Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 117 (2006) 369–375

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Towards practical application of lanthanum chromite catalysts for diesel particulate combustion

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

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

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 (SO_2 and water), was studied on some promising catalysts ($LaCrO_3$, $La_{0.9}CrO_3$, $La_{0.9}Na_{0.1}CrO_3$, $La_{0.9}Rb_{0.1}CrO_3$, $La_{0.8}Cr_{0.9}Li_{0.1}O_3$) for diesel particulate combustion. The catalytic activity was almost completely retained. The catalyst $La_{0.8}Cr_{0.9}Li_{0.1}O_3$ 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.

Keywords: Diesel particulate; Lanthanum chromite; Catalytic combustion; Catalyst stability

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

---

[*] 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.2006.05.034

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 SO_2-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 ($LaCrO_3$, $La_{0.9}CrO_3$, $La_{0.9}Na_{0.1}CrO_3$, $La_{0.9}Rb_{0.1}CrO_3$, $La_{0.8}Cr_{0.9}Li_{0.1}O_3$) 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 HNO_3/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 N_2 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 conductibility (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 O_2 flow (40 ml/min) up to 750 °C. After 30 min stay in O_2 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 O_2 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 m^2/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 cm^3/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 CO_2 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 CO_2 amount produced per run were calculated and the selectivity of carbon combustion towards CO_2 (η_{CO_2}) was estimated.

2.4. Catalyst ageing procedure

A catalyst used for combustion of soot in diesel emissions may loose 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. SO_2, H_2O), 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: