

# NO<sub>x</sub> AND DIESEL SOOT ABATEMENT OVER CATALYTIC TRAPS BASED ON MIXED TRANSITION METAL OXIDES

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## Abstract

Nanostructured perovskite-type oxides catalysts La<sub>1-x</sub>A<sub>x</sub>Ni<sub>1-y</sub>B<sub>y</sub>O<sub>3</sub> (where A = Na, K, Rb and B = Cu; x = 0, 0.2 and y = 0, 0.05, 0.1), prepared by the solution combustion synthesis method and characterized by BET, XRD, FESEM, and catalytic activity tests in microreactors, proved to be effective in the simultaneous removal of soot and NO, the two prevalent pollutants in diesel exhaust gases in the temperature range 350–450 °C. The best compromise between soot and nitrogen oxide abatement was shown by La<sub>0.8</sub>K<sub>0.2</sub>Ni<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>3</sub> catalyst which displayed the higher catalytic activity towards carbon combustion and the highest NO conversion activity (CO<sub>2</sub> peak temperature = 368°C; max NO conversion = 92% at 400°C).

An *in situ* SCS method was tailored to the preparation of a La<sub>0.8</sub>K<sub>0.2</sub>Ni<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>3</sub>-catalyzed trap based on a SiC wall-flow monolith. 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 2-fold reduction of the regeneration time compared to the case of a non-catalytic trap, with consequent saving of post-injected fuel. Moreover, during the regeneration phase the presence of the catalyst enabled a NO conversion of about 45%.

## Introduction

The industrialization and particularly the increase of road traffic in developed or developing Countries have been accompanied by a negative impact on the air quality, the environment and human health. Diesel engines have both carbon monoxide and unburned hydrocarbons outlet concentrations much lower than those produced by spark-ignition engines. However, even the most recent diesel engines (e.g. common rail) generate nitrogen oxides and carcinogenic particulate, whose size (50–200 nm) falls in the so-called lung-damaging range [1]. The automotive industry is currently facing serious challenges to meet the specific requirements of future regulations concerning both NO<sub>x</sub> and particulate emissions. Less than 0.025 g km<sup>-1</sup> for particulate and 0.25 g km<sup>-1</sup> for NO<sub>x</sub> will be prescribed by the pending 2005 EEC 98/69 regulations. These limits cannot be accomplished by either engine modifications [2] or fuel pre-treatments [3] or more simply by a better tuning of the combustion process [4]: a convenient way of treating diesel off-gases has thus to be worked out. In this context, diesel particulate traps appear to be mandatory to most researchers in the field and the Authors have already been involved for several years in some European R&D programs (CATATRIP, DEXA-cluster) aiming at the development of catalytic traps [5]. Catalysis can indeed play a significant role, by possibly achieving as good results as those obtained with catalytic converters in gasoline-fired engines [6]. Research in this field is carried out worldwide towards two different solutions:

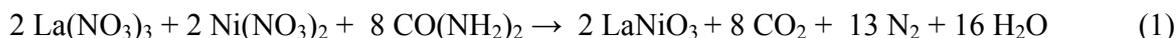
1. Filtration of particulate in a first catalytic converter (the soot is trapped and burned out owing to the presence of a catalyst thoroughly deposited onto the filter [7]), whereas NO<sub>x</sub> are eliminated in a second catalytic converter either by reaction with suitable reducing agents (light hydrocarbons, fuel, ammonia, etc. [8]) or by direct decomposition [9].
2. Contemporary removal of soot and nitrogen oxides in a single suitably catalysed trap [10].

This latter way is clearly more ambitious than the former one, and has been very recently explored in view of the considerable advantages it might enable in terms of both investment cost and pressure drop reduction. It is well known that 10–15% of NO<sub>x</sub> is generally reduced during regeneration of soot laden traps. This reduction mostly involves NO<sub>2</sub> molecules by direct reaction with soot to form NO and to a lesser extent N<sub>2</sub> and N<sub>2</sub>O [11]. This reaction, exploited in the so-called CRT system by Johnson Matthey [12], stands at the grounds of the present study. Despite the existence of several technical problems to be solved (e.g. find out the best catalyst deposition on the trap, the best trap design so as to allow an intimate contact between the reactants and the catalyst itself, etc.), the more urgent research topic to be addressed for the time being is the development of a suitable catalyst, capable of promoting both soot oxidation and NO<sub>x</sub> reduction at comparatively low temperatures (possibly within the range typical of diesel exhaust: 150–380°C). On the grounds of a previous work of ours [13], perovskite-type oxides seem to be the most promising catalysts for such a purpose. In the present work, La<sub>1-x</sub>A<sub>x</sub>Ni<sub>1-y</sub>B<sub>y</sub>O<sub>3</sub> (where A = Na, K, Rb and B = Cu; x = 0, 0.2 and y = 0, 0.05, 0.1) perovskite catalysts were prepared, characterized and tested for their activity in the simultaneous abatement of NO<sub>x</sub> and soot. On the basis of the experimental work here reported some conclusions are then drawn concerning the catalysts tested.

