Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 119 (2007) 257–261

CATALYSIS TODAY

www.elsevier.com/locate/cattod

$LiCoO_2$ catalyst for diesel particulate abatement

D. Fino [*], E. Cauda, D. Mescia, N. Russo, G. Saracco, V. Specchia

Materials Science and Chemical Engineering Department, Politecnico di Torino,
Corso Duca degli Abruzzi 24, 10129 Torino, Italy

Abstract

This paper concerns the development of a $LiCoO_2$ catalyst which shows appreciable activity towards the catalytic combustion of soot already at 300 °C. An *in situ* combustion synthesis method was then tailored to the preparation of a $LiCoO_2$-catalysed trap based on a silicon carbide wall-flow monolith. Engine bench tests on this catalytic trap (trap loading with soot and then its regeneration induced by a temperature rise entailed by catalytic combustion of post-injected fuel) showed that the presence of the catalyst in the wall-flow trap enables both a more complete regeneration (78% opposed to just 52% of the non-catalytic trap) and a reduction of the regeneration time, with consequent saving of post-injected fuel.

Keywords: Diesel particulate; Catalytic combustion; $LiCoO_2$; Catalytic wall-flow trap

1. Introduction

Diesel engines provide the society with great benefits since they are widely used to transport goods and people. The diesel engine is being increasingly used to power passenger cars and vans; particularly 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 diesel engine emissions, which include carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x) and particulate matter (PM). Diesel particulate consists mostly of carbonaceous soot and a volatile organic fraction (VOF) 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, diesel particulates are highly detrimental to human health and have been classified as likely carcinogenic [2]. In general, diesel particulate matter smaller than 10 μm (PM10) do not only penetrate deep in the lungs but remain there longer than larger particles. Moreover, it also contains large quantities of organic materials that may have significant long-term health effects. As a consequence, 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 for next generation vehicles.

The control of emissions from Diesel engines presents many challenges for the engineers and catalyst developers. The use of 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 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. This paper describes the encouraging results obtained with an innovative catalyst based on lithium cobaltite. An analysis on the reaction mechanism is also provided and the prevalent importance of suprafacial oxygen species on the soot oxidation activity is hypothesized.

2. Materials and methods

2.1. Catalyst development

After a wide screening of soot–combustion catalysts [4–6], some delafossites were selected as the most promising ones.

---

[*] Corresponding author. Tel.: +39 011 5644710; fax: +39 011 5644699.
E-mail address: debora.fino@polito.it (D. Fino).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.08.029

Powders of these catalysts ($LiCrO_2$, $LiCoO_2$, $LiNiO_2$) were obtained by an in-house developed method (solution combustion synthesis [6]) based on the highly exothermic and self-sustaining reactions occurring between metal nitrate precursors and urea (see [7] for details). This technique is particularly suited to produce bulk catalysts based on foamy aggregates of nanosized crystals. Layers of these catalysts coated onto the soot trap channels could effectively improve the local catalyst–soot contact conditions, a critical issue in this field, and keep pressure drop at an acceptable level. The preparation of lithium cobaltite is considered as an example:

$$6LiNO_3 + 6Co(NO_3)_2 + 14N_2H_4CO \rightarrow 6LiCoO_2 + 28H_2O + 14CO_2 + 23N_2$$

The catalyst was then ground in a ball mill at room temperature. X-ray diffraction (PW 1710 Philips diffractometer) was used to check the achievement of the delafossite oxides structure. The specific surface area of the prepared catalyst was evaluated using a Micrometrics ASAP 2010 BET analyzer. Direct observation of the nanosized spinels crystals was performed by transmission electron microscopy (TEM, Philips CM 30T). Conversely, a field emission scanning electron microscope (FESEM, Leo 50/50 VP with Gemini column) was used to analyze the microstructure of the catalysts crystal aggregates.

The activity of the prepared catalyst towards soot combustion was analyzed 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 [4]: air was fed at the constant rate of 50 N cm^3 min^{-1} to the fixed bed constituted of a mixture of carbon and powdered catalyst (1:9 mass basis) [4]. Moreover, the activation energy of soot combustion over the prepared catalysts was measured via the Kissinger method [8] on the grounds of DSC runs carried out in a Perkin-Elmer DSC-Pyris equipment according to the operating procedures described by Fino et al. [9].

Finally, some temperature-programmed desorption analyses were performed in a Thermoquest TPD/R/O 1100 analyzer, equipped with a thermal conductibility (TCD) detector. The catalysts were purged with He and then saturated with O_2 at room temperature; they were then heated up to 1100 °C and the O_2 desorbed during heating was detected by the TCD detector [6]. X-ray diffraction was once again performed on the catalysts which underwent TPD analysis, to assess whether the delafossite structure had been retained or not, and to check the possible appearance of new phases.

