

Diesel Particulate Traps Regenerated by Catalytic Combustion

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Abstract—The development of catalytic means for the regeneration of particulate-laden traps for diesel exhaust cleaning is the main topic of this paper. All the steps of the catalytic trap preparation are dealt with, including: the synthesis and choice of the proper catalyst and trap materials, the development of *in situ* catalyst deposition, and the bench testing of the derived catalytic traps. Two different traps were considered (i.e., silicon carbide and cordierite wall-flow monoliths operating via a shallow-bed filtration mechanism), whereas the best catalyst selected was the perovskite $\text{LaCr}_{0.9}\text{O}_3$. The filtration efficiency and the pressure drops of the catalytic and non-catalytic monoliths were evaluated on a diesel engine bench under various operating conditions. On the basis of the obtained results the catalysed SiC converter was found to be the most satisfactory converter to be placed on the exhaust line of the modern common-rail diesel-engine cars.

Key words: Particulate, Wall-Flow Monolith, $\text{LaCr}_{0.9}\text{O}_3$, SiC, Cordierite

INTRODUCTION

The particulate matter (PM) emitted by diesel engines is a serious problem in urban areas. The fuel efficiency, the simplicity and durability of diesel technology are attractive properties; however, these engines produce soot and NO_x . Concerns about the health effects of diesel particulate emissions have led to progressively tighter PM emission standards, which can be met only through new technological advances and fuel modifications. Concomitant reduction in emission nitrogen oxides needs to be achieved because they contribute to formation of ozone and acid rains.

To meet the new emission standards (EURO IV legislation, to be enforced in 2005), various approaches are being considered. Some of these, such as lowering the sulphur content of the fuel or improving the engine design, are currently being implemented, but may not be sufficient. Moreover, reducing PM emissions through changes in fuel or engine design is often achieved at the price of increasing the NO_x produced.

A promising approach to lower PM emissions is to use a particulate filter alone or in conjunction with a catalyst. Particulate filters are made of temperature-resistant porous material such as ceramics with an as-high-as-possible filtration area so as to decrease the pressure drop and the related fuel penalty.

Although a filter is effective in lower PM emissions, technical problems are associated with its use. Over time, the filter tends to become clogged with trapped particles, increasing the exhaust back pressure and reducing the engine efficiency, which in turn leads to greater fuel consumption. This soot can be eliminated by combustion (filter regeneration). However, soot cannot be burned off effectively at temperatures that are likely to occur during normal driving conditions. A way to improve the filter system and addressing the regeneration demands is to use the filter lined with a catalyst [van

Setten et al., 2001]. The role of the catalyst is to enhance the combustion of the soot collected on the filter by reducing its ignition temperature so that the PM can burn off during normal driving conditions.

Several approaches are being developed and tested at our labs to provide realistic solutions for reducing emissions to environmentally acceptable levels:

- catalytic traps made of a ceramic foam lined with suitable catalysts (e.g. Cs and V compounds) which filter particulate according to a deep filtration mechanism, as described in Saracco et al. [1999a];
- catalytic foam or wall-flow traps combined with the use of fuel additives mixed with the fuel via a dosing system: the additive lowers the spontaneous combustion temperature of the particulate down to 450 °C (a temperature that can be reached in highway driving). This last system has been recently introduced by Peugeot-Citroën for light-duty diesel engines [Gieshoff et al., 2001];
- catalytic traps based on a wall-flow monolith (shallow-bed fil-

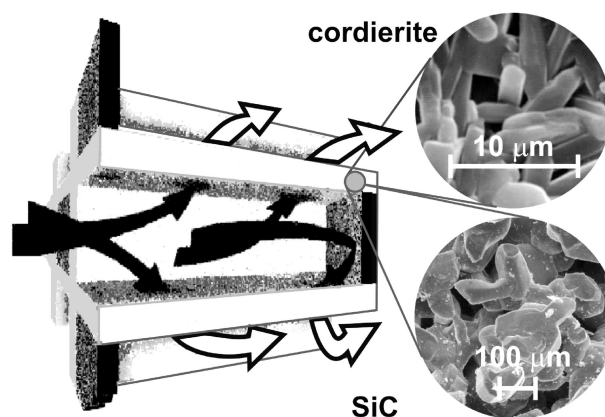


Fig. 1. Sketch of wall-flow monolith filtration mechanism with two SEM views of silicon carbide and cordierite channel walls.

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tration) combined with an oxidation catalyst deposited onto it (e.g. $\text{LaCr}_{0.9}\text{O}_3$ on SiC or $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ monoliths). A sketch concerning this last trap concept is shown in Fig. 1, which also includes micrographs of the structure of the filter.

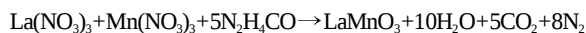
This contribution describes the encouraging results obtained with these last traps, which can be periodically regenerated by a peculiar use of last generation Common-Rail Diesel engines: post injection of fuel, which gets then burned out by a specific catalytic converter so as to heat up the downstream trap until catalytic combustion of soot is ignited.

EXPERIMENTAL PROCEDURES

1. Catalyst Preparation and Characterisation

A series of perovskite samples ($\text{LaMn}_{1-x}\text{O}_3$, $\text{La}_{1-x}\text{A}_x\text{MnO}_3$, $\text{LaMn}_{1-x}\text{B}_x\text{O}_3$, $\text{LaCr}_{1-x}\text{O}_3$, $\text{LaCr}_{1-x}\text{B}_x\text{O}_3$ and $\text{LaFe}_{1-x}\text{O}_3$, with different x values, $\text{B}=\text{Mg}$, V , Cr , Mn , Fe and $\text{A}=\text{K}$, Rb , Ca , Sr ; see later Fig. 4) were prepared via a highly exothermic and self-sustaining reaction (*combustion synthesis*; Merzahanov, 1996) to obtain nanosized particles of catalyst. The synthesis process consists of two reactions: the first concerns the real perovskite synthesis starting from the metal precursors, while the second one concerns the reaction between nitrates and urea. The entire combustion process is over within few minutes.

As an example, fine-particle LaMnO_3 has been synthesized by quickly heating an aqueous concentrated solution containing stoichiometric amounts of metal nitrates and urea. The mixture was located in an oven at 600°C for a few minutes in a capsule, so as to ignite the very fast reaction:



The catalysts were then ground in a ball mill at room temperature. X-ray diffraction (PW1710 Philips diffractometer) was used to examine whether the desired perovskite structure of each catalyst synthesized was actually achieved.

2. Screening Activity Tests for the Selection of the Best Catalyst

The catalytic activity of the prepared catalysts was tested in a temperature-programmed-reaction (TPR) apparatus [Fino et al., 2002a]. Air was fed at the constant rate of $50\text{ ml}\cdot\text{min}^{-1}$ via a set of mass flow meters to a fixed-bed reactor enclosed in a U-shaped quartz tube. The tubular quartz reactor was loaded with 50 mg of a 1 : 9 by weight mixture of carbonaceous materials and powdered catalyst and 200 mg of SiO_2 granules (0.2–0.7 mm); this inert material was adopted to reduce the specific pressure drops across the reactor and to prevent thermal runaways.

Experiments were performed by using, instead of real diesel soot, an amorphous carbon having the following properties: average particle size=45 nm; 0.34 wt-% ashes after calcination at 800°C ; 12.2 wt-% of moisture lost after drying at 110°C . This material was chosen over its real counterpart so as to avoid any interfering effect due to the presence of adsorbed hydrocarbons, sulfates or fly-ashes present in real diesel soot. Furthermore, the amorphous carbon employed is more difficult to burn than real diesel soot which renders the achieved results conservative.

A proper and reproducible degree of mixing between catalyst and carbon was obtained by grinding carefully together such sub-

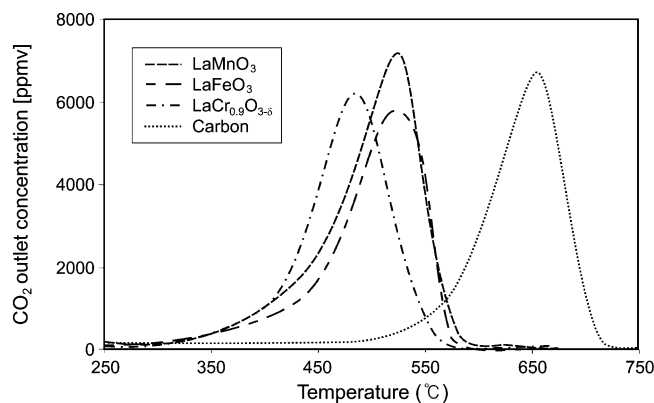


Fig. 2. TPR runs performed with LaMnO_3 , LaFeO_3 and $\text{LaCr}_{0.9}\text{O}_3$ perovskite catalysts; TPR non-catalytic carbon combustion is also drawn for a comparison.

stances for 15 min in a ball mill. The catalyst-carbon- SiO_2 fixed-bed was sandwiched between two quartz-wool layers, while the tip of a K-type thermocouple was located well inside the bed itself. The reaction temperature was controlled through a PID-regulation system and varied during each TPR runs from 200 to 700°C at a $5^\circ\text{C}\cdot\text{min}^{-1}$ rate.

The outlet gas composition was checked through CO_2 NDIR continuous analyzers (Hartmann & Braun URAS 10E). The signal from the analyzer was sent to a computer-controlled data acquisition system to collect CO_2 concentrations as a function of the bed temperature. The inlet and outlet flow rates were measured by means of a digital-flow meter.

Screening tests were performed in the TPR apparatus according to the standard operating procedures listed above in order to determine some critical performance parameters of each of the prepared catalysts (e.g., catalytic activity toward carbon combustion, selectivity to CO_2 , optimal operating temperature range, etc.). The aim of these tests was to find the most promising catalysts for diesel particulate combustion. Fig. 2 shows, as an example, typical TPR plots obtained for some of the tested catalysts (LaMnO_3 , LaFeO_3 and $\text{LaCr}_{0.9}\text{O}_3$ perovskite catalyst) and for the non catalytic combustion of soot (run performed in the absence of any catalyst). The role of the catalysts can be clearly perceived. Besides, an index of their activity can be found in the peak temperature (T_p) of their TPR plot: the lower the T_p value, the higher the catalyst activity.

3. In situ Catalyst Deposition within the Traps

The best catalyst selected ($\text{LaCr}_{0.9}\text{O}_3$, as later detailed) was deposited by *in situ* combustion synthesis directly over the wall-flow filters. The ceramic support was dipped in the aqueous solution with precursors (exactly the same used for powdered catalyst production) and then placed into an oven at 600°C . The aqueous phase was rapidly brought to the boiling point, then the precursor mixture was ignited and the main synthesis reaction took place *in situ*.

Two different ceramic supports have been selected: a cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) filter produced by CORNING and a silicon carbide (SiC) filter industrialised by IBIDEN (for both monoliths: cell structure=14/200, diameter 30 mm, length=6–12"; pore diameter of channel walls=9 μm , porosity of channel walls=42%). A good chemical compatibility between catalysts and ceramic materials was in fact assessed by means of XRD analysis after a suit-

able thermal treatment. Powders of both wall-flow materials were mixed with $\text{LaCr}_{0.9}\text{O}_3$ (weight ratio of 1 : 1) and kept for 2 hours at 900 °C. The mixed powders were then characterised by XRD analysis in order to investigate the possible formation of new crystalline species by chemical reaction with the catalyst. Finally, this ceramic material-catalyst mixture was mixed with carbon so as to obtain samples for TPO analysis and assess the change of catalytic activity eventually occurred.

Conversely, the catalytic traps obtained underwent a microstructural and morphological characterisation by means of electron microscopy and energy dispersive analysis.

A final adhesion test was carried out by simulating the typical engine vibrations using an ultrasonic bath and weighting the samples after different periods to verify the bond of the catalytic layer to the support and eventual loss of solid materials.

4. Diesel Engine Bench Tests

The developed traps were tested in the pilot plant sketched in Fig. 3 on real diesel exhaust gases (Kubota 1,000 cc IDI engine, capable of up to 23.5 hp at 3,000 rpm), where the temperature and gas composition before and after the trap can be controlled and monitored as well as the filtration efficiency and the evolution of the pressure drop through the trap (a sign of soot accumulation therein). A detailed description of the pilot plant was provided by Fino et al. [2002a].