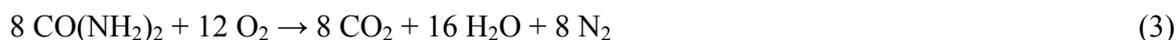
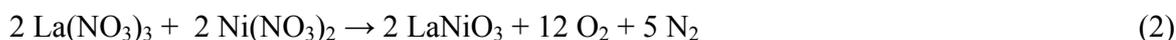
## Experimental

### *Catalysts preparation, characterization and catalytic activity assessment*

Several La-Ni perovskite samples (La<sub>1-x</sub>A<sub>x</sub>Ni<sub>1-y</sub>B<sub>y</sub>O<sub>3</sub> where A = Na, K, Rb and B = Cu; x = 0, 0.2 and y = 0, 0.05, 0.1) were prepared via a highly exothermic and self-sustaining reaction, the so-called “*solution combustion synthesis*” method [14]. This technique is particularly suitable for production of nanosized particles of catalyst. The combustion synthesis process can be formally split into two steps (the preparation of LaNiO<sub>3</sub> is here considered as an example):



The whole reaction can be formally regarded as the combination of two different contributions:



The first one is the endothermic reaction (2) for the real perovskite synthesis starting from the metal nitrate precursors, while the second is exothermic and accounts for the reaction (3) between oxygen derived from nitrates decomposition and urea. Some direct combustion of urea with atmospheric oxygen cannot of course be excluded as the preparation is carried out in air within an electric oven kept at 500°C hosting the precursors mixture placed in a porcelain pot. The overall set of reactions is

markedly exothermic, which leads within the reacting solid mixture to a thermal peak well exceeding 1000°C for a few seconds. To increase this sudden heat release, a varying amount of  $\text{NH}_4\text{NO}_3$  was also added and kept into account in the fuel-to-oxidisers ratio.

Under these conditions nucleation of perovskite crystals is induced, their growth is limited, and nanosized grains can be obtained, as earlier anticipated. After preparation, all catalysts were ground in a ball mill at room temperature and submitted to physical and chemical characterization. The nanostructured nature of the catalyst is pursued so as to increase the number of contact point between the catalyst and the particulate, a key feature of the reaction pathway, as later discussed.

The catalytic activity of the prepared catalysts was tested in a Temperature-Programmed Reaction (TPR) apparatus. A standard gas mixture (1000 ppm NO; 10 vol.%  $\text{O}_2$ , He = balance) was fed at the constant rate of  $100 \text{ ml}\cdot\text{min}^{-1}$  via a set of mass flow meters (Brooks) to a fixed-bed reactor enclosed in a quartz tube placed in an electric oven. The tubular quartz reactor was loaded with 50 mg of a 1:9 by weight mixture of carbon and powdered catalyst and 150 mg of  $\text{SiO}_2$  granules (0.3–0.7 mm); this inert material was added 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 (printex U by Degussa) 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 preferred so as to avoid any interfering effect due to the presence of adsorbed HCs, sulfates or fly ashes present in real diesel soot. Moreover, the carbon employed is more difficult to burn than diesel soot, which renders the achieved results conservative [5]. A proper and reproducible mixing between catalyst and carbon was routinely carried out grinding carefully together such substances for 15 min in a ball mill. These mixing conditions are normally addressed as “tight-contact” ones [7] and were ensured in the present study because they allow a better reproducibility. The real soot-catalyst contact conditions in a real catalytic trap are though less intensive. The catalyst–carbon– $\text{SiO}_2$  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 based on the measurements of an external K-type thermocouple and varied during each TPR runs from 200 to 700°C at a  $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  rate. A 30 min stay at 200°C under He flow was adopted as a common pre-treatment in order to eliminate possible contaminants such as adsorbed water. The analysis of the outlet gas was performed via a  $\text{N}_2\text{O}/\text{CO}/\text{CO}_2$  NDIR analyzer and a  $\text{NO}/\text{NO}_2$  chemiluminescence analyzer. The temperature of maximum  $\text{CO}_2$  production (Tp) and of maximum NO conversion could be pointed out as indexes of catalytic activity.

### ***Catalytic trap preparation and Diesel engine bench tests***

The best catalyst selected ( $\text{La}_{0.8}\text{K}_{0.2}\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}_3$ , as detailed later) was deposited by *in situ combustion synthesis* 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 (CTI, 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 selected catalyst. The load of catalyst deposited was assessed by gravimetric analysis and resulted equal to 4.8 wt%.

The developed trap was tested over real Diesel exhaust gases on an engine bench (Kubota 1000 cc 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 is provided in [15].

