

Towards practical application of lanthanum chromite catalysts for diesel particulate combustion

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Abstract

The effect of specific aging protocols (thermal treatment at 400 °C for 96 h and 650 °C for 24 h) in the presence of potentially deactivating species present in diesel exhaust gases (SO₂ and water), was studied on some promising catalysts (LaCrO₃, La_{0.9}CrO₃, La_{0.9}Na_{0.1}CrO₃, La_{0.9}Rb_{0.1}CrO₃, La_{0.8}Cr_{0.9}Li_{0.1}O₃) for diesel particulate combustion. The catalytic activity was almost completely retained. The catalyst La_{0.8}Cr_{0.9}Li_{0.1}O₃ was found to allow the best compromise between satisfactory catalytic activity and stability. This catalyst was then deposited on a SiC wall-flow trap, submitted to the same aging treatments and then tested in a diesel engine bench showing satisfactory stability. Engine bench tests on this catalytic trap (trap loading and regeneration inducing a temperature increase by the catalytic combustion of suitably post-injected fuel) showed that the presence of the catalyst in the wall-flow trap enabled both a more complete regeneration and a significant reduction of the regeneration time compared to that of a non-catalytic trap, with a consequent saving of post-injected fuel.

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1. Introduction

Diesel engines provide the society with great benefits since they are widely used to transport goods and people. The Diesel engine is also being increasingly used to power passenger cars and vans. In several European countries, the current penetration of the Diesel engine into the light-duty and passenger cars market exceeds 50% market share. In recent years, increasing attention has been paid to the emissions from Diesel engines which include carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x) and particulate matter (PM), which consists mostly of carbonaceous soot and a soluble organic fraction (SOF) of hydrocarbons condensed or adsorbed over the soot. The US Environmental Protection Agency, EPA, estimates that 20% of all particulates are due to heavy-duty diesel truck engines alone [1]. Furthermore, they believe that diesel particulates are highly detrimental to human health and have classified it as a likely carcinogen [2]. In general, diesel particulate matter smaller than 10 μm, PM₁₀, not only penetrates deeper and remains longer in the lungs than larger

particles, but it also contains large quantities of organic materials that may have significant long-term health effects. In response, a 90% reduction in particulate emissions has been mandated for diesel trucks by 2007 and legislators in the United States and Europe have imposed severe emission limits.

The control of emissions from Diesel engines presents many challenges for the engine engineers and catalyst developers. The use of a multifunctional catalytic filter that combines filtration and oxidation of the captured particulate matter seems to be the most promising technique in this context [3]. The key challenge is to find a catalyst that decreases the combustion temperature of soot as much as possible so as to limit the energy requirements of periodic trap heating for regeneration purposes. Catalytic traps based on wall-flow ceramic monoliths (shallow-bed filters), combined with an oxidation catalyst deposited onto their inlet channel walls, are being developed and tested at our labs. These traps can be periodically regenerated by a peculiar use of last generation Common-Rail Diesel engines: some fuel is post-injected and gets burned out over an oxidation catalyst thereby heating up the flue gases and the particulate-laden trap until catalytic combustion of soot is ignited.

Focusing on diesel particulate, recent articles of ours concerned the development of perovskite catalysts, which showed high diesel particulate combustion activity as well as

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the analysis of their reaction mechanism, dominated by their capability of weakly chemisorbing suprafacial oxygen species spilling-over the particulate [4,5]. The present work is focused on the stability of the most interesting catalysts produced, aged at different operating temperatures and gaseous atmospheres: dry, wet and SO₂-laden air. The catalysts stability to repeated reaction cycles was also tested. On the basis of the obtained results, the suitability of the mentioned catalysts for application in the treatment of actual diesel exhaust will be finally discussed.

2. Experimental

2.1. Catalyst preparation

A series of perovskite samples (LaCrO₃, La_{0.9}CrO₃, La_{0.9}Na_{0.1}CrO₃, La_{0.9}Rb_{0.1}CrO₃, La_{0.8}Cr_{0.9}Li_{0.1}O₃) were prepared via a highly-exothermic and self-sustaining reaction, according to the *combustion synthesis* method [6]. A concentrated aqueous solution of various precursors (metal nitrates and urea) was located in a oven at 600 °C for few minutes in a crucible, so as to ignite the highly-exothermic and self-sustaining reactions. These catalysts were found to display a good activity towards the catalytic oxidation of soot in earlier investigations [4,5].