The wall-flow was located along the main line of the main ex-

haust stream. The exhaust gas superficial velocity across the trap could be controlled at a desired value by measuring the exhaust flow rate through a volumetric flow controller connected to a throttling control valve placed on by-pass exhaust stream. The pressure drop across the trap could be measured by means of differential pressure transducers (VIKA), whereas the trap inlet and outlet temperature was measured by K-type thermocouples at axial positions. The soot concentration in the exhaust gases was measured by isokinetic sampling of a small flue-gas flow rate through a suction pump and collecting the suspended particulate using a two-filter system (PALL-FLEX 47 TX 40 HI 20-W). Finally, gas phase composition could be monitored through continuous analyzers by Elsag-Bailey (NDIR for NO, CO, CO₂, SO₂; FID for overall HC; paramagnetic for O₂).

The standard bench test procedure can be described as follows. The traps were at first loaded by letting rather cold (about 200 °C) exhaust gases flow throughout it until a 110-160 mbar pressure drop is reached (corresponding to a particulate hold-up of about 10 g·L⁻¹). Then, regeneration is induced by post injecting some fuel with a metering pump in the exhaust gases and by burning these HC with an oxidizing honeycomb catalyst (OXICAT by Johnson Matthey) placed just upstream the trap. The time needed for a complete trap regeneration (e.g., combustion of the soot hold-up) is an index of the catalyst performance. The higher the catalyst activity the lower the time required.