The gas superficial velocity across the trap could be controlled 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 suitable differential pressure transducers (VIKA), whereas K-type thermocouples were mounted at axial position just upstream and downstream the trap so as to measure the local temperatures. 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 120-130 mbar pressure drop was reached (corresponding to a particulate hold-up of about  $10 \text{ g}\cdot\text{L}^{-1}$ ). 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 so as to get to an inlet trap temperature of about  $550^\circ\text{C}$ . The time needed for the complete trap regeneration (e.g. combustion of soot hold-up) is an index of catalyst performance. 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, or lower, to that measured at the beginning of the loading phase. As far as the NO conversion is concerned, the temperature and gas composition before and after the trap were controlled and monitored, in order to evaluate the catalytic activity towards NO reduction. A twin run on a virgin, non catalytic trap was also performed for the sake of comparison.

## Results and discussion

All perovskite catalyst samples were found to be well crystallized by XRD analysis (Figure 1). All diffraction peaks expected according to the reference JPCDS card ( $\text{LaNiO}_3$ : PDF 33-0711) were observed. No secondary phases could be detected by this technique. X-ray diffraction has a  $\pm 4\%$  precision and therefore the presence of amorphous phases cannot be completely excluded. Besides, chemical analysis (dissolution + atomic absorption,  $\text{O}_2$  titration) confirmed, with its intrinsic precision ( $\pm 5\%$ ), that the amount of the various constituting elements (La, Ni, Na, K, Rb, Cu, O) was consistent with that used in the precursors and was compatible with the phases detected by XRD. In the present context, perovskite crystals having a size of the same order of magnitude as that of the particulate agglomerate 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. Figure 2A shows a FESEM picture of  $\text{LaNiO}_3$  perovskite-type catalyst produced via combustion synthesis. It refers to the catalyst that showed the highest BET area among those prepared (see Table 1). This FESEM enlightens a very foamy structure, a typical feature of catalysts synthesised by SCS. This should once again remarkably favour the contact between soot and catalyst even under loose contact conditions and, once coated upon the wall flow trap channel walls, it should allow just a slight increase of pressure drop. Figure 2B shows a close view of the same catalyst. The perovskite crystals of the considered catalyst have a size below 100 nm, which is perfectly in line with the dimensions of particulate nuclei and is in substantial agreement with the specific surface area measured. Anyhow the perovskite crystals of all catalysts prepared have a size ranging between 60 and 100 nm, which satisfies the above requirement.