The obtained catalysts were then ground in a ball mill at room temperature and submitted to physical and chemical characterisation.

2.2. Catalyst characterisation

X-ray diffraction (PW 1710 Philips diffractometer) was used to check the achievement of the oxide structure.

Compositional analysis (dissolution in HNO₃/HCl followed by atomic absorption analysis with a Perkin-Elmer 1100B spectrometer) performed on all prepared samples, confirmed that the overall amounts of the various elements of interest (La, Li, Cr, Na, Rb) were consistent with that used in the precursors and was compatible with the phases detected by X-ray diffraction (sensitivity: 4%).

Field emission scanning electron microscope (FESEM—Leo 50/50 VP with GEMINI column) was employed to analyze the microstructure of the crystal aggregates of the catalysts as prepared and after aging.

Conversely, transmission electron microscopy (TEM—Philips CM 30 T) was employed to assess the size and morphology of the oxide crystals themselves.

The specific surface areas of the prepared catalysts were evaluated from the linear parts of the BET plot of N₂ isotherms, using a Micromeritics ASAP 2010 analyzer. For bulk and non-porous catalysts as perovskite or delafossite ones the specific surface area can be directly related to the average crystal size.

Oxygen temperature programmed desorption experiments were also performed on the catalysts in a Thermoquest TPD/R/O 1100 analyser, equipped with a thermal conductivity (TCD) detector. A fixed bed of catalyst powders was enclosed in a quartz tube and sandwiched between two quartz wool layers;

prior to each temperature programmed desorption (TPD) run, the catalyst was heated under an O₂ flow (40 ml/min) up to 750 °C. After 30 min stay in O₂ flow at this temperature as a common pre-treatment, the reactor temperature was then lowered down to room temperature by keeping the same flow rate of oxygen, thereby allowing complete oxygen adsorption over the catalyst. Afterwards, helium was fed to the reactor at 10 ml/min flow rate and kept up for 1 h at room temperature in order to purge out any excess oxygen molecule. The catalyst was then heated up to 1100 °C at a constant heating rate of 10 °C/min using helium under a flow rate of 10 ml/min. The O₂ desorbed during the heating was controlled by the TCD detector.

2.3. Catalytic activity assessment

The activity of the prepared catalysts towards soot combustion was analysed by temperature programmed combustion (TPC) carried out in a fixed-bed micro-reactor, according to the standard operating procedures described in detail by Fino and Specchia [7] air was fed at the constant rate of 50 ml/min to the fixed bed constituted of a mixture of carbon and powdered catalyst (1:9 mass basis). All experiments were performed by using, instead of real diesel soot, an amorphous carbon by Cabot Ltd. (particle average diameter: 45 nm in diameter; BET specific surface area: 200 m²/g; ashes content after calcination at 800 °C: 0.34%; adsorbed water moisture at room temperature: 12.2 wt.%; no adsorbed hydrocarbons and sulphates). This allows to regard as conservative the results obtained, since amorphous carbon is more difficult to burn than real diesel soot.

The reaction temperature was controlled through a PID-regulated oven and varied from 200 to 700 °C at a 5 °C min⁻¹ rate, meanwhile feeding air at a 50 N cm³/min flow rate. The analysis of the outlet gas was performed via NDIR analysers (ABB).

A TPC run was also performed in the absence of the catalyst so as to set a reference for comparison.

The peak temperature T_p of the TPC plot of the outlet CO₂ concentration was taken as an index of the catalytic activity: the lower the T_p value, the higher the catalytic activity. Furthermore, on the grounds of the area of the TPC plots, estimates of the overall CO₂ amount produced per run were calculated and the selectivity of carbon combustion towards CO₂ (η_{CO_2}) was estimated.

