

Mild Catalytic DPF Regeneration and Related CO Emissions in Commercial Vehicles

G. Villata, A. Tarabocchia and V. Bozzolini

Centro Ricerche Officine Metallurgiche Cornaglia

J. Caroca, N. Russo, D. Fino, G. Saracco and V. Specchia

Politecnico di Torino

Copyright © 2008 SAE International

ABSTRACT

$\text{La}_{1-x}\text{A}_x\text{Ni}_{1-y}\text{B}_y\text{O}_3$ nanostructured perovskite-type oxides catalysts (where A = Na, K, Rb and B = Cu; $x = 0, 0.2$ and $y = 0, 0.05, 0.1$), also supporting 2% in weight of gold, were prepared via the so-called “*Solution Combustion Synthesis (SCS)*” method, and characterized by means of XRD, BET, FESEM-EDS and TEM analyses. The performance of these catalysts towards the simultaneous oxidation of soot and CO was evaluated. The 2 wt.% Au- $\text{La}_{0.8}\text{K}_{0.2}\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}_3$ showed the best performance with a peak carbon combustion temperature of 367 °C and the half conversion of CO reached at 141 °C. The same nanostructured catalyst, deposited by *in situ* SCS directly over a SiC filter and tested on real diesel exhaust gases, fully confirmed the encouraging results obtained on the powder catalyst.

INTRODUCTION

The particulates in the exhaust gases from diesel engines are a potential risk to public health. These emissions contribute to the overall suspended particulates in urban areas. However, due to their small size, they can penetrate into lungs and induce severe diseases [1]. The main targets, concerning particulate emissions control, are defined by future soot particulate emissions standards. Up-to-date information about these standards can be found on the net [2]. One of the technologies available to control diesel particulate emissions is the employment of filters to capture soot particles from the exhaust stream. The filter must be regenerated periodically or continuously by burning the trapped soot in order to prevent a too high back-pressure increase [3, 4]. The exhaust gas temperatures at the filter location often do not attain the level required

for the regeneration, even at the maximum allowable back-pressure. Therefore, auxiliary systems, such as an electrical heater or a fuel burner, must be installed to ignite trapped diesel soot. These auxiliary systems are designed to heat the exhaust gases up to the regeneration temperature (>600 °C), and consequently, this operation is exposed to a certain risk, because of the exceptionally hot exhaust jet generated. On the other hand, the combustion temperature of diesel particulate matter can be lowered by using an oxidation catalyst. The catalytic regeneration of soot traps reduces operational risks as well as energy consumption to such an extent that a fully passive regeneration (i.e. without auxiliary systems) might be achieved. 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. These catalysts can be either deposited on a ceramic support (wall-flow filter) thereby obtaining a catalytic trap, or generated inside the combustion chamber by using a proper metal-organic precursor of the catalyst, that must be added to the fuel [5]. In this last case, the catalyst particles get in tight contact with soot and are carried by the exhaust gases towards the filtering device where soot combustion occurs [5-7]. Several kinds of catalysts have been tested: perovskite type oxides [8-11], spinel type oxides [12, 13], alkaline or heavy metal oxides [14-20], mixtures of halides with vanadates or molybdates [21-26], precious metals [27, 28]. A comparison among the performances of the different catalysts proposed to date should be made bearing in mind that not only the catalytic activity, but several other characteristics must be taken into account: thermal stability, chemical reactivity towards both the ceramic supports and the chemical species contained in the emissions, cost, etc. The direct catalytic combustion of diesel particulate is a