Finally, all measurements have been carried out by using as a

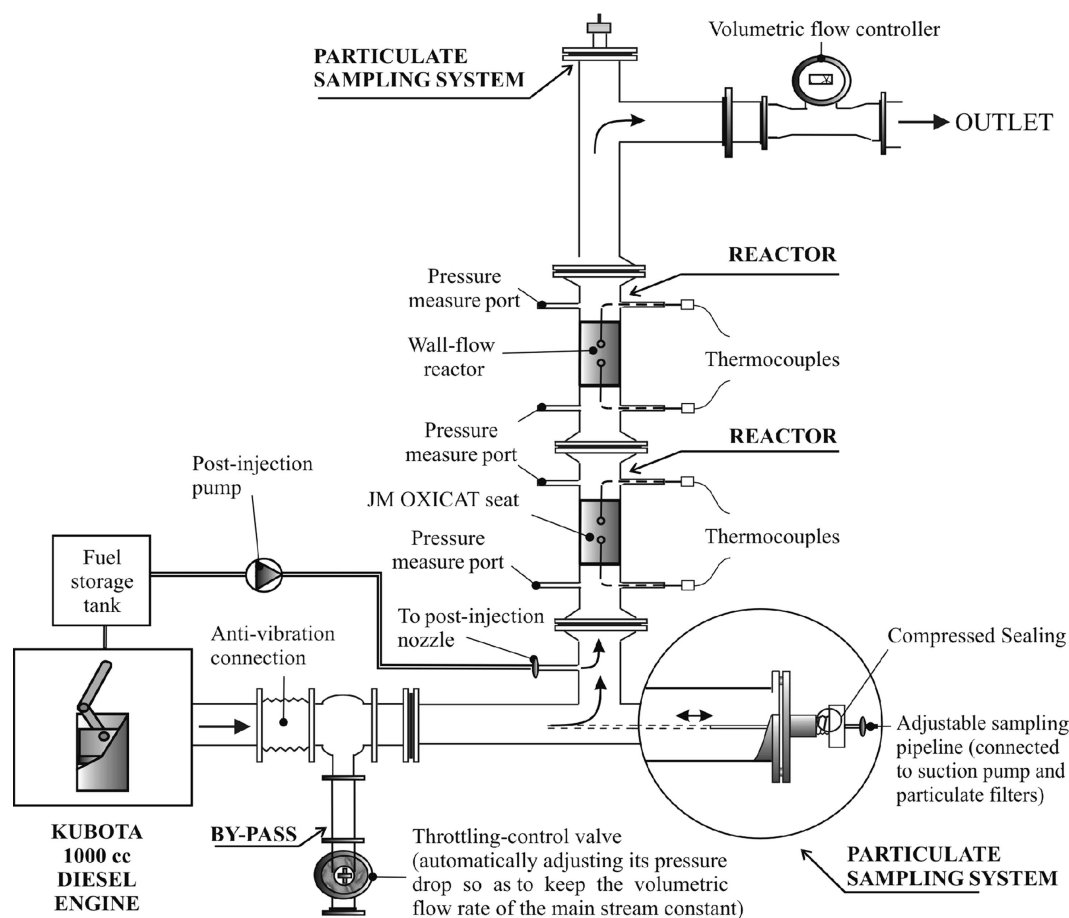


Fig. 3. Schematic view of the engine-bench pilot plant.

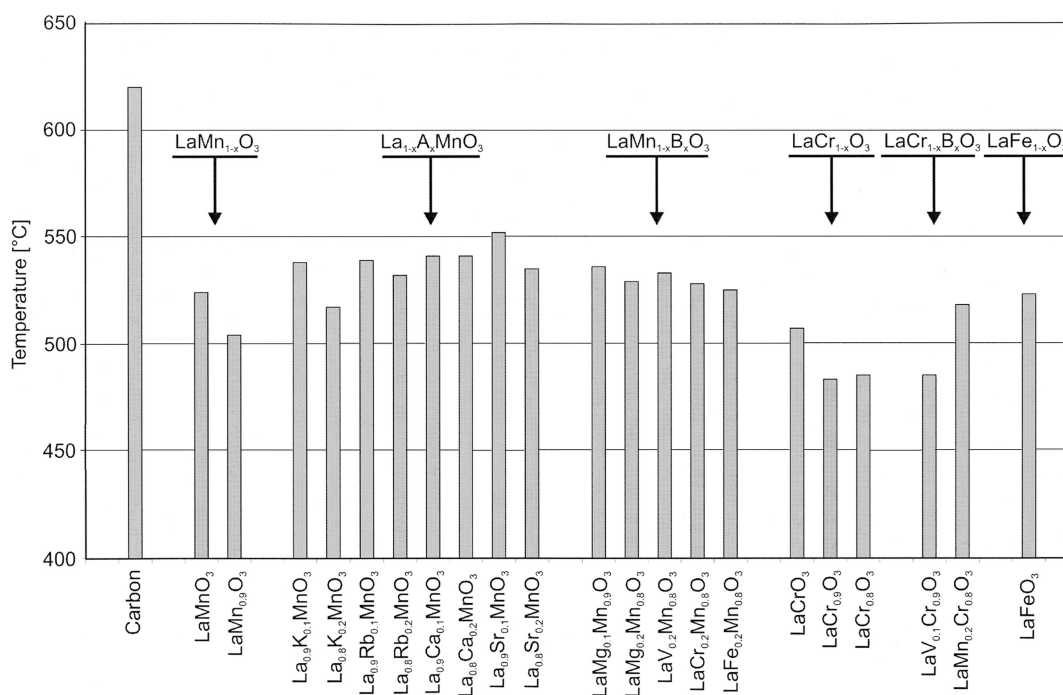


Fig. 4. Results of the screening tests on the activity (TPR peak temperature) of the various perovskite catalysts developed.

fuel the low sulphur (<50 ppmw) diesel produced by Haltermann named “CEC RF 06 99 BATCH 5” in line with the pending 2005 EEC regulations.

RESULTS AND DISCUSSION

Fig. 4 summarizes the TPO peak temperature values of all the perovskite catalysts tested. These materials show peak TPR temperatures significantly lower than 650 °C, characteristic of non-catalytic combustion. The superior activities of LaCr_{1-x}O₃ and LaCr_{1-x}B_xO₃ perovskites can be clearly noticed.

LaCr_{0.9}O₃ in particular shows significant catalytic activity (e.g. CO₂ production) at 400 °C in air and at the operating conditions employed, entails a CO₂ production peak temperature (T_p) at only 480 °C. Owing to the nature of chromium, this transition metal can in part undergo a valence shift from Cr³⁺ to Cr⁴⁺ so as to re-establish electroneutrality, despite the substoichiometric composition of the above mentioned chromite. The presence of Cr⁴⁺ was demonstrated to promote an increase of catalytic activity towards carbon combustion [Saracco et al., 1996]. The most likely explanation is that the perovskite can act as an oxygen pump towards the soot. Oxygen can indeed be made available to PM combustion in combination with a temporary shift of Cr valence from 4+ back to 3+. Oxygen molecules coming from the gaseous atmosphere can re-oxidise the perovskite and set back Cr⁴⁺ species.