2.4. Catalyst ageing procedure

A catalyst used for combustion of soot in diesel emissions may lose its activity due to several reasons: temporary temperature rise-up to unusual values (>600 °C, due to the sudden burning of a large soot aggregates), poisoning effect caused by some components of diesel exhausts (e.g. SO₂, H₂O), prolonged working time at high temperature. In line with earlier investigations on other soot-combustion catalysts [8], in order to consider separately the effect of each of these factors, aging treatments were performed under these conditions:

- thermal ageing in dry air at 400 and 650 °C for 96 and 24 h, respectively;
- thermal ageing at the same temperature and time values under wet air, containing 12 vol.% of moisture obtained by humidification in thermostasized bubble column;
- thermal ageing at the same temperatures in air containing 500 ppmv SO₂, a value much larger than current SO₂ levels in exhaust gases (a few ppms), fixed for the sake of accelerating the possible effect of this specific poison.

All these treatments were carried out in a tubular furnace with a gaseous flow of 100 ml/min. In addition, the possible loss of catalytic activity due to prolonged catalyst operation was checked. Purpose, the catalysts were mixed with carbon (weight ratio 9:1) and kept at 650 °C for 1 h to achieve the complete carbon combustion. This treatment was repeated by using the same catalyst sample so as to carry out up to six consecutive combustion cycles. Most of the physical and chemical characterisation analyses described above were replicated on aged samples.

2.5. Catalytic trap preparation

The best catalyst (La_{0.8}Cr_{0.9}Li_{0.1}O₃) was deposited by *in situ* combustion synthesis [9], directly over the wall-flow filters. The ceramic support was dipped in the aqueous solution of its precursors and then placed into an oven at 600 °C. The aqueous phase was rapidly brought to boil, the precursors mixture ignited and the synthesis reaction took place *in situ*. The support selected was a silicon carbide (SiC) filter produced by IBIDEN (cell structure = 14/200, diameter 30 mm, length = 6–12 in., pore diameter of channel walls = 9 μm, porosity of channel walls = 42%) which was found to be chemically compatible with the selected catalyst. The load of catalyst deposited was assessed by gravimetric analysis (5.2 wt.%). The morphology of the deposited catalyst layer was analysed by FESEM observation, whereas catalyst adhesion to the monolith was assessed by a tailored ultrasonic bath test procedure [9].

2.6. Catalytic trap ageing procedure

The catalytic trap was submitted to thermal ageing at 650 °C in air for 72 h and in air containing 500 ppmv of SO₂ for 24 and 72 h. These treatments were carried out in a furnace with a gaseous flow of 100 ml/min.

2.7. Diesel engine bench tests

The developed trap was tested over real diesel exhaust gases on an engine bench (Kubota 1000 cm³ IDI engine, capable of up to 23.5 hp at 3000 rpm), where the temperature and gas composition before and after the trap can be controlled and monitored, as well as the evolution of the pressure drop through the trap (a sign of soot accumulation therein). A detailed description of the plant was provided by Fino and Specchia [7].

The exhaust gas superficial velocity across the trap could be controlled at a fixed value by measuring the exhaust flow rate

through a volumetric flow controller connected to a throttling valve placed on a 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 temperatures were measured by K-type thermocouples mounted at axial position. The soot concentration in the exhaust gases before and after the trap was measured by isokinetically sampling a small flue-gas flow rate through a pump and by collecting the suspended particulate on a two-filter system (PALLFLEX 47 TX 40 HI 20 W); the two measures allow to determine the filtration efficiency. Finally, gas phase composition could be monitored through a continuous analyser by Elsag-Bailey (NDIR for NO, CO, CO₂, SO₂; FID for overall HC; paramagnetic for O₂). In line with the pending 2005 EU regulations, all the tests were carried out by using a low-sulphur (<50 ppmw) diesel oil produced by Agip Petroli.

The following standard bench test procedure was adopted. The trap was loaded by letting comparatively cold exhaust gases flow through it until a 90–120 mbar pressure drop was reached (corresponding to a particulate hold-up of about 10 g/l). Then, regeneration was induced by post-injecting some fuel with a metering pump and by burning it with an oxidizing honeycomb catalyst (OXICAT by Johnson Matthey) placed just upstream the trap. The time needed for the complete trap regeneration (e.g. combustion of soot hold-up) is an index of catalyst performance as well as of completeness of soot combustion. The higher the catalyst activity the lower the time required to regenerate the trap. The completeness of the regeneration process was indicated by the decrease of the trap pressure drop till a value practically equal to that measured at the beginning of the loading phase.