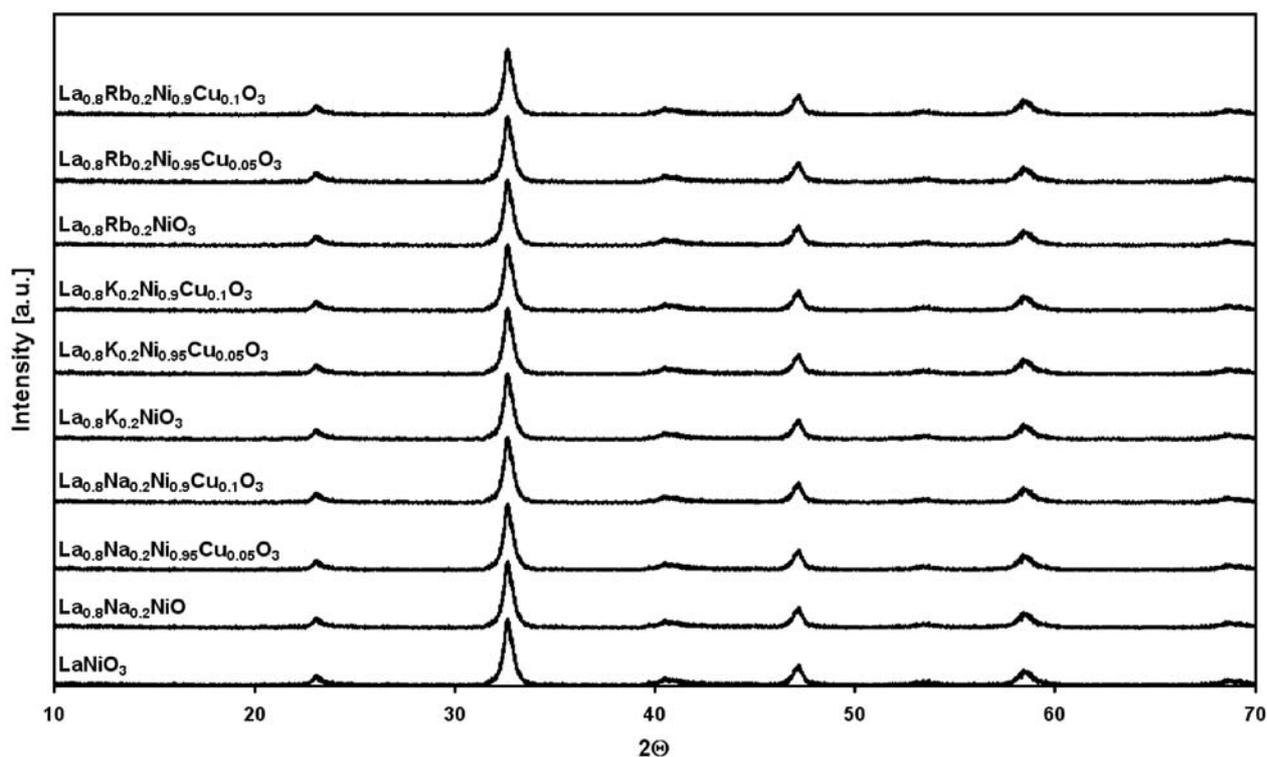


Figure 1 XRD spectra of the prepared perovskite catalysts.

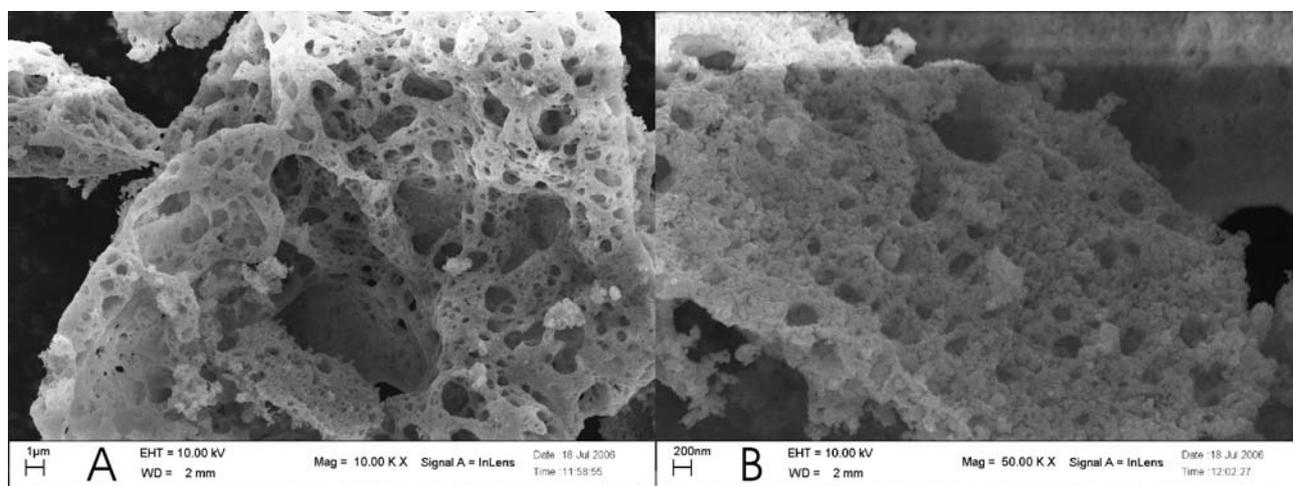


Figure 2 FESEM view of  $\text{LaNiO}_3$  catalyst crystal agglomerates obtained by solution combustion synthesis. A) 10000x; B) 50000x.

Shifting to the activity screening results, Table 1 summarizes the BET specific surface area, the carbon combustion peak temperatures, the maximum NO conversion and the relative peak temperature of all the catalysts investigated. A detailed investigation was carried out on these oxides by temperature programmed oxidation of soot and reduction of  $\text{NO}_x$  (TPR) tests in fixed bed microreactors.

Table 1 Catalysts characterization and activity results

Catalyst	BET [m <sup>2</sup> /g]	T <sub>p</sub> [°C]	Max NO conversion [%]	T of max NO conversion [°C]
LaNiO <sub>3</sub>	15.4	410	33	423
La <sub>0.8</sub> Na <sub>0.2</sub> NiO <sub>3</sub>	5.9	399	67	429
La <sub>0.8</sub> Na <sub>0.2</sub> Ni <sub>0.95</sub> Cu <sub>0.05</sub> O <sub>3</sub>	4.9	395	68	425
La <sub>0.8</sub> Na <sub>0.2</sub> Ni <sub>0.9</sub> Cu <sub>0.1</sub> O <sub>3</sub>	5.2	394	69	421
La <sub>0.8</sub> K <sub>0.2</sub> NiO <sub>3</sub>	4.5	358	74	380
La <sub>0.8</sub> K <sub>0.2</sub> Ni <sub>0.95</sub> Cu <sub>0.05</sub> O <sub>3</sub>	4.8	373	83	403
La <sub>0.8</sub> K <sub>0.2</sub> Ni <sub>0.9</sub> Cu <sub>0.1</sub> O <sub>3</sub>	4.7	368	92	400
La <sub>0.8</sub> Rb <sub>0.2</sub> NiO <sub>3</sub>	3.8	369	63	427
La <sub>0.8</sub> Rb <sub>0.2</sub> Ni <sub>0.95</sub> Cu <sub>0.05</sub> O <sub>3</sub>	4.0	378	66	389
La <sub>0.8</sub> Rb <sub>0.2</sub> Ni <sub>0.9</sub> Cu <sub>0.1</sub> O <sub>3</sub>	4.1	394	68	423

As expected, all the catalysts significantly lowers the combustion peak temperature compared to that of the non catalytic combustion (T<sub>p</sub> = 650 °C; not reported).

