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Diesel particulate abatement via catalytic traps

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Abstract

This paper concerns the development of catalytic traps for diesel particulate removal from the exhaust gases of light-duty vehicles. The studied traps were realised with ceramic (ZTA and mullite) foam structure, on which two different kinds of catalysts, one based on caesium metavanadates and the other on pyrovanadates, were deposited. Catalyst activity was checked through simple TPO experiments, whereas the performance of catalytic trap prototypes was tested in a pilot plant, where a soot laden gas flow was produced by acetylene combustion.

The traps activated through ternary $Cs_4V_2O_7$+AgCl+CsCl catalyst allowed one to burn out catalytically the soot filtered, thereby keeping pressure drop throughout the trap at acceptable levels for vehicle applications (i.e. below 100 mm H_2O). This was achieved at about 370°C, a temperature close to the temperature range of the newest diesel passenger cars (180–350°C).

A mathematical model has been assembled and validated by the data obtained with the pilot plant. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Diesel particulate; Soot; Catalytic combustion; Caesium vanadates; Foam trap

1. Introduction

The new generation of diesel engines (common-rail with direct injection) allows one to achieve very high energetic efficiency and quite limited pollutant emissions: both carbon monoxide and unburned hydrocarbons outlet concentrations are in fact lower than those produced in spark ignition engines. However, diesel engines produce specific pollutants that are hazardous for human health (i.e. NO_x, soot, etc.). Among them, diesel particulate is believed to be very dangerous, because it can be inhaled and captured in alveolar region of the lungs, where it might give rise to carcinogenic effects, owing to the polycyclic aromatic hydrocarbons and to nitro-compounds adsorbed on its surface. For this reason, US, Japan and Europe have adopted severe standards for particulate in diesel light-duty vehicle emissions: starting from January 2000 the highest level admitted in Europe will be 0.04 g/km. Even more severe limits have been fixed for year 2005. To meet these requirements, different systems (fuel additives, injection of oxidising agents, etc.) have been proposed. Among them, the catalytic traps seem to be one of the best alternatives on the grounds of their simplicity, easy handling, high abatement efficiency and comparatively low cost. The catalyst contained in such device should lower down soot ignition temperature (550°C for non-catalytic combustion) to the values characteristic of diesel exhaust (180–350°C), thereby enabling diesel soot combustion when it impacts the pore walls of the catalytic trap. The success of catalytic traps requires the development of catalysts suitable to display a good activity already in the temperature range 250–350°C and with a good stability and durability

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under practical working conditions. Several catalysts capable of appreciably lowering down the ignition temperature of carbonaceous materials were proposed and their catalytic mechanism well investigated: precious metals (Pt, Pd) [1]; oxides of transition metals (i.e. V, Mn, Fe, Cu, Cr, Mo) [2–6]; alkali-metal-based compounds [7]; more complex catalysts based on the combination of some of the compounds mentioned above [8–14].

The good performance of the most promising of these last mentioned multi-component catalysts was, in most cases, attributed to the formation of low-melting eutectic liquids [15]. Such liquid phases can wet the surface of the solid carbon particles promoting their combustion. Saracco et al. [16] observed this mechanism for several binary catalysts based on the coupling of alkali-metal vanadates and halides. A previous systematic study about the intrinsic activity of metavanadates [17] allowed us to assess a performance hierarchy among different compounds of this class, the catalytic activity increasing with the electropositivity of the alkali metals. Furthermore, catalysts based on $CsVO_3$+KCl and KVO_3+KCl showed a satisfactory thermal stability (in the temperature range 380–600°C) under gaseous atmosphere containing some typical components of diesel emissions [18]. More recently, new catalysts based on typical components of alkali metal have been developed [19] achieving better results; this happened in the context of an industrial-type BRITE-EURAM project (CATATRAP) which involves, beyond our group, several partners from the automotive, catalyst and trap manufacturing industries. In addition to these catalysts based on caesium metavanadates and pyrovanadates forming a liquid phase at low temperature, they were also found to show an acceptable stability. The catalyst loss by evaporation was negligible since its vapour pressure was low at regular diesel working temperature.

In this paper, the activity of catalysts based on both meta- and pyro-vanadates will be compared by means of temperature programmed oxidation (TPO) experiments. Afterwards, the performance of catalytic traps obtained using these two kinds of catalysts on two different ceramic–foam supports will be assessed, and a mathematical model validated with the abatement results thereby obtained.