A twin run on a virgin, non-catalytic trap was also performed for the sake of comparison. Besides, six repeated bench tests were performed with the same catalytic trap in order to investigate its performance after prolonged usage. The same catalyst ageing procedure employed on the powders was applied to twin catalytic traps, as well.

3. Results and discussion

Fig. 1 shows the TPC plots obtained with each catalyst tested, whose peak temperatures are listed in Table 1 together with the T_p value of non-catalytic combustion (650 °C). As expected, all the catalysts significantly lower the combustion peak temperature compared to that of the non-catalytic combustion. An activity order can be outlined as follows:

- (1) the La_{0.8}Cr_{0.9}Li_{0.1}O₃ shows by far the best activity ($T_p = 408$ °C);
- (2) the other perovskite catalysts characterized by lanthanum deficiency (i.e. La_{0.8}CrO₃, La_{0.9}CrO₃, La_{0.9}Na_{0.1}CrO₃, La_{0.9}Rb_{0.1}CrO₃, La_{0.9}K_{0.1}CrO₃) exhibit quite similar activities (T_p ranging from 441 to 455 °C);
- (3) the unsubstituted LaCrO₃ chromite is by far the less active catalyst ($T_p = 495$ °C);
- (4) the ageing treatment in the presence of SO₂ and H₂O leads to a limited deactivation of the catalysts;

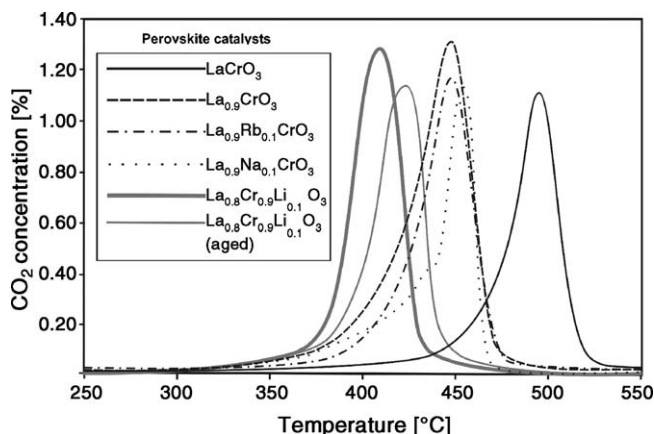


Fig. 1. Results of the TPC runs performed with all the selected perovskite catalysts. The curve related to the best performing catalyst ($\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$) are reported in grey, for this case only, the performances as prepared and after ageing at $650\text{ }^\circ\text{C}$ for 24 h in air.

(5) the CO_2 selectivity of the best performing catalyst ($\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$) as prepared was 96%, the other catalysts being characterised by lower values but never less than 87% (LaCrO_3).

A possible reason of the different behaviour of the $\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$ catalyst might be linked to the relative amount of active oxygen species present on the catalyst surface, ready to spill-over the carbon and promote its combustion [10]. A previous study [4], focused on perovskite catalysts, showed that these materials were able to deliver oxygen species, depending on temperature:

- α -Oxygen: low-temperature suprafacial species, weakly chemisorbed on the surface of the perovskite, desorbed in the $300\text{--}600\text{ }^\circ\text{C}$ range, and related to surface oxygen vacancies;
- β -Oxygen: high-temperature intrafacial one, less easy to desorb and therefore more bound to the perovskite structure, desorbed above $600\text{ }^\circ\text{C}$ and related to the bulk nature of the catalyst.

The $\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$ catalyst, which showed the best catalytic performance, can chemisorb suprafacial oxygen species more than the others because it maintains its electroneutrality by means of oxygen vacancies instead of increasing the oxidation state of the B site.