An activity order can be outlined as follows:

- 1) The La<sub>0.8</sub>K<sub>0.2</sub>Ni<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>3</sub> catalyst appears to be the one displaying a very high catalytic activity towards carbon combustion combined with the highest NO conversion activity, as well (T<sub>p</sub> = 368°C; max NO conversion = 92% at 400°C). For this reason, further investigations at a catalytic trap level were carried out on this catalyst only;
- 2) the other perovskite catalysts characterized by both lanthanum and nickel substitutions with alkali metals and copper, respectively, exhibit quite similar activity (T<sub>p</sub> ranging from 358 to 399°C; max NO conversion ranging from 63 to 83% );
- 3) the un-substituted LaNiO<sub>3</sub> is by far the less active catalyst (T<sub>p</sub> = 410°C; max NO conversion = 33% at 423°C) despite its high specific surface area.

In line with earlier papers of ours [14], it can be deduced that substitution of part of lanthanum with a lower valence alkali metal brings about formation of high valence nickel to maintain electro-neutrality and possibly to more active or more concentrated oxygen species over the catalyst surface. It seems to be clear that the presence of alkali metals at the A site is also directly involved with the activity towards the NO conversion. Moreover, increasing the amount of copper in the substituted perovskite structures a further improvement of the maximum NO conversion was observed.

Figure 3 shows the catalytic activity of the K-substituted perovskites compared with the unsubstituted one. A synergetic effect of potassium and copper in ensuring a peculiar activity for the simultaneous abatement of soot (lower TPO peak temperatures) and NO<sub>x</sub> (highest values of maximum NO conversion) is evident. It seems clear that the two reaction processes (soot combustion and NO reduction) occur simultaneously. In particular, for the most active catalyst the early stages of soot combustion, at temperatures below 350°C, seem to involve a certain amount of oxygen derived from NO<sub>x</sub> reduction. This effect seems to progressively vanish as long as the combustion progresses and higher temperatures are reached. It is very likely that a key player in the NO<sub>x</sub> reduction and soot oxidation processes is NO<sub>2</sub> whose production gets maximized in the 300-400°C as a consequence of kinetics limitations (below 300°C) and thermodynamic ones (above 400°C, [16]). Deeper investigations are needed to elucidate this point in line with an earlier paper of ours [13].