2. Materials and methods

2.1. Catalysts preparation

The caesium metavanadate and pyrovanadate ($CsVO_3$, $Cs_4V_2O_7$) were prepared by melting together vanadium pentoxide (V_2O_5) and caesium carbonate (Cs_2CO_3); meta- or pyro-vanadate were obtained by properly varying the ratio between the precursors. After solidification, these vanadates were annealed at about 50°C below the respective melting points ($CsVO_3$=641°C; $Cs_4V_2O_7$=890°C, as reported in the literature and/or measured on the prepared salts by a heating microscope or a differential scanning calorimeter). The purity of each obtained vanadate was checked by X-ray diffraction analysis (XRD), using Philips PW1710 diffractometer equipped by a monochromator (Cu Kα radiation).

The activity of $CsVO_3$ and $Cs_4V_2O_7$ can be improved by coupling these compounds with KCl and AgCl+CsCl, respectively, in order to achieve binary/ternary eutectics. Binary and ternary catalysts were prepared by mixing in a mortar, respectively, $CsVO_3$ with KCl (molar ratio 1:1) and $Cs_4V_2O_7$ with a AgCl+CsCl mixture (molar ratio of 1:1 between the chloride mixture and the vanadate). The mixture between AgCl and CsCl had the binary eutectic composition (molar ratio of 7:3).

The two- and three-component catalysts were prepared by melting of mixed salts and slowly cooling down to room temperature; the composition of these catalysts based on eutectics were checked by XRD as well. The partial melting of binary and ternary catalysts was investigated by a heating microscope.

2.2. TPO experiments

The catalytic activity of these compounds towards carbon combustion was investigated by TPO experiments. The samples for TPO tests were obtained by supporting each catalyst on alpha alumina powder (size range: 100–200 μm). These specimens were prepared by impregnating the alumina with aqueous solutions of vanadates and appropriate salts (catalyst/alumina weight ratio of 1:1), drying at 120°C and annealing for 4 h at 50°C below the vanadate or the eutectic melting point.

Summarising, four different kind of catalysts were investigated:

- pure caesium metavanadate supported on α-Al_2O_3 powder;
- pure caesium metavanadate+KCl supported on α-Al_2O_3 powder;
- pure caesium pyrovanadate supported on α-Al_2O_3 powder;
- pure caesium pyrovanadate+AgCl+CsCl mixture supported on α-Al_2O_3 powder.

A XRD analysis was carried out after each preparation in order to check reactions eventually occurring between the catalyst components during alumina impregnation, drying and annealing.

Each catalyst listed above was accurately mixed with carbon powder in a mortar; a catalyst/carbon weight ratio of 4:1 was adopted. In this way, a constant weight ratio of 2:1 between catalytically active substance and carbon was achieved for all mixtures. Amorphous carbon particles of about 45 nm diameter, with 0.34% of ashes and 12.2% of adsorbed moisture, were used.

The catalyst–carbon mixtures were subjected to TPO runs; three tests were carried out for each mixture and the results averaged. During the TPO measurements the mixture was heated at constant rate (5°C/min) under an air flow, while measuring the amount of CO_2 produced at each temperature.

The TPO equipment consisted of the following items: a quartz tubular fixed bed reactor inserted in a PID controlled oven; a mass flow meter delivering synthetic air (21 vol.% of oxygen, 79 vol.% of helium); a thermocouple inserted in the fixed bed for temperature measurement; a CO_2 IR analyser (Hartman & Braun URAS 10 E) positioned on the gas flow at the exit of the reactor.

The fixed bed, a mixture of catalyst+carbon sample (50 mg) with 150 mg of SiO_2 pellets (0.3–0.7 μm in size), was kept inside the reactor between two layers of quartz–wool. After an isothermal pre-treatment at 200°C (30 min under an argon flow) the flow of synthetic air was delivered (100 Nl/min) and the temperature was risen up to 700°C at the rate of 5°C/min. The combined measurement of the sample temperature and CO_2 outlet concentration, recorded by a data acquisition system, allowed one to evaluate

- the temperature at which 5% of the initial carbon was burned to CO_2;
- the peak temperature, corresponding to the maximum rate of carbon conversion to CO_2, a simple index of catalytic activity;
- the fraction of carbon converted to CO_2, by comparing the integral amount of CO_2 produced with the carbon content in the initial sample.

2.3. Trap selection and catalytic trap preparation

Following TPO test, the four catalysts mentioned above ($CsVO_3$; $CsVO_3$+KCl; $Cs_4V_2O_7$; $Cs_4V_2O_7$+AgCl+CsCl) were used for the preparation of the catalytic foam traps. The foam supports were chosen because they offer a good compromise between filtration efficiency and required pressure drop, enabling a good penetration and dispersion of particulate within the porous structure and favouring the contact between the particulate and the deposited catalyst [20].

Two kinds of filters can be used to actually guarantee a good filtration efficiency: ceramic foams and wall-flow filters. The latter ones present a good filtration behaviour, but soot–catalyst contact would be very poor as highlighted in Fig. 1. Wall-flow filters can instead be used in addition to fuel additives: in this context soot–catalyst contact is very good, because the catalytic materials (introduced as additives in fuel tank) are intimately mixed with the soot.

Conversely, foams allow good contact between soot and deposited catalyst, since they guarantee a deep bed and not shallow-bed filtration mechanism. However, the inner foam struts can strongly influence trap performances; for this reason two kinds of foams, built with two different materials (ZTA and mullite), were tested.

The metavanadate based catalysts were deposited (20 wt.%) inside ceramic traps based on zirconia-toughened α-Al_2O_3 (ZTA) having a foam-like structure (manufacturer: ACF-Selee, Hedersonville, NC; porosity ε_0=80%; 65 pores per inch; size: cylindrical; diameter=55 mm; thickness=23 mm; density ρ_t=900 kg m^{-3}; thermal conductivity k_t=1.13 W m^{-1} K^{-1}). ZTA was preferred over other substrates (e.g. cordierite) for its negligible reactivity towards the employed catalytic compounds. The deposition procedure was optimised so as to achieve a catalyst distribution as even as possible throughout the trap body. The two compounds were added in series

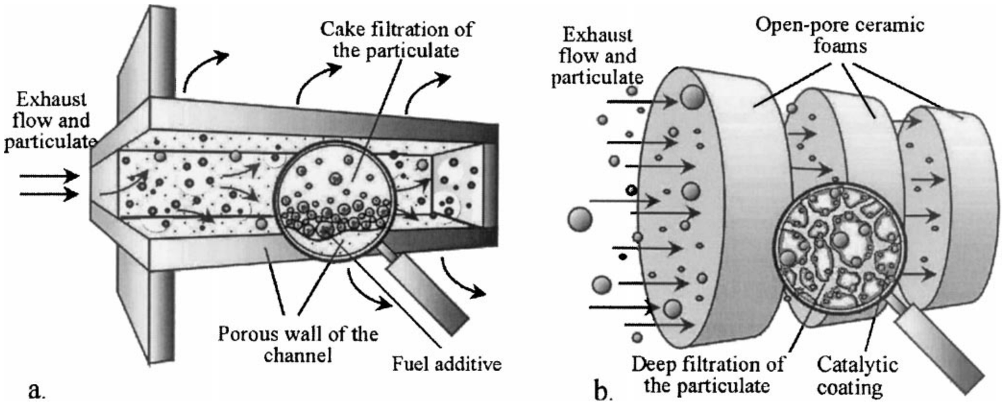

Fig. 1. Different filtration methods for (a) wall-flow filter and (b) foam.

(vanadates first) through wet impregnation followed by microwave drying. As suggested by Bos et al. [24], such drying technique allowed one to get an even catalyst distribution, as checked by SEM-EDS analysis on cross-sections of the catalytic traps. A final heat treatment at 700°C was carried out for 2 h.

The pyrovanadate showed a very good compatibility with mullite (manufacturer: Centro Ricerche Fiat (CRF), Orbassano, Italy); for this reason, only cylindrical mullite foams (50 mm diameter; 17 mm long; 45 pores per inch; ε_0=80%; ρ_t=3156 kg m^{-3}; k_t=4.3 W m^{-1} K^{-1}) were adopted as supports for the pyrovanadate based catalysts. Moreover, the mechanical foam properties are: compression strength, 1.39 and 4.9 MPa for ZTA and mullite, respectively; bending strength, 1.69 and 1.70 MPa for ZTA and mullite, respectively.

The caesium pyrovanadate was deposited inside the mullite foam with the same procedure used for metavanadate, but the final heat treatment was carried out at 900°C. Moreover the AgCl+CsCl mixture, because of its very low solubility, was impregnated by distributing eutectic powder onto one flat side of the disc foam, then heating the coated trap up to chlorides mixture melting point and keeping it at this temperature level for half an hour. The same procedure was repeated for the other flat side.