Nevertheless, it is surprising how this catalyst is more active than catalysts belonging to LaMn_{1-x}O₃ perovskite system, which are much better catalysts for the combustion of methane or light hydrocarbons [Saracco et al., 1999b]. Further investigations are essential to explain this behaviour.

Anyhow, on the grounds of its superior activity, LaCr_{0.9}O₃ was selected for the catalytic activation of wall-flow monoliths. To these

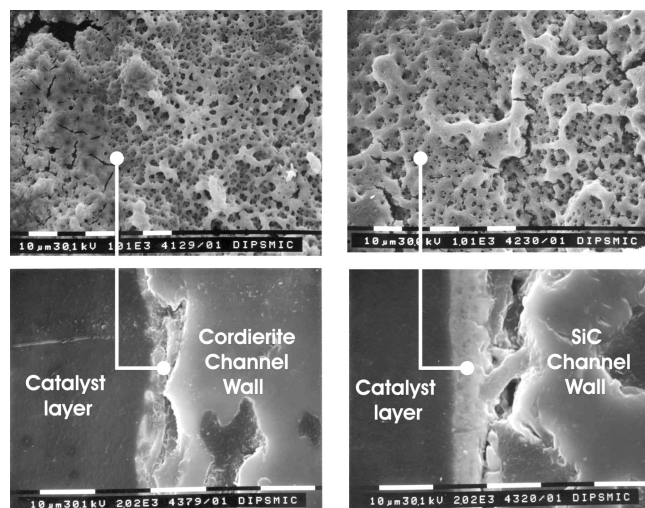


Fig. 5. Front and cross-section SEM views of layers of LaCr_{0.9}O₃ catalyst deposited on the inlet channel walls of the traps developed. Left: cordierite channel wall; right: silicon carbide channel wall.

merits, Fig. 5 shows SEM pictures of catalysts lined via *in situ* deposition on the upstream channel-walls of cordierite and silicon carbide wall-flow traps: the catalyst is in both cases strongly bonded to the support and the microstructure obtained appears extremely foamy. During combustion synthesis, the decomposition of reacting precursors generates a large amount of gaseous products in a very short period of time, which leads to a spongy catalyst morphology. This feature represents a great advantage, as it favours the contact between the catalyst and the soot that accumulates over it.

In order to correlate the concentration of the precursor solution with the load and the thickness of the catalyst deposited onto the

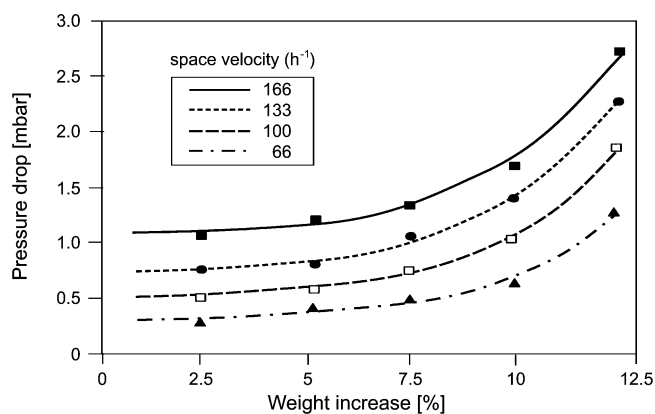


Fig. 6. Pressure drop throughout catalytic cordierite wall-flow monoliths as a function of the deposited catalyst weight and of the space velocity of air (room temperature).

monolith, a systematic study by combined SEM observation and gravimetric analysis was carried out. Catalyst layers with thickness ranging from 0.5 to 30 μm were obtained using precursor solution with a concentration from 50 up to 200 g/l. Moreover, the permeability of the wall-flow monolith with different catalyst load was assessed at different space velocity. The results obtained for cordierite are shown in Fig. 6: it can be seen that, despite the weight increase of the catalyst until 7.5%, the pressure drops are not significantly influenced. Conversely, starting from about 10% weight content, higher catalyst loads entail a steeper increase of pressure drop to values which may be unsatisfactory for a catalytic trap, as a consequence of the progressive plugging of the very small channel-wall pores (9 μm). Comparable results have been obtained for cordierite. Thus for our tests a catalyst load of 10 wt% has been chosen in order to maximise the catalytic wall-flow monolith performance without a remarkable permeability reduction.