Moreover, this catalyst is able to weakly chemisorb α -oxygen species in the temperature range of interest of the

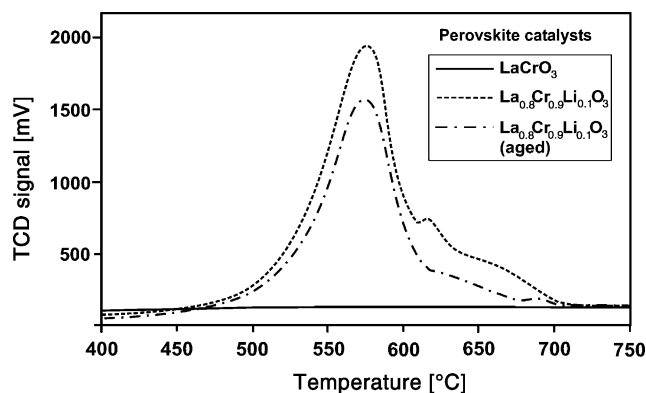


Fig. 2. Results of the temperature-programmed desorption tests of the $\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$ (fresh and after ageing at $650\text{ }^\circ\text{C}$ in the presence of SO_2) and the fresh LaCrO_3 catalyst.

catalytic soot combustion and that these oxygen species were directly involved in the combustion process. Oxygen TPD runs were carried out on purpose in order to possibly detect and quantify any oxygen species weakly chemisorbed over the two of the catalysts under investigation: the reference LaCrO_3 , and the most active $\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$.

The results of these TPD runs are shown in Fig. 2. A remarkable difference can be noticed in the behaviour of the two catalysts. The perovskite basic catalyst showed a very limited desorption of α -oxygen, whereas a significant presence of these oxygen species was noticed for the other one. These oxygen species and their mobility over the catalyst surface should be the primary responsible for the good performance of the $\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$ catalyst as opposed to the LaCrO_3 one. The most active single-phase catalyst ($\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$) is clearly characterized by the highest amount of weakly chemisorbed α -oxygen which can possibly undergo *spill-over* over the carbon particulates in contact with the catalyst. This should maximize the number of reaction events per unit time and carbon mass thereby boosting reaction kinetics at temperatures even lower than those at which it is desorbed in TPD runs owing to the favourable reaction thermodynamics. In other words, during TPD experiments the only free energy available to oxygen to leave the catalyst is thermal energy. During reaction runs, carbon provides additional free energy to α -oxygen and help exploiting it at temperatures lower than those at which it is desorbed during simple TPD runs.

A pre-requisite for practical applicability of a catalyst is not only its activity but also its stability. As mentioned earlier, no serious deactivation was found after any of the tested ageing

Table 1
TPC peak temperatures ($^\circ\text{C}$) after different ageing treatments

T_p ($^\circ\text{C}$)	Fresh	96 h $400\text{ }^\circ\text{C}$ dry	96 h $400\text{ }^\circ\text{C}$ wet	96 h $400\text{ }^\circ\text{C}$ SO_2	24 h $650\text{ }^\circ\text{C}$ dry	24 h $650\text{ }^\circ\text{C}$ wet	24 h $650\text{ }^\circ\text{C}$ SO_2
No catalyst	650	–	–	–	–	–	–
LaCrO_3	495	529	522	505	532	536	505
$\text{La}_{0.9}\text{CrO}_3$	447	457	456	458	479	477	465
$\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$	455	492	474	478	489	487	470
$\text{La}_{0.9}\text{Rb}_{0.1}\text{CrO}_3$	448	465	470	446	472	477	466
$\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$	408	425	433	434	429	434	422