2.2. *Catalytic trap development*

The $LiCoO_2$ catalyst was deposited by *in situ* solution combustion synthesis [4] 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 Céramiques Techniques et Industrielles (Salindres, France) (cell structure = 14/200, diameter 58 mm, length = 150 mm; pore diameter of channel walls = 9 mm, porosity of channel walls = 40%) which was found to be chemically compatible with the catalyst. The load, adhesion and the thickness of the catalyst deposited onto the monolith were measured by gravimetric analysis, ultrasonic bath test and FESEM observation, respectively. The amount of delafossite deposited was 10 wt.% for the catalytic trap tested as described in the following.

The developed trap was tested over real Diesel exhaust gases on an engine bench (Kubota 1000 cm^3 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 filtration efficiency and 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 [4]. The catalytic wall-flow was located along the main line of the exhaust stream. 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 soot concentration in the exhaust gases was measured by isokinetic sampling of a small flue-gas flow rate through a pump and by collecting the suspended particulate using a two-filters system. Finally, the gas phase composition could be monitored through continuous analyzers (ABB). According to a standard loading-regeneration procedure, the trap is loaded by letting comparatively cold exhaust gases flow through it until a 120 mbar pressure drop is reached. Then, regeneration is induced by post-injecting some fuel with a metering pump and by burning it with an oxidizing honeycomb catalyst (by Johnson Matthey Ltd.) placed upstream the trap. The time needed for a complete trap regeneration (e.g. combustion of trapped soot) is an index of catalyst performance. The higher the catalyst activity the lower the required regeneration time. The completeness of the regeneration process, measured by weighting the trap before and after regeneration, is to be considered a further sign of an effective catalyst performance.

3. Results and discussion

A crucial factor affecting the catalytic combustion of soot lies in the contact conditions between the catalyst and its carbonaceous counter part. Fig. 1A shows a SEM picture of $LiCoO_2$ delafossite catalyst produced via solution combustion synthesis. Its microstructure appears foamy. During combustion synthesis, the decomposition/combustion 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 formation of rough interfaces for the catalyst powder agglomerates, which in turn intensify the contact conditions between the catalyst and the soot that accumulates over them. In the present context, delafossite crystals having a size of the same order of magnitude of that

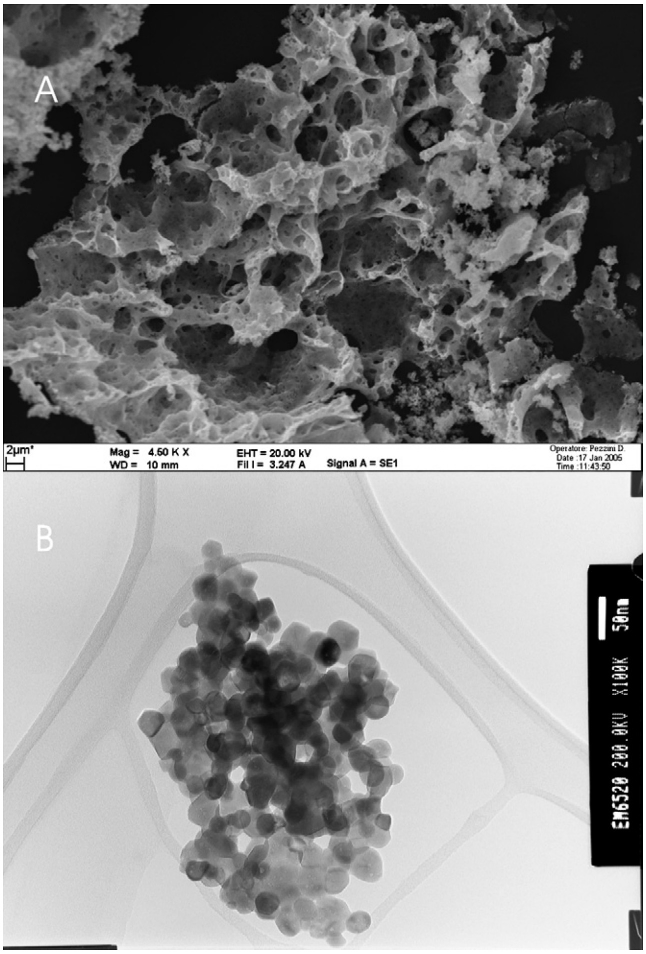

Fig. 1. Electron microscopy results concerning the $LiCoO_2$ catalyst: (A) FESEM view of the catalyst microstructure; (B) TEM micrograph of the catalyst crystals.