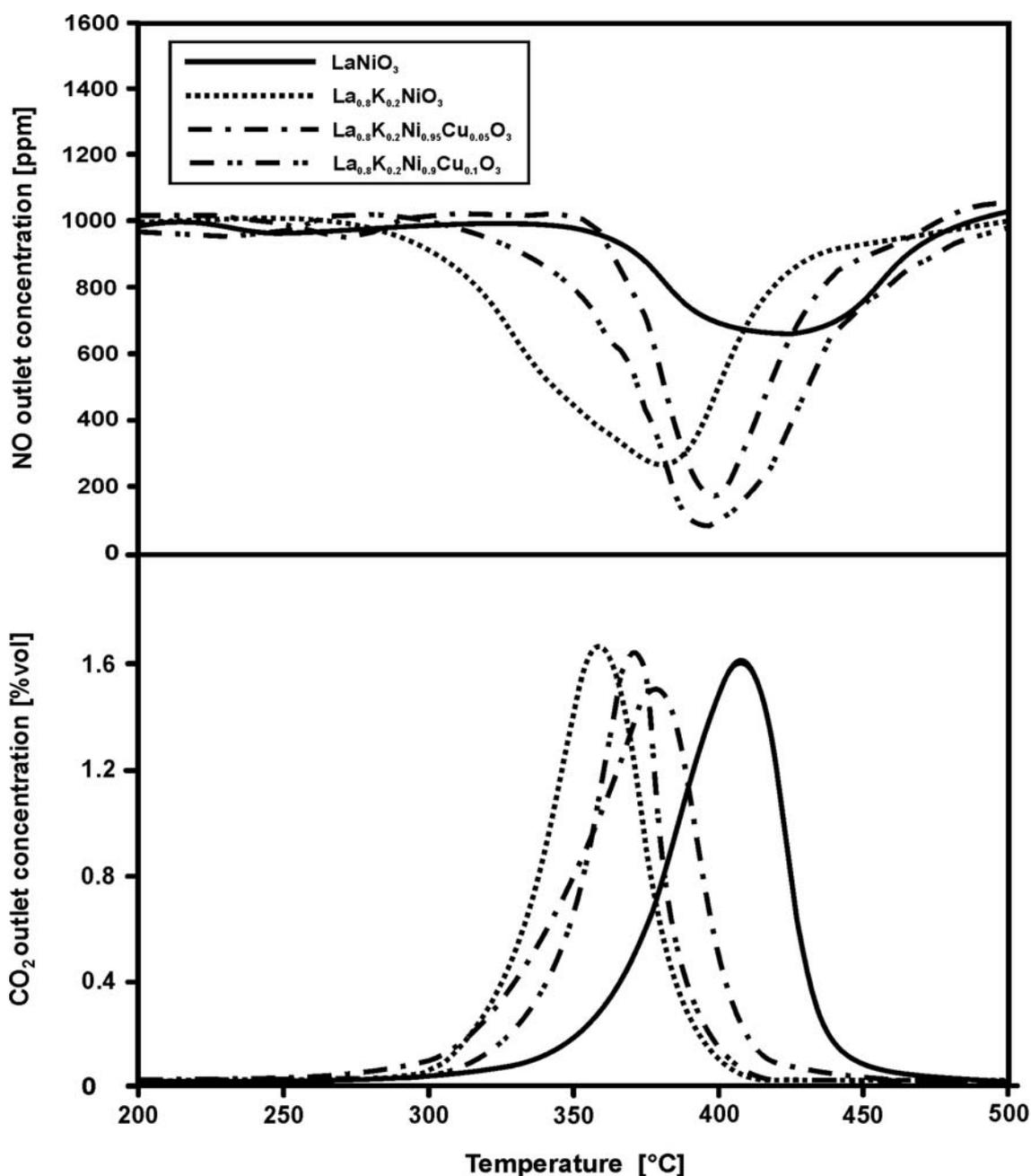


Figure 3 Results of the TPR runs performed with some selected catalysts for the simultaneous abatement of soot and NO.

Figure 4 shows the complete set of gas outlet concentrations plots of the various components involved in a standard TPR run on the La<sub>0.8</sub>K<sub>0.2</sub>Ni<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>3</sub> catalyst but it is representative of the catalytic behaviour of all the prepared catalysts. The scenario is rather complex. CO<sub>2</sub> is generally by far the main carbon oxidation product with a selectivity well exceeding 95%. A certain role of CO as a reducing agent may be present.

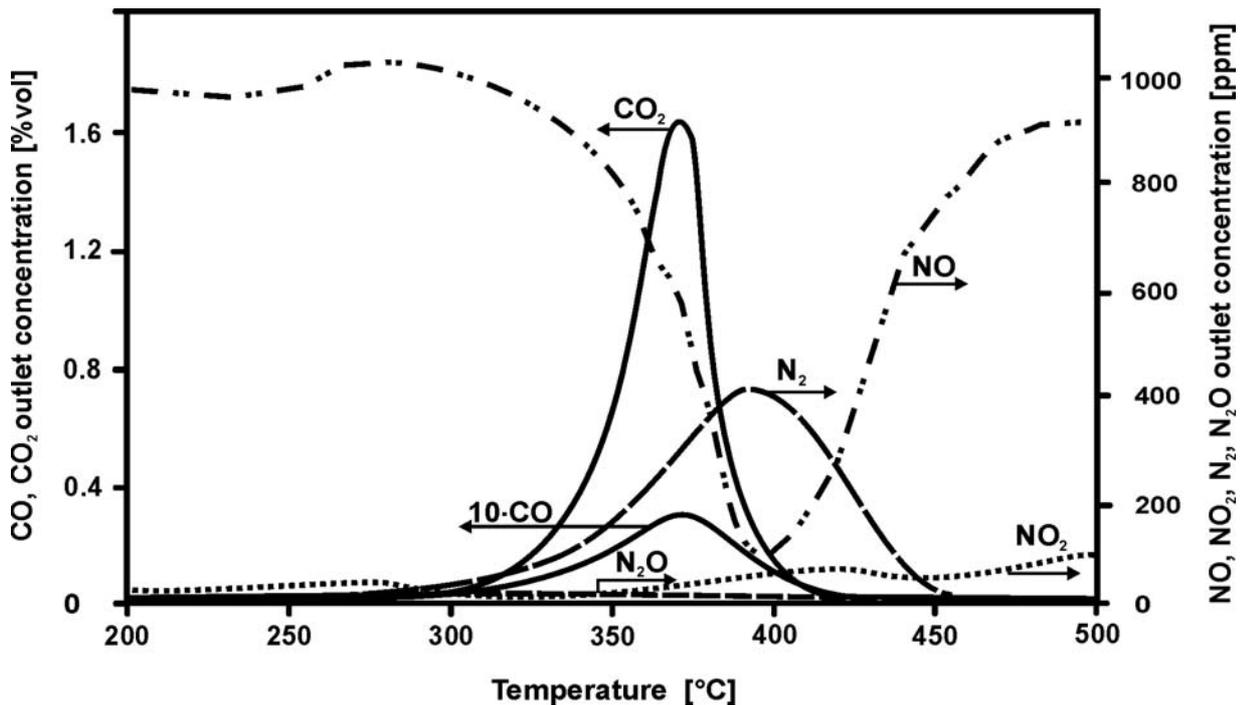


Figure 4 Concentration plots of the outlet gaseous species in a TPR run performed with the  $\text{La}_{0.8}\text{K}_{0.2}\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}_3$  catalyst.