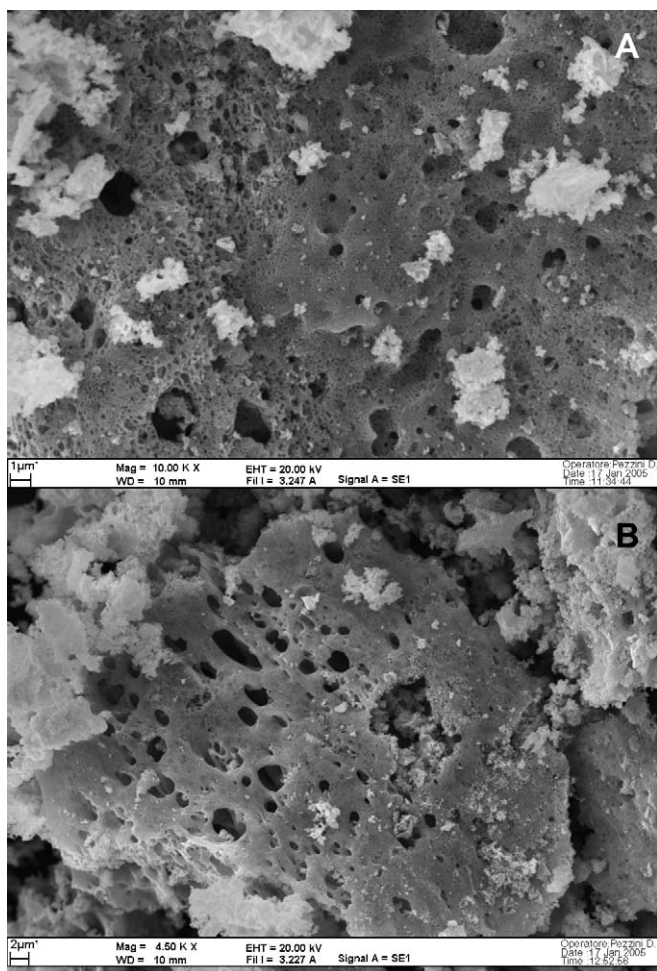


Fig. 3. FESEM views of the $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ catalyst as prepared (A) and after ageing at $650\text{ }^\circ\text{C}$ for 24 h in air (B).

protocols. The highest deactivation (limited, however, to an increase of about $40\text{ }^\circ\text{C}$ of the T_p value, see Table 1) was noticed for high temperature hydrothermal ageing, which mostly affected the specific surface area of the catalyst and slightly reduced the selectivity to CO_2 (η_{CO_2}). Further runs were then performed in order to check whether the catalyst remains stable after repeated carbon combustion cycles. After each combustion cycle a portion of the catalyst was used to perform a standard TPO run in order to detect any possible variation of the catalytic activity. In order to draw a comparison, the same sequence of combustion cycles was carried out also on all the catalysts selected. The obtained T_p data confirm that the activity remains almost unaffected.

FESEM views of the microstructure of the crystal aggregates of the $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ catalyst (Fig. 3) did not show any particular modification after ageing. A similar behaviour was noticed for all the other catalysts prepared. The microstructure remained very foamy, a typical feature of combustion synthesised catalysts which should remarkably favour the contact between soot and catalyst even under loose contact conditions. Conversely, the TEM micrographs of $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ reported in Fig. 4 clearly demonstrate that the significant reduction in the BET surface area of the catalysts before and after ageing at $650\text{ }^\circ\text{C}$ in air, reported in Table 2, was mostly ascribable, as expected, to a certain growth of the perovskite crystals. This BET specific surface area decrease did not significantly affect the catalytic activities, possibly because the increase in crystal dimensions did not change remarkably the catalyst–carbon contact conditions.

A question still to be clarified lies in the effect of water vapour, that seems to be slightly detrimental. To these merits, if the runs at $650\text{ }^\circ\text{C}$ under dry or humid conditions are compared, this effect cannot be primarily attributed to specific surface area reduction, as both the ageing tests mentioned lead approxi-