Shifting to the analysis of the performance of the developed trap systems, Fig. 7 compares the results of the induced regeneration runs obtained with a catalytic and a non-catalytic cordierite wall-flow monolith. After loading of the trap up to about 110 mbar pressure drops, the regeneration is achieved only for the $\text{LaCr}_{0.9}\text{O}_3$ -catalysed trap, as soon as an inlet trap temperature of about 600 °C is reached by fuel-post-injection (the fuel penalty is about 20% of the

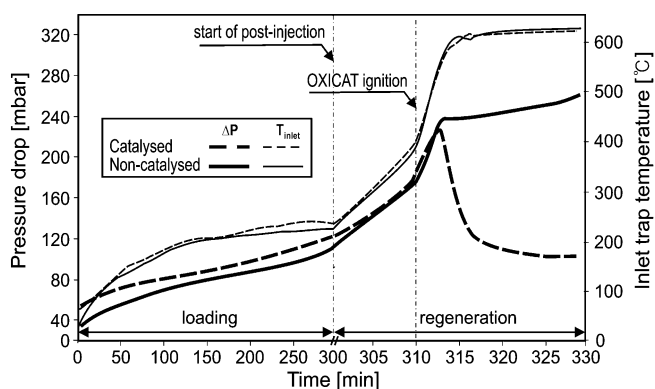


Fig. 7. Trap loading and regeneration cycles for a catalytic ($\text{LaCr}_{0.9}\text{O}_3$) and a non-catalytic wall-flow trap (Cordierite by Corning).

entire diesel burned) and its catalytic combustion over the OXICAT monolith. Conversely, the non-catalytic wall-flow progressively increases its pressure drop since soot accumulation in the monolith becomes higher and higher. This negative feature is complex to explain and is related to several factors influencing soot combustion kinetics (e.g., temperature, oxygen content in the flue gases). The need to burn out a significant flow rate of fuel so as to rise the exhaust gas temperature from 200 to 600 °C, leads to an almost complete depletion of the oxygen concentration downstream the OXICAT converter (only 0.5 vol% against the 9 vol% value emitted by the engine). While the catalyst succeeds to capitalise only this small amount of O_2 , this is simply not enough for the non-catalytic combustion. Furthermore, the temperature of the exhaust gases is higher than that at which the $\text{LaCr}_{0.9}\text{O}_3$ catalyst starts to be active (about 400 °C), but lower than that of maximum rate of non catalytic combustion measured by TPR experiments (about 650 °C; Fig. 2). For all the above reasons it turned out to be necessary to inject an additional air stream in the exhaust gases ahead of the OXICAT converter so as to regenerate the non-catalytic cordierite trap. This post injection of air led to an oxygen concentration of about 3 vol% entering the trap itself.

Direct visual observation of the inlet of both catalytic and non-catalytic traps (Fig. 8) shows, however, that regeneration is not complete. Soot combustion starts in the central monolith area. As soon as the soot is removed from the channels located in axial position, the exhaust hot gases concentrate their flow in that region owing to the reduced pressure drop and this makes the regeneration of the remaining parts of the trap difficult, not only because of the lower temperature of the peripheral zones of the trap, but also due to a poor oxygen concentration in this region. However, the regenerated zone is wider for the catalytic trap than for the non-catalytic one.