2.4. Pilot plant tests

The catalytic traps thereby obtained were tested in a tailor-made laboratory scale pilot plant already described in [21]. It is based on an acetylene-burner capable of generating a particulate-rich stream to be fed to the catalytic trap. As measured by SEM observation, the particle diameter of the produced soot was ranging between 0.075 and 0.275 μm, quite representative of the actual particulate size distribution in the diesel exhaust gases of modern passenger cars. Further, acetylene generated soot is more difficult to burn than diesel particulate since it has no adsorbed organic compounds, which are well known to lower the catalytic combustion temperature of soot. As a consequence, the particulate abatement results obtained in these experimental conditions can be regarded as conservative.

The experiments were carried out in the pilot plant as follows:

- the catalytic ceramic trap was located above the burner inside a foam holder surrounded by an electrical heating device;
- the burner was fed by acetylene and air, and the exhaust gas was preliminarily analysed by filtration (filters type: Pall TXHi20-ww) and weighting, which allowed one to evaluate the particulate feed concentration;
- the catalytic trap temperature was risen up to a pre-fixed set-point value by the external heater and the burner flue gases delivered through the trap; a temperature control system regulating the power delivered to the external heaters maintained the trap temperature at the set-point value during the test;
- the outlet stream flowing from the catalytic trap was once again analysed in order to evaluate the residual particulate concentration.

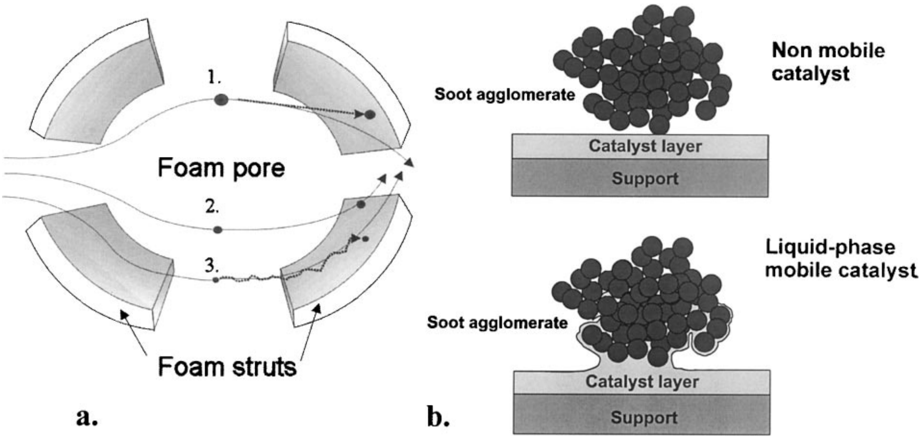

Fig. 2. (a) Filtration mechanisms: (1) inertial impaction; (2) interception; (3) Brownian diffusion. (b) Soot–catalyst contact with or without mobile catalyst.

For each set of operating conditions and catalyst type, the pressure drop across the trap and the particulate abatement efficiency vs. time were measured.

The pilot plant allowed one to assess the performance of the different catalytic traps through the comparison of the temperature at which a stationary trap pressure drop value was achieved; when this happened, most of the particulate flowing through the trap burned out and the pressure drop remained constant (i.e. constant soot accumulation inside the trap). On the contrary, if the catalyst did not display a sufficient catalytic activity at a given temperature, the particulate quickly accumulated inside the trap and the pressure drop increased. Then, the minimum temperature, which allowed one to achieve the above mentioned “steady-state” condition was assumed as an index of the catalytic performance of the trap.

A model was also assembled, solved by the finite difference method, and validated by fitting the experimental data. The model includes differential heat and mass balance equations inside the catalytic foam. Particularly, inertial impaction, interception and Brownian diffusion were considered as basic mechanisms for diesel particulate trapping (Fig. 2a) [22], whereas the reaction kinetics expression was adapted from literature [23]. The reaction rate was set to be proportional to the contact area between soot and catalytic material, variable depending on the catalyst mobility. If the catalyst is in a solid state, the contact with soot is in fact very poor and limited to the very small zones in which the soot touches the catalyst. Whereas, using a mobile catalyst, a wet phase is formed, so that the catalytic material can wrap the soot agglomerate covering the entire external soot surface. In this context, Fig. 2b shows how, employing a mobile catalyst, the soot–catalyst contact area reaches its maximum.