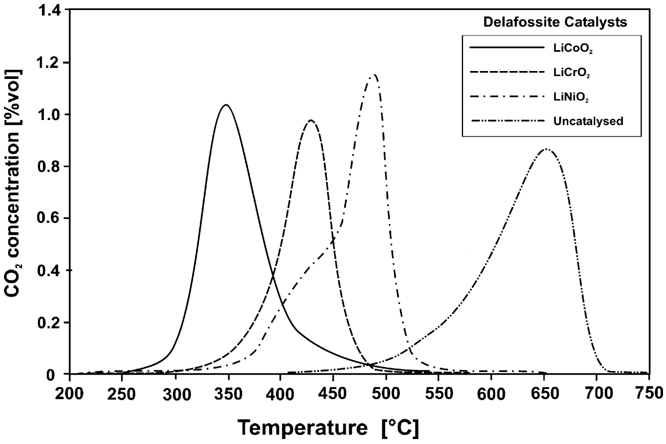

Fig. 2. Results of the TPC runs performed with all the selected delafossite catalysts. The curve related to non-catalytic combustion of carbon is also reported as a reference.

of the particulate are expected to provide the highest specific number of contact points between the soot directly captured over the catalyst layer and the crystals constituting such a layer. The TEM picture in Fig. 1B shows that most of the delafossite crystals have a size ranging between 10 and 20 nm, which satisfies the above requirement. Moreover, this particle size is in line with the BET surface areas of the various delafossite prepared catalysts (19–26 m^2/g). Such specific surface area values are equal to the geometrical surface area of the delafossite crystals as they do not show any internal porosity.

An index of catalyst activity can be found in the CO_2 peak temperature (T_p) of their TPC plot (Fig. 2): the lower the T_p value, the higher the catalyst activity. According to the data plotted in Fig. 2, the catalysts are characterised by TPC peak temperatures significantly lower than 650 °C (non-catalytic combustion). The superior activity of $LiCoO_2$ delafossite can clearly be noticed. In particular, it shows a T_p of just 347 °C. This higher activity cannot be explained on the grounds of a higher specific surface area, since the most active $LiCoO_2$ catalyst was exhibiting the lowest BET value (19 m^2/g). This also entails that the presence of nanoscopic catalyst particles is a pre-requisite for obtaining a high catalytic activity but it cannot explain on its own the significantly different behaviours observed for the different catalysts.

As expected, all catalysts lower the activation energy towards carbon combustion compared to the non-catalytic combustion. Besides, $LiCoO_2$ activation energy is 119 kJ/mol versus 157 kJ/mol of the non-catalytic combustion of soot [9]. However, the activation energies of the two other catalysts (124 kJ/mol for $LiCrO_2$ and 135 kJ/mol for $LiNiO_2$) are higher but the increase over $LiCoO_2$ is not pronounced. Therefore, the different delafossites, as a key feature of the reaction mechanism they entail, seem to be capable of delivering oxygen species of a rather similar nature or reactivity to the carbon particulates. The reactivity of the oxygen species delivered by $LiCoO_2$ should be slightly higher than that of O_2 species released by its catalytic counterparts. However, to fully explain the difference in catalytic activity, it might be guessed that the superior activity of cobaltite should be due, at least in part, to a particularly high specific surface concentration of such active oxygen species.

Temperature-programmed desorption (TPD) studies were quite helpful to better elucidate this issue. Previous investigations [5,6], focused on perovskite catalysts, showed indeed that these materials can weakly chemisorb oxygen species (named α oxygen) in the temperature range of interest of the catalytic soot combustion. Furthermore, these oxygen species were proven to be directly involved in the combustion process [10]. Oxygen TPD runs were thus carried out on purpose in order to possibly detect and quantify any oxygen species weakly chemisorbed over the three catalysts under investigation. The results of these TPD runs are shown in Fig. 3. The temperatures of practical interest are, as later analyzed in pilot plant experiments, below 600 °C, were suprafacial oxygen species should dominate the combustion process [5,6]. A remarkable difference can be noticed in the behaviour of $LiCoO_2$ and $LiCrO_2$ catalysts, compared to that of $LiNiO_2$. The latter catalyst showed a very limited desorption of α oxygen, whereas a significant presence of these low-temperature oxygen species was noticed for the $LiCrO_2$ delafossite one [11]. Besides, if the attention is focused on the temperature range 200–350 °C, where the most active