Another parameter affecting regeneration completeness is the thermal conductivity of the trap constituting material. The higher the thermal conductivity the more readily the heat released by soot combustion in a channel is transferred to adjacent channels, thereby igniting regeneration therein. As underlined in a previous paper [Fino et al., 2002b], cordierite materials are characterised by a rather low thermal conductivity value: $2.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, about 20 times less than SiC, which displays a thermal conductivity value of $55 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

As a consequence of this superior property of SiC, the regeneration of both catalytic and non-catalytic SiC wall-flow monoliths is nearly complete. As shown in Figs. 8, 9, after loading of the SiC-based traps up to a pressure drop of about 150 mbar (higher than

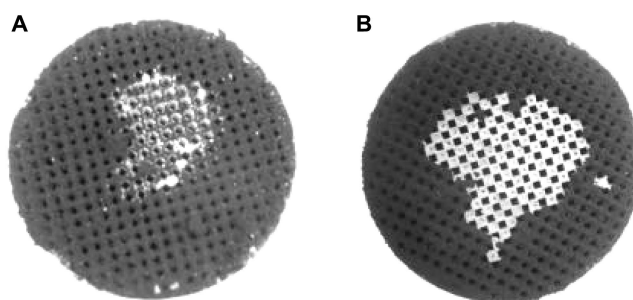


Fig. 8. View of cordierite wall-flow monolith after regeneration; A. non-catalysed trap; B. $\text{LaCr}_{0.9}\text{O}_3$ -catalysed trap. Inlet side in front of viewer.

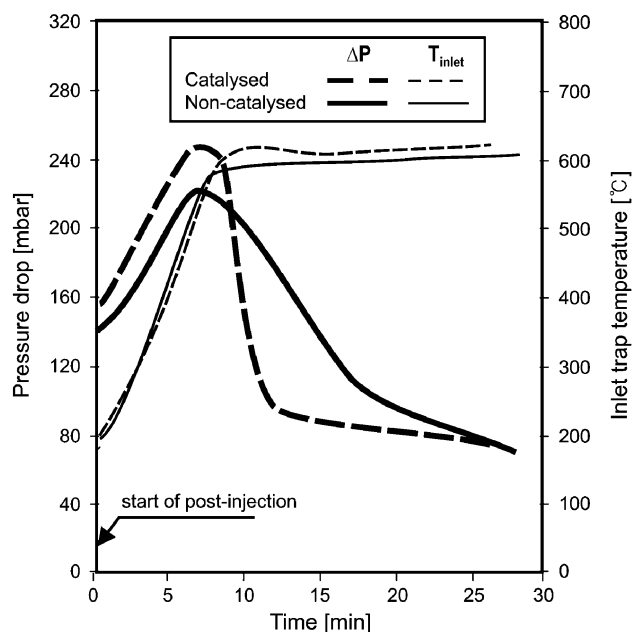


Fig. 9. Trap regeneration for a catalytic ($\text{LaCr}_{0.9}\text{O}_3$) and a non-catalytic wall-flow trap (SiC by Ibiden).

those on cordierite since SiC is characterised by a superficial filtering area about 2/3 that of former), both counterparts get regenerated at standard test conditions with no need of air post-injection. One may guess that successful regeneration for the non-catalytic SiC trap occurs, as opposed to the cordierite filter, because, due to the lower filtration area of the Ibiden SiC monolith, the trapped soot is flushed by a higher specific oxygen flow rate, which possibly helps sustaining the combustion of soot once ignited. The regeneration of the $\text{LaCr}_{0.9}\text{O}_3$ -catalysed trap is much faster than that with the non-catalytic ceramic filter, as soon as an inlet trap temperature of about 600 °C is reached by fuel-post-injection and catalytic combustion. By these means, it becomes possible to save a significant amount of fuel at any filter regeneration, therefore reducing running costs. It has to be kept in mind, however, that part of the fuel saving cost is compensated by a slight decrease of filter permeability owing to the presence of the catalyst.

CONCLUSIONS

Nanosized particles of several perovskite for diesel particulate combustion have been obtained by combustion synthesis, and the best one was lined via an ad-hoc developed technique over the channel walls of cordierite and SiC wall-flow traps. The results achieved for the SiC-catalysed monoliths suggest that this should be the best technical answer to defeat the serious problem of PM abatement to level less than 0.025 g/km, as required by the 2005 EEC regulations.

Both experimental and modelling studies are currently in progress to develop new and more active catalysts, to further improve the deposition technique for the sake of reducing the entailed pressure drop increase, and to design a trap structure optimised for this promising regeneration process.

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