The complete set of model equations was published earlier in [21] and is not reported here for the sake of briefness. Beyond the above filtration and reaction mechanisms, such model accounted, through an ad hoc defined Froude number, for the possibility of re-suspending, back into the flame gas, the particulate deposited over the pore walls. As a small though important improvement of the earlier model, the particulate size distribution, instead of a single average particle diameter, was considered here. The aim of this model improvement was also to predict whether the trap design could influence the abatement of the most dangerous soot (i.e. particle size <100 nm), which can reach the alveolar region of the lungs.

3. Results and discussion

XRD analysis results, not reported here for the sake of briefness, allow one to exclude any significant interaction between the $Cs_4V_2O_7$-based catalysts and the foam substrate. This is due to high purity of mullite powder (>99%) used in the foam production. As a counterpart, the CRF process based on mullite

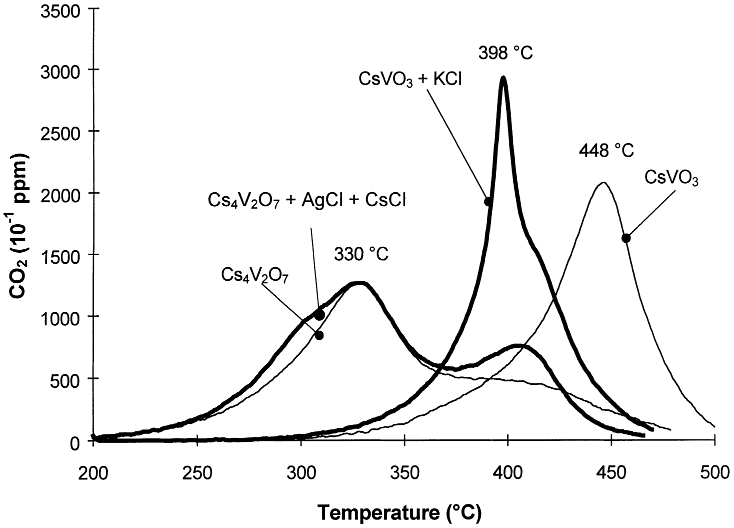

Fig. 3. TPO runs of caesium metavanadate- and pyrovanadate-based catalysts supported on α-Al_2O_3 (50 wt.%).

powder precursor however involves high costs and high sintering temperature (about 1600°C). On the other hand, other commercial and cheaper mullite foams were found to possess an unacceptably high level of free silica, due probably to an incomplete reaction with the corresponding amount of Al_2O_3 precursor to form mullite. SiO_2 displays a pronounced reactivity towards all the catalysts.

The TPO runs carried out for each catalyst are shown in Fig. 3. These results show that pyrovanadate is more active ($T_{50\,\mathrm{wt.\%}}$=330°C) than metavanadate ($T_{50\,\mathrm{wt.\%}}$=448°C). However, the performance of metavanadate is appreciably enhanced ($T_{50\,\mathrm{wt.\%}}$=398°C) when the catalyst achieves mobility through the formation of molten eutectic, involving KCl and the metavanadate. The activity of $Cs_4V_2O_7$ towards carbon combustion is already appreciable at 250°C, temperature easily achieved inside the car exhaust pipes. This is particularly evident analysing $T_{5\,\mathrm{wt.\%}}$ temperature at which the 5 wt.% of the carbon present in TPO reactor is converted: these values are summarised in Table 1.

As regards the caesium pyrovanadate, the formation of molten ternary eutectic is not so plain as for the metavanadate. The catalyst $CsVO_3$+KCl in fact gives a large amount of liquid at 389°C that is well below the melting point of pure metavanadate, whereas the ternary catalyst ($Cs_4V_2O_7$+AgCl+CsCl) gives a very small amount of eutectic liquid (just sufficient to be detected by heating microscope) at about 280°C. Moreover, the already tight contact conditions between catalyst and carbon in the TPO analysis diminishes the effects of the catalyst mobility, as it is particularly evident for the more active catalysts.

A good feature shown by $Cs_4V_2O_7$+AgCl+CsCl is the very low temperature at which all carbon present in the reactor is oxidised to CO_2 (above 450°C, no CO_2 is detected by IR analyser using this mobile catalyst). This can be due to the better mobility of this catalyst compared to pure $Cs_4V_2O_7$; the latter needs, in fact, a higher temperature level to completely burn out the soot particles.