However, this role should be minor as it is known that NO reduction by CO on metal oxide catalysts (e.g. [18]) is strongly inhibited by the presence of oxygen, which was accounting for 10 vol% of the feed gas mixture in any TPR experiment performed. The main product of NO reduction is  $\text{N}_2$ .  $\text{N}_2\text{O}$  formation is rather low (less than 30 ppm). Conversely, nitrogen dioxide concentrations, formed to some extent from the fed NO and  $\text{O}_2$  according to the  $\text{NO} + 1/2\text{O}_2 \leftrightarrow \text{NO}_2$  equilibrium, generally increases with the T. By the way,  $\text{NO}_2$  should actually contribute to direct carbon combustion, but with minor impact on  $\text{N}_2$  generation as the main reduction product in this case is known to be NO itself.

Shifting to the analysis of the developed trap systems performance, Figure 5 compares the results of the runs obtained with the catalytic and the reference, non-catalytic SiC wall-flow monolith. 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 trap temperatures up to  $550^\circ\text{C}$ , as a common operating condition.

However, the regeneration of the  $\text{La}_{0.8}\text{K}_{0.2}\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}_3$ -catalysed trap was much faster than that of the non-catalytic ceramic filter, which resulted in a nearly twofold shorter soot combustion period (evaluated from the maximum of the pressure drop curve till its end). By these means, it becomes possible to save a significant amount of fuel at any filter regeneration, thereby reducing the operating costs. It has to be kept into account, however, that the part of fuel saving is compensated by a very small decrease of filter permeability for the presence of the catalyst which brings about a slightly higher back pressure. Another important feature lies in the more complete regeneration of the catalytically-promoted trap: the pressure drop value after regeneration is about 20 mbar lower than that of the non-catalytic trap. As a consequence of this higher completeness in the regeneration, a lower

regeneration frequency can be expected for the catalytic trap, compared to the non-catalytic one, which should result in further savings in post-injected fuel.

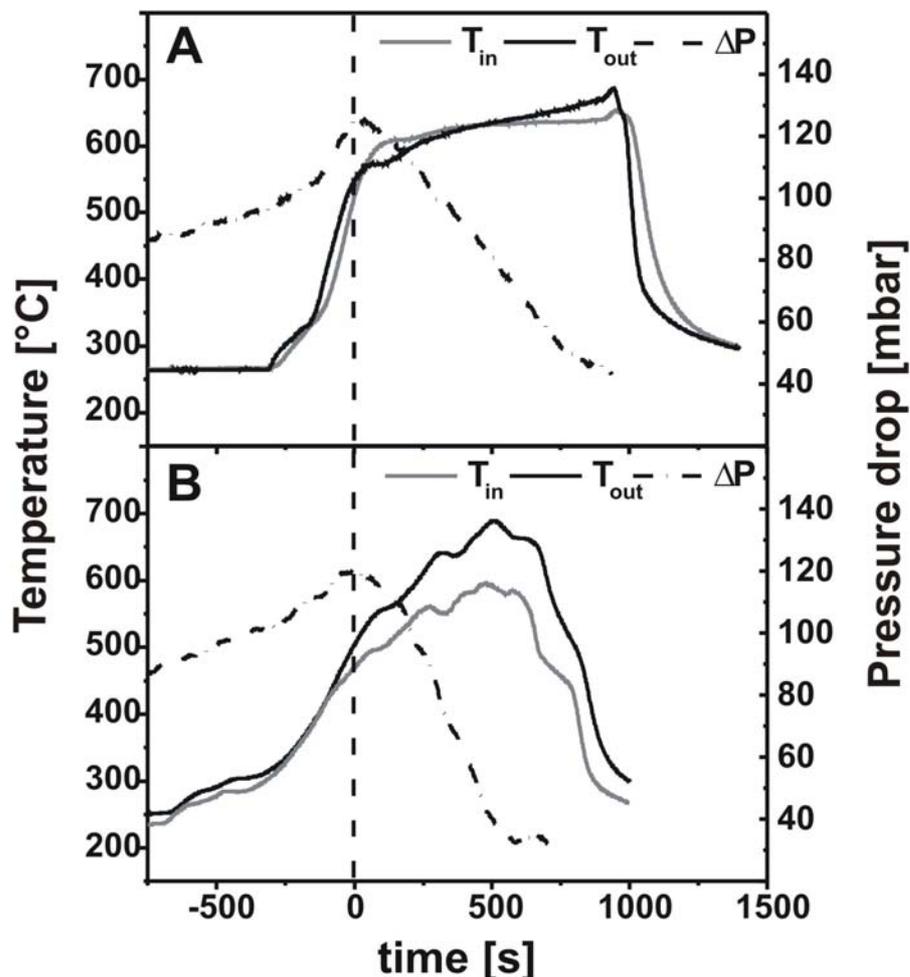


Figure 5 Results of loading and regeneration runs for the (A) non-catalysed and the (B) catalysed ( $\text{La}_{0.8}\text{K}_{0.2}\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}_3$ ) wall-flow traps.