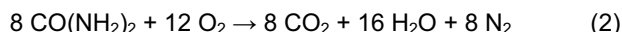
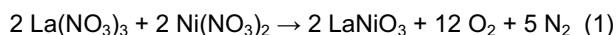
process based on a heterogeneous reaction involving solid particles of soot, gaseous oxygen and, of course, the solid catalyst. In order to promote this process, the catalyst must get in contact with soot particles [25]. This may actually be favoured by the synthesis of foamy microstructures of nanosized catalyst crystals as those typically obtained by solution combustion synthesis (SCS) methods [29, 30]. Furthermore, the interaction between the catalyst and the oxygen contained in diesel exhausts is believed to play an important role in the combustion of soot, in particular when the catalyst acts as an oxygen pump [31] and even promotes oxygen spill-over [32]. On the other hand, during the regeneration phase of the catalytic Diesel Particulate Filter (DPF) high amounts of carbon monoxide can be emitted and should be valuable to reduce this emission by designing a multifunctional catalyst for the simultaneous abatement of soot and CO. Over the past few years supported gold catalysts gained in interest due to their surprisingly high catalytic activity towards various reactions [33]. Among these reactions, one of the most interesting is low temperature CO oxidation [34–38]. The catalytic performance of gold strongly depends on the particle size, in such a way that smaller particles entail higher activities [39]. Gold-based catalysts containing nanoparticles can catalyse many reactions under conditions where bulk metallic gold is inactive. It is generally known that the addition of a metal to oxides (e.g. PGMs on CeO₂ and/or La₂O₃ [40, 41]) can modify the intrinsic catalytic properties of the oxides, possibly increasing the activity, selectivity or stability of the obtained products. As far as the reaction mechanism is concerned, up to now it has not been well recognized if the reaction proceeds exclusively on metallic gold particles [33, 42] or it may possibly occur preferentially at the edges of gold particle involving either sites on the adjacent support or on gold atoms influenced by the support [43]. Furthermore, it has been pointed out that the reaction may occur only on the support, involving adsorbed CO molecules migrated from the gold particles by spillover and oxygen species of the support [34]. Clearly, these mechanisms could coexist. In all the cases, the interface between the gold particles and the supports plays a determinant role in the catalytic activity of the sample.

The work presented in this paper deals with the development of supported gold perovskite catalysts, finally deposited on a DPF and tested on a real diesel engine, for the simultaneous abatement of soot and CO during the regeneration phase of the catalytic trap. The key feature of this investigation lies in the innovative method used to prepare the above multifunctional catalysts (solution combustion synthesis - SCS [29]) in a single step, i.e. in a more rapid and straightforward manner than those involving a more complex *modus operandi*.

MATERIALS AND METHODS

CATALYSTS PREPARATION AND CHARACTERIZATION

Several La-Ni perovskite samples (La_{1-x}A_xNi_{1-y}B_yO₃ where A = Na, K, Rb and B = Cu; x = 0, 0.2 and y = 0, 0.05, 0.1) have been prepared by SCS from an aqueous solution of nitrates (acting as oxidizers) and urea (acting as a sacrificial fuel). According to this method the reagents (Fluka extra pure grade) are dissolved into distilled water. The obtained solution is then placed into an oven kept at a constant temperature (600 °C) in air. The solution is quickly brought to boil; it then froths and swells until chemical reaction starts. Combustion is over in a few seconds, resulting in easily-crumbling foam of nano-sized particles with large specific volume and surface area [29]. Taking LaNiO₃ synthesis as an indication, the SCS preparation route can be formally regarded as the combination of two different contributions:



The exothermic reaction (2), namely urea combustion, provides the heat necessary to the completion of the decomposition reaction (1), i.e. the endothermic transformation of nitrate into the desired oxide. The Au-based catalysts (2 wt.% Au-La_{1-x}A_xNi_{1-y}B_yO₃ where A = Na, K, Rb and B = Cu; x = 0, 0.2 and y = 0, 0.05, 0.1) were prepared according to the same reaction written above, by adding HAuCl₄ to the aqueous solutions in order to directly obtain perovskite carriers supporting 2 wt.% of gold. The catalysts were then calcined in air at 500 °C for 4 h as a common stabilisation treatment. This method, suitably adapted according to an *in situ* version, has proved to be amenable for deposition of mixed oxides of catalysts within wall-flow diesel particulate traps based on SiC or cordierite [44]. Field Emission Scanning Electron Microscopy (FESEM) and energy dispersion spectroscopy (EDS) (Hitachi, model S4700 FESEM) were used to investigate the morphology as well as the elemental composition and distribution of all the catalysts prepared. Direct observation of the obtained nanosized Au clusters was performed by Transmission Electron Microscopy (TEM; Philips CM 30 T). All the catalysts were then ground in a ball mill at room temperature and characterized. X-ray diffraction (PW1710 Philips diffractometer equipped with a monochromator for the Cu K_α radiation) was used on all the fresh catalysts to examine whether the desired oxide structure was actually achieved. The BET specific surface areas of the prepared catalysts were evaluated from the linear parts of the BET plot of the N₂ isotherms, using a Micromeritics ASAP 2010 analyser.