The effect soot–catalyst contact condition is more evident for the catalytic foams tested in pilot plant (Fig. 4). In this context, carbon–catalyst contact is poorer than that in TPO test; therefore, the catalyst mobility in the coated trap plays a much more

Table 1
Results of TPO runs on the studied catalysts

Catalyst	$T_{5\,\mathrm{wt.\%}}$	$T_{50\,\mathrm{wt.\%}}$	Fraction of carbon converted to CO_2
$CsVO_3$	359	448	~1
$CsVO_3$+KCl	343	398	~1
$Cs_4V_2O_7$	256	330	0.98
$Cs_4V_2O_7$+AgCl+CsCl	252	330	~1

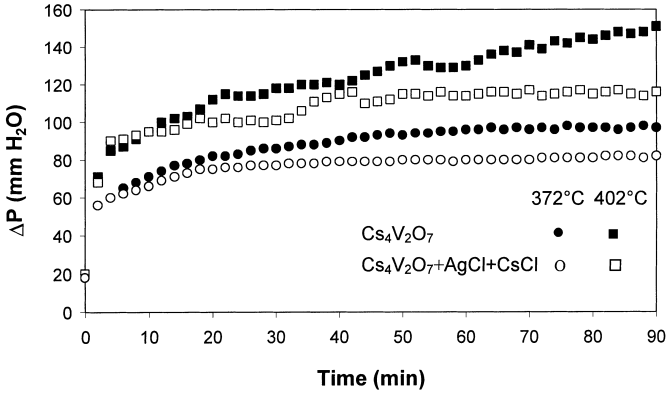

Fig. 4. Pressure drop across the mullite trap at two different temperatures with $Cs_4V_2O_7$+AgCl+CsCl and $Cs_4V_2O_7$ catalyst. Soot feed concentration=0.13 g/N m^3.

important role. When the catalyst based on caesium pyrovanadate is deposited on the ceramic foam, the contact between soot and catalyst is strongly affected by liquid phase formation. This should be the major factor responsible for the better performance of the AgCl+CsCl-added catalyst, as shown in Fig. 4 comparing curves at 372 and 402°C. At both temperatures, the pressure drop measured across the trap using $Cs_4V_2O_7$ with AgCl and CsCl is lower than the one obtained with pure $Cs_4V_2O_7$. During these kinds of tests high soot abatement efficiencies are reached: for instance, using pure pyrovanadate, at 372°C the global conversion at steady-state was 80%, whereas at 402°C it reached 85%.

Although 372°C may seem a bit too high compared to the temperature range typical of exhaust gases, we must remember the following:

1. As mentioned earlier, the soot generated by burning acetylene has no adsorbed hydrocarbons, which are well known to largely favour soot combustion.
2. The soot concentration of 0.13 g/N m^3 is higher than the average one in normal diesel engine conditions (~0.055 g/N m^3, measured during ECE-EUDC standard cycle).
3. The soot production occurred continuously during the tests, whereas in diesel particulate, emissions are substantially limited to the time periods where a high engine torque is required.

Fig. 4 clearly shows that $Cs_4V_2O_7$+AgCl+CsCl gives a superior performance. Besides, its chemical compatibility with mullite support is rather good; conversely, its deposition procedure is more complex than that for the catalysts due to the very low solubility of AgCl and CsCl. This superior performance of $Cs_4V_2O_7$+AgCl+CsCl is confirmed by the data shown in Fig. 5. It can be noticed that using $Cs_4V_2O_7$+AgCl+CsCl supported on mullite at 400°C, the pressure drop is limited for a long time to about 80 mm H_2O, whereas at the same temperature using $CsVO_3$+KCl supported on ZTA, the pressure drops are much higher. The better performance obtained with the former system is due in part to the higher activity catalyst and in part to the better foam properties. This is particularly clear observing the pressure drops across the trap without catalyst: those of mullite foam are in fact lower than the ZTA ones.