As far as the NO conversion is concerned (figure not reported) a reduction of nitrogen oxide emitted during regeneration for the catalytic trap as opposed to the non catalytic one was observed. As a consequence of the poorer catalyst-soot contact conditions and the higher temperature, the results are less encouraging than those obtained during TPR experiments. During the regeneration phase the NO conversion is about 45% which is interesting, even if quite lower than the 92% value recorded for the TPR runs. In any case, even under loose contact conditions the catalysts are generally performing significantly better than the reference non catalytic combustion/reduction. This helps reduce the NO emissions in the loading but especially during the regeneration phase, where they were found to be quite significant.

## Conclusions

Some perovskite-type catalysts were prepared, characterised and tested for potential application in the treatment of diesel exhaust gases as promoters of both NO<sub>x</sub> and soot removal. A common feature of all the catalyst tested was the simultaneity of the denoxing and the soot combustion reactions, but those catalysts containing both K and Cu elements showed particularly high NO reduction activity and low TPO peak temperature. In this context, the present investigation proved that a wall-flow ceramic filter catalysed with the La<sub>0.8</sub>K<sub>0.2</sub>Ni<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>3</sub> obtained by *in situ* combustion synthesis looked very promising, as it entailed a two-fold 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. Moreover, the La<sub>0.8</sub>K<sub>0.2</sub>Ni<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>3</sub>-catalysed trap facilitates the conversion of NO especially during the regeneration phase.

An experimental test campaign is currently in progress to better verify this potential at a catalytic trap level on real exhaust gases. Alongside with this, mechanistic studies are in progress to better understand the reaction mechanism leading to simultaneous NO<sub>x</sub> reduction and soot oxidation in this rather complex solid-solid-gas system.

## References

1. L. Shirnamé-Moré, Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects, *A Special Report of the Institute's Diesel Working Group*, Health Effects Institute, Cambridge, MA, pp. 221–242 (1995).
2. T. Kawatani, K. Mari, I. Fukano, K. Sugakawa, T. Koyama, SAE Paper no. 932654 (1993).
3. K. Slodowske, An engine manufacturer's prospective on diesel fuels and the environment, in: *Proceedings of the SAE Panel Presentation at SAE Fuels and Lubricant Meeting*, Detroit, 20 October (1993)
4. H. Hiroyasu, M. Arai, H. Nakanishi, SAE Paper no. 800252 (1980).
5. D. Fino, N. Russo, C. Badini, G. Saracco, V. Specchia, *AIChE J.*, 49 (2003) 2173.
6. P. Marecot, A. Fackhe, L. Pirault, C. Geron, G. Mabilon, M. Prigent, J. Barbies, *Appl. Catal. B*, 5 (1994) 57.
7. B.A.A.L. Van Setten, M. Makkee, J.A. Moulijn, *Catal. Rev. - Sci. Eng.*, 43 (2001) 489.
8. S.L. Andersson, P.L.T. Gabrielson, C.U.I. Odenbrand, *AIChE J.*, 40 (1994) 1911.
9. C.Y. Lee, K.Y. Chai, B.H. Ha, *Appl. Catal. B*, 5 (1994) 7.
10. K. Yoshida, S. Makino, S. Sumiya, G. Muramatsu, R. Helferich, SAE Paper no. 892046 (1989).
11. B.J. Cooper, J.E. Thoss, SAE Paper no. 890404 (1989).
12. R. Allanson, B.J. Cooper, J.E. Thoss, A. Uusimäki, A.P. Walker, J.P. Warren, SAE Paper no. 2000-01-0480 (2000).
13. D. Fino P. Fino, G. Saracco, V. Specchia, *Appl. Catal. B*, 43 (2003) 243.
14. N. Russo, D. Fino, G. Saracco, V. Specchia, *J. Catal.*, 229 (2005) 459.
15. D. Fino, P. Fino, G. Saracco, V. Specchia, *Chem. Eng. Sci.*, 58 (2003) 951.
16. J. Despres, M. Koebel, M. Elsener, *PSI Scientific Report 2001*, 5 (2002) 64.
17. D. Fino, N. Russo, G. Saracco, V. Specchia, *J. Catal.*, 217 (2003) 367.
18. B. Viswanathan, *Catal- Rev. - Sci. Eng.* 34 (1992) 337.