CATALYTIC ACTIVITY TEST

The catalytic activity towards carbon combustion has been tested in a Temperature-Programmed Combustion (TPC) apparatus (Fig. 1). This equipment consists of a fixed bed inserted in a quartz microreactor (i.d.: 4 mm). The fixed bed was prepared by mixing 50 mg of a 1:9 by weight mixture of carbon and powdered catalyst with 150 mg of silica pellets (0.3–0.7 mm in size, this mixture

material was adopted to reduce the specific pressure drops across the reactor and to prevent thermal runaway. Amorphous carbon particles by Cabot Ltd. of about 45 nm in diameter, with BET specific surface area of 200 m²/g, with 0.34% of ashes after calcination at 800 °C and 12.2wt% of adsorbed water moisture, without adsorbed hydrocarbons and sulfates, were used for the sample preparation. The tight contact conditions between catalyst and carbon obtained in the ball mill allow good reproducibility which is a *conditio sine qua non* to draw reliable comparisons between the intrinsic activity of different catalysts. The TPC reactor temperature was controlled through a PID-regulated oven and it was increased from 200 to 700 °C at a 5 °C/min rate, under an air flow of 100 Nml/min. The analysis of the outlet gas of the reactor was performed by means of a CO₂/CO NDIR analyzer (ABB). A computer was used to record both the fixed-bed temperature (measured by a thermocouple put nearby the bed) and the concentration of CO₂ in the outlet gas as a function of time (i.e. vs. the programmed temperature).

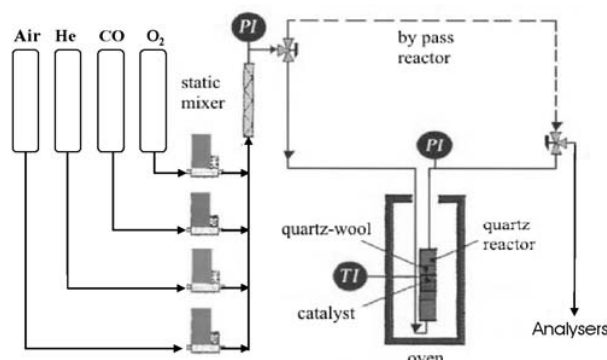


Fig. 1. Schematic view of the Temperature-Programmed Combustion (TPC) apparatus.

The temperature corresponding to the CO₂ concentration peak (T_p) was taken as an index of the catalytic activity of each tested catalyst: the lower the T_p value, the higher the catalytic activity. A TPC run was also performed in the absence of the catalyst so as to set a reference for comparison. 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 was estimated. The activity of the prepared catalysts towards CO oxidation was evaluated by the same TPC apparatus according to the following standard operating procedure: a gas mixture (2300 ppm CO; 7 vol.% O₂, He = balance) was fed, via a set of mass flow controllers, to the catalytic fixed-bed microreactor enclosed in a quartz tube placed in an electric oven (W/F = 0.12 g s/cm³). The tubular quartz microreactor was loaded with 800 mg of pelletised catalyst (0.2–0.5 mm granules obtained by sequential pressing, crushing and sieving). The

reaction temperature was varied from room temperature to 600 °C at a 5 °C/min rate. The CO conversion was monitored with the same NDIR analyser.

CATALYTIC TRAP PREPARATION

The catalyst which showed the best performance (2 wt.% Au-La_{0.8}K_{0.2}Ni_{0.9}Cu_{0.1}O₃) was deposited by *in situ* SCS directly over a ceramic wall-flow filter. The filter was dipped in an aqueous solution of the catalyst 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 NGK (cell structure = 17/200, diameter = 172 mm, length = 280 mm; pore diameter of channel walls = 23 µm, porosity of channel walls = 52%) which was found to be chemically compatible with the selected catalyst. The amount of perovskites deposited was about 5wt%, as assessed by gravimetric analysis. The morphology of the deposited catalyst layer was analysed by FESEM observation. A foamy structure of the catalyst is indeed a pre-requisite to obtain good catalyst-to-particulate contact conditions and a rather low pressure drop throughout the channel walls. Finally, catalyst adhesion to the monolith was assessed by a tailored ultrasonic bath test procedure [45].

ENGINE BENCH TESTING

The developed trap was tested over real Diesel exhaust gases on an engine bench (Iveco F1C Unijet 4 cyl., 3000 cc, 122 kW at 3500 rpm, maximum torque 380 N·m), where the temperature and gas composition upstream and downstream 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 reported in Fig. 2 was provided by Fino et al. [45]. 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 “EURO 5” 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 about a 80-90 mbar pressure drop was reached (corresponding to a soot hold-up of about 8 g·L⁻¹). A pre-test activity was carried out in order to correlate the final pressure drop reached during the loading phase, with the corresponding soot mass accumulated, by means of gravimetric analysis. This procedure was adopted both for catalytic and bare traps. Any appreciable change was observed for coated and virgin trap; a “mild”