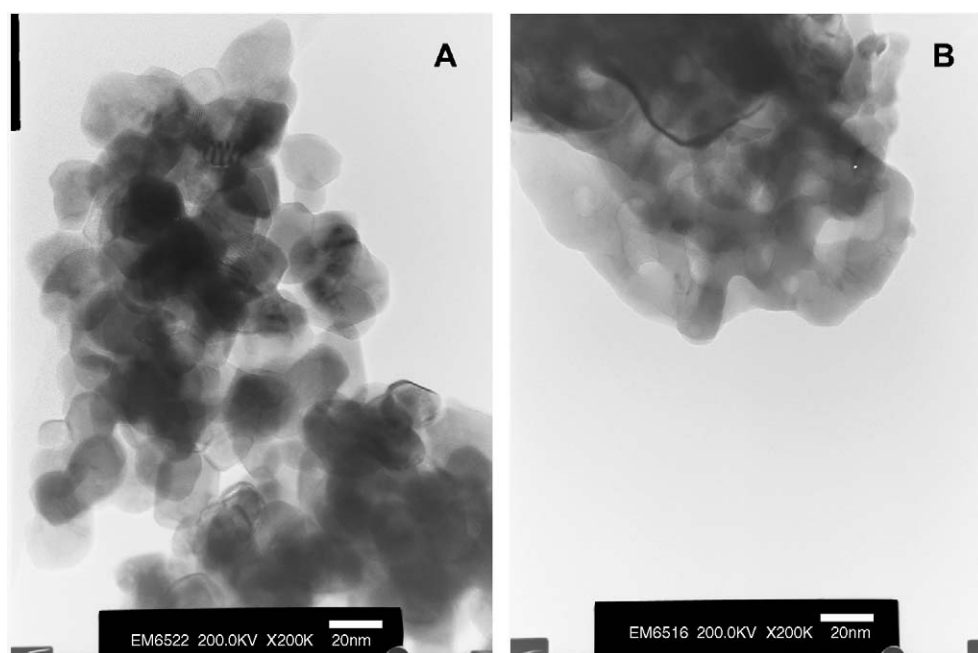


Fig. 4. TEM micrographs of the $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ catalyst as prepared (A) and after ageing at $650\text{ }^\circ\text{C}$ for 24 h in air (B).

Table 2
BET values of the different catalysts after ageing

BET (m ² /g)	Fresh	96 h 400 °C dry	96 h 400 °C wet	96 h 400 °C SO ₂	24 h 650 °C dry	24 h 650 °C wet	24 h 650 °C SO ₂
LaCrO ₃	17.53	16.35	16.98	16.04	10.44	9.45	15.84
La _{0.9} CrO ₃	16.46	14.23	13.95	13.27	9.22	9.13	13.04
La _{0.9} Na _{0.1} CrO ₃	17.09	18.06	16.67	16.43	6.94	6.43	15.23
La _{0.9} Rb _{0.1} CrO ₃	7.72	7.25	7.07	6.84	4.88	4.49	6.62
La _{0.8} Cr _{0.9} Li _{0.1} O ₃	12.96	11.05	12.98	11.22	8.93	10.56	11.17

mately to same reduction value. A modification of the surface active sites has to be thought of. Specific investigations are needed to better clarify this point.

A peculiar feature of the ageing experiments was the effect of the presence of SO₂ in the atmosphere. It is worth noticing that SO₂ hampered to some extent the effect of thermal ageing at 650 °C by limiting the BET area decrease after the 24 h stay at 650 °C and by entailing a very limited increase in the T_p temperature.

A possible explanation for this behaviour might lie in the formation of sulphates, over the crystal surface, which hamper grain growth and catalyst sintering. In order to ascertain this, specific XRD analyses were performed. The XRD spectra (not shown) of the “as-prepared” and of the aged catalysts at 650 °C under SO₂-rich atmosphere put into evidence the presence of sulphate species after ageing on all the catalysts tested, which confirmed the above interpretation [11]. It may be guessed that the presence of such sulphate species may interfere with the capability of the catalyst to deliver active oxygen species to carbon. However, a specific TPD run carried out on the SO₂-aged La_{0.8}Cr_{0.9}Li_{0.1}O₃ catalyst led to the encouraging plot shown in Fig. 2, which shows just a limited decrease of the overall amount of chemisorbed oxygen and then explains the very limited decrease of catalytic activity noticed (Table 1).

On the grounds of these rather promising results, catalytic trap preparation and bench testing were undertaken with confidence. Due to standardised vibration tests, the adhesion of

the deposited catalytic layer was found to be rather good (catalyst loss lower than 0.8 wt.% after tests representative of an entire operating lifetime of a trap [9]).

Coming to the analysis of the performance of the developed trap systems, Fig. 5 compares the results of the loading and regeneration runs performed with the La_{0.8}Cr_{0.9}Li_{0.1}O₃ fresh and aged-catalysed and the non-catalytic SiC wall-flow monolith. A striking difference can be noticed for the catalysed and the virgin traps. A rather high fuel post-injection is required (0.13 kg/kg of exhaust gases), leading to inlet trap temperatures well exceeding 600 °C, to achieve regeneration of the uncatalysed trap.

This scenario is significantly influenced by the presence of the catalyst. The La_{0.8}Cr_{0.9}Li_{0.1}O₃ catalyst could in fact induce trap regeneration with a lower fuel post-injection rate (0.10 kg of fuel per kg of exhaust gases) sufficient to increase the inlet trap temperature to just 550 °C. Furthermore, regeneration is faster and more complete than for the non-catalytic trap. It is probable that the catalytic reaction starts operating even below 400 °C during the post-injection phase. However, to achieve a rapid and complete regeneration 550 °C need to be approached. Under these operating conditions it is likely that portions of soot might get burned by non-catalytic direct oxidation with oxygen owing to some localised over-heating. The role of the catalyst remains though essential either to initiate and support soot combustion or to lead regeneration to a higher degree of completeness.