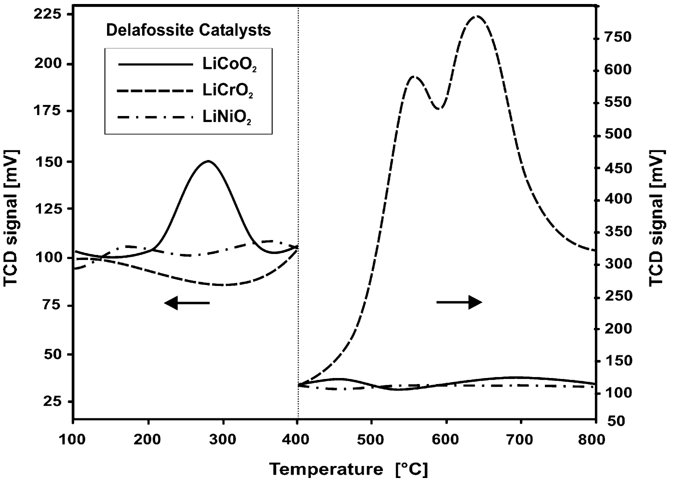

Fig. 3. Results of oxygen temperature-programmed desorption (TPD) tests on all the developed catalysts.

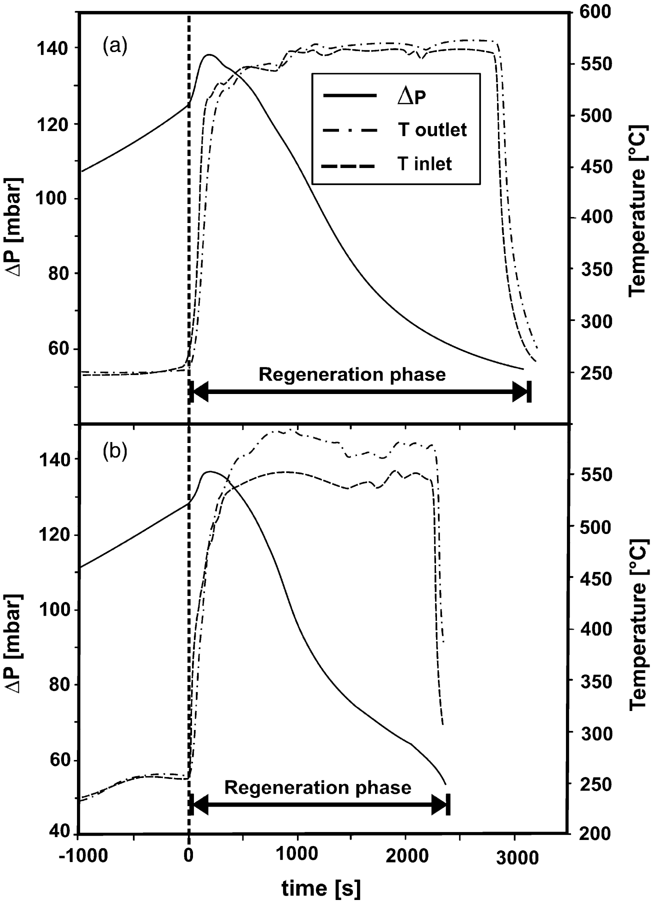

Fig. 4. Results of loading and regeneration runs for: (a) non-catalytic SiC wall-flow trap; (b) the $LiCoO_2$-catalysed trap.

delafossite tested in TPC experiments displayed its best soot combustion activity (see the CO_2 peaks in Fig. 2), Fig. 3 shows that only $LiCoO_2$ exhibits a significant oxygen desorption in this very low temperature range. Such α-type weakly chemisorbed species should likely be responsible for the good TPC performance of the $LiCoO_2$ catalyst. These α-type oxygen may likely undergo *spillover* [12] over the carbon agglomerates in contact with the catalyst. This would result in an increase of the number of sites in which the carbon particles are simultaneously attacked by oxygen, to the benefit of reaction kinetics. These promising results paved the way towards $LiCoO_2$-catalytic trap preparation and bench testing.

Shifting to the analysis of the wall-flow monolith deposited by *in situ* solution combustion synthesis with the $LiCoO_2$ catalyst, Fig. 4 compares the results of the runs performed with the catalytic and the reference, non-catalytic silicon carbide wall-flow monoliths. The results are rather encouraging. After trap loading up to a pressure drop of about 120 mbar (the graph shows only the last part of the loading phase), the post-injection of about 0.095 kg of fuel per kg of exhaust gases was operated in both cases. This entailed a rapid increase in the inlet (and outlet) trap temperatures, as measured by a thermocouple inserted some 10 mm inside one of the central channels of the trap. Upon reaching a temperature level just exceeding 550 °C the regeneration of the both traps got fully started.