In both cases, the model agreement with the experimental data is rather good and it could be used to improve the trap design, because structural trap parameters (e.g. pore size or porosity) can strongly influence the performance obtainable with this kind of filter. For this purpose, with a proper choice of the pore density, the filter length and diameter, it is possible to reach a good compromise between pressure drop and filtration efficiency. Besides, the catalytic combustion effectiveness can be influenced by the trap design, because the soot/catalyst contact depends on particle penetration into the trap. For this reason, the trap structure has to guarantee the best particulate dispersion onto the internal surface in order to fully exploit the potential of the deposited catalyst. Foams of different basic materials, with the same ppi

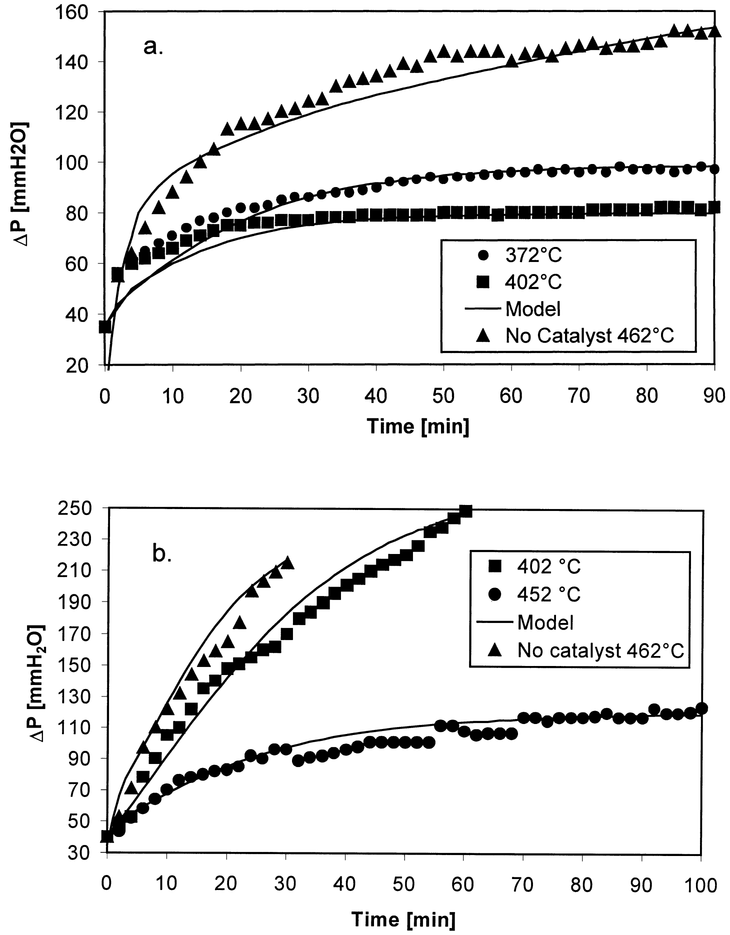

Fig. 5. Pressure drop across the trap. (a) Cs pyrovanadate on mullite foam: soot feed concentration=0.13 g/N m^3; (b) Cs metavanadate: soot feed concentration=0.11 g/N m^3.

number, do not possess, generally, equivalent pore structure due to the different rheological properties of the slurries employed during the foam manufacturing process.

As a last issue, it was noticed both experimentally and by modelling that the foam filters employed could abate nearly all particulate sizes with equivalent selectivity.

4. Conclusions

Two different catalytic compounds, caesium metavanadate and pyrovanadate, have shown good thermal stability and catalytic activity in diesel soot abatement. They were thus deposited on ceramic traps to be tested in a pilot plant. Both caesium metavanadate and pyrovanadate were able to catalyse soot oxidation, keeping the pressure drop across the catalytic trap at a tolerable level for diesel-engined passenger cars. The $Cs_4V_2O_7$-based catalysts entailed a better performance than $CsVO_3$-based ones. However, to obtain these results at a temperature range similar to that of diesel engine (180–350°C), it is still necessary to reach a catalytic activity and catalyst/soot contact better than those achieved. Particularly, the formation of liquid phase among the catalyst components has been demonstrated to enhance the contact surfaces permitting a higher soot abatement (see the better performance of AgCl+CsCl-added $Cs_4V_2O_7$ as opposed to pure $Cs_4V_2O_7$).

It has finally to be underlined that a high catalytic activity is not sufficient to obtain high diesel soot abatement, but has to be coupled with a suitable filter design. The trap should be capable of being properly penetrated by the soot in the porous activate matrix, so that it can get into contact with most of the catalyst deposited. For such a design purpose, a model has been proposed and validated with success. By using this tool, it should be possible to tailor the trap geometry as well as its basic structural parameters (e.g. porosity, pore size) so as to reach the best compromise between low pressure drop and high abatement efficiency.

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