As far as the effect of ageing treatments on the trap are concerned, they were carried out at 650 °C both in presence and

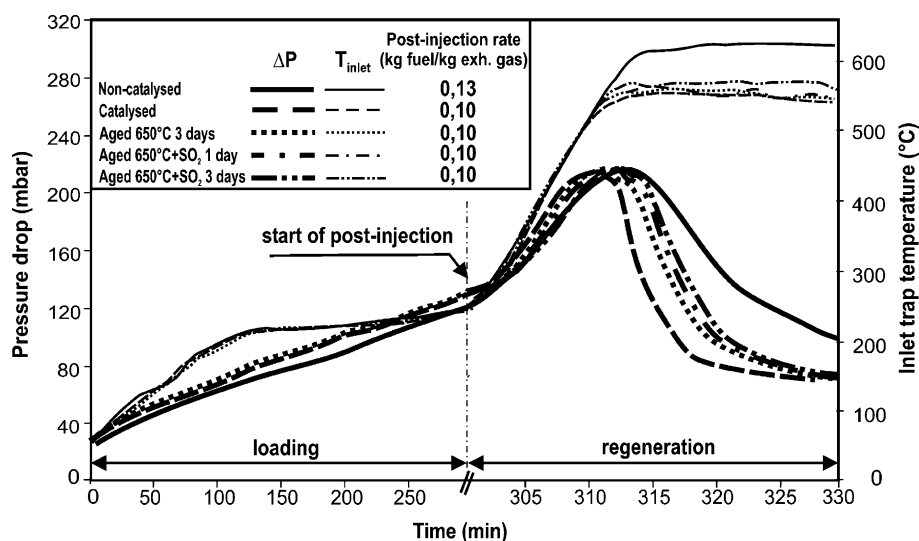


Fig. 5. Results of loading and regeneration runs for the catalysed (La_{0.8}Cr_{0.9}Li_{0.1}O₃) SiC wall-flow trap before and after thermal ageing in air at 650 °C for 72 h, in air containing 500 ppmv of SO₂ for 24 and 72 h and for the non-catalytic one.

absence of SO₂ in order to better evaluate both effects. They did not induce significant deactivation: the regeneration starting temperatures, times and completeness remained nearly the same of the fresh catalytic trap for an equal amount of post-injected fuel (0.10 kg of fuel per kg of exhaust gases). However, as opposed to the runs performed on powder catalysts, the activity of the catalysed filters after SO₂ aging slightly decreased, to an extent proportional to the duration of exposition. Conversely, the regeneration time increased up to 20% after six repeated combustion cycles.

4. Conclusions

The deactivation of a series La–Cr perovskite catalysts for diesel particulate combustion was investigated. Thermal ageing under different conditions and poisoning with SO₂ have been performed both on catalyst powders and on La_{0.8}Cr_{0.9}Li_{0.1}O₃ catalysed traps. The presence of water vapour does not practically modify the catalytic activity towards the particulate combustion. The high temperature aging treatments entailed the highest reduction of the BET surface area. An increase of the crystal size after all thermal treatment was confirmed by TEM micrographs, too. However, the highest increase of T_p did not overpass 40 °C, which keeps the activity of the aged catalysts still at quite interesting levels for practical application. The ageing of catalysts lined on a wall-flow trap lead to somehow different results: thermal aging did not modify the activity of the trap during the regeneration possibly on the grounds of a stabilization effect of the ceramic structured support. Conversely, the activity of the catalytic trap gets a bit

worse after the SO₂ poisoning. In line with Rosso et al. [12], catalyst promoters are being developed to cope with this slight deactivation. The progressive reduction of S content in the fuel (<10 ppmw are expected for EURO V legislation to be enforced in 2008) may also be helpful in this context.

An experimental test campaign is currently in progress to verify this potential at a catalytic trap level on real exhaust gases. Moreover, any possible loss of toxic chromium species will be ascertained at this level.

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