The difference between the inlet and outlet temperatures of the non-catalytic trap remained rather small even when soot combustion started. On the contrary, the increase of the outlet temperatures over the inlet ones of the $LiCoO_2$-catalytic trap was significantly higher than that reached for the virgin trap as a likely consequence of a higher amount of heat released by soot combustion, i.e. a more rapid and complete regeneration. It has to be stressed that since the operating temperature of the catalytic and non-catalytic traps is imposed to be the same, the effect of the presence of the catalyst can only be assessed by a reduction of the different regeneration time. To these merits, the regeneration of the $LiCoO_2$-catalysed trap is definitely faster than that of the non-catalytic ceramic filter as it can be assessed by comparing the pressure drop decrease curves in Fig. 4a and b. By decreasing the regeneration time and the residual soot concentration in the trap the presence of the catalyst enables significant fuel savings, thereby reducing the operating costs.

Besides, from the temperature plots in Fig. 4b it can be noticed how the trap outlet temperature begin to overpass the inlet one already at about 450 °C. This is a clear effect of the presence of the catalyst, already active well below that temperature.

As underlined in a previous paper of ours [13] soot combustion starts in the central monolith part. As soon as the soot is removed from the channels located in the axial position, the exhaust hot gases concentrate their flow mainly in that region owing to the reduced pressure drop and this makes the regeneration of the remaining parts of the trap difficult, mostly because of the lower temperature of the peripheral zones of the trap, but also due to a lower overall amount of oxygen passing through these zones. The presence of the $LiCoO_2$ catalyst may indeed allow to burn more soot and this generates more heat thereby entailing to achieve temperatures high enough to regenerate also the "cold" and less flushed zones of the trap. However, regeneration is indeed a very complex and activated phenomenon which depends on a number of variables and, once initiated, takes advantage of the heat released by the burnt soot to emphasize combustion kinetics. It is tricky and almost impossible to reach at a trap level the results obtained in the TPC tests under tight contact conditions. However, the particular nature of the catalyst which enables spillover of active oxygen species and its rough morphology which increases the number of catalyst–soot contact points, can actually help to reduce this gap [12]. These are surely the reasons why at the end of the regeneration phase 78% of the soot was converted in the catalysed trap, as opposed to just 52% of the non-catalytic one.

4. Conclusions

The development of the common-rail engines has deeply changed the perspectives in the diesel-exhaust treatment field, by enabling a momentary rise of the exhaust gas temperature for trap regeneration purposes, even if this implies a certain fuel penalty. In this context, the present investigation proved that a wall-flow ceramic filter catalysed with $LiCoO_2$ obtained by *in situ* solution combustion synthesis entailed a reduction of the time required for trap regeneration (and of the related fuel penalty) as well as a much more complete regeneration compared to that of a non-catalytic trap.

An experimental test campaign is currently in progress to verify this potential at a catalytic trap level on real exhaust gases. Alongside with this, modelling studies are currently in progress to design a trap structure optimized for this promising regeneration route.

References

[1] US EPA, Federal Register, Rules and Regulations, I.B.3, vol. 66, no. 12, January 18, 2001.

[2] Review of EPA's Health Assessment Document for Diesel Exhaust, EPA 600/8-90/057E, 2000.

[3] M.R. Heidi, A. Hongmei, J.M. Paul, Appl. Catal. B: Environ. 44 (347) (2003).

[4] D. Fino, V. Specchia, Chem. Eng. Sci. 59 (2004) 4825.

[5] D. Fino, N. Russo, G. Saracco, V. Specchia, J. Catal. 217 (2003) 367.

[6] N. Russo, D. Fino, G. Saracco, V. Specchia, J. Catal. 229 (2005) 459.

[7] A. Civera, M. Pavese, G. Saracco, V. Specchia, Catal. Today 83 (2003) 199.

[8] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.

[9] D. Fino, N. Russo, C. Badini, G. Saracco, V. Specchia, AIChE J. 49 (2003) 2173.

[10] T. Seyama, Catal. Rev. Sci. Eng. 34 (1992) 281.

[11] E. Cauda, D. Mescia, D. Fino, G. Saracco, V. Specchia, Ind. Eng. Chem. Res. 44 (2005) 9549.

[12] B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, Catal. Rev. Sci. Eng. 43 (2001) 489.

[13] D. Fino, P. Fino, G. Saracco, V. Specchia, Korean J. Chem. Eng. 20 (2003) 445.