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Ceramic papers as flexible structures for the development of novel diesel soot combustion catalysts

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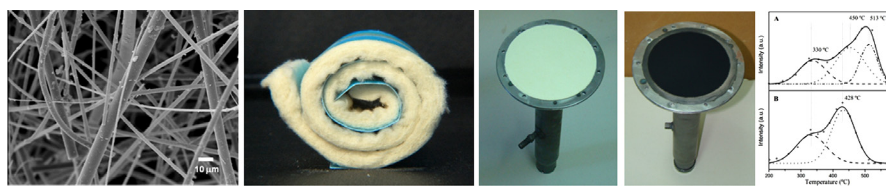
HIGHLIGHTS

- Flexible ceramic papers were prepared for diesel soot abatement.
- Cobalt and cerium oxides were impregnated to develop catalytic activity.
- Cerium nanoparticles, added to confer mechanical resistance, allowed anchoring catalytic species.
- A filter designed from catalytic papers properly resisted testing bench experiments.

GRAPHICAL ABSTRACT



Catalytic ceramic paper with an open structure. | Flexible developed ceramic papers. | Soot filter based on a ceramic paper before and after a testing bench experiment. TPO curves.

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ABSTRACT

Currently, the most adequate technology for the abatement of particles coming from diesel engines is the one that employs catalytic filters. This work proposes the preparation of catalytic ceramic papers to be employed in the development of new catalytic filters. To this end, the papermaking technique was employed. The resulting papers were flexible, easy to handle and presented suitable mechanical properties to resist the tests from a test bench in which they were placed inside a metal housing, at the exhaust pipe outlet of a Corsa 1.7 vehicle. These optimal mechanical properties were obtained through the incorporation of a suspension of CeO_2 nanoparticles during the papermaking process. It was found that the nanoparticles covered the ceramic fibers completely and that their excess accumulated under the form of patches. In order to promote the filter continuous regeneration, once the ceramic papers were formed they were impregnated with a cobalt salt which, after a calcination stage, produced oxidic clusters in tight contact with the CeO_2 nanoparticles. The papers thus obtained exhibited a maximum soot combustion temperature close to 400 °C, being T_{50} = 376 °C for the more active catalytic ceramic paper, in the presence of NO (1000 ppm) in the feed. Even though more tests are necessary to determine filtration efficiency, preliminary experiments carried out in the test bench proved that the ceramic papers properly resisted the high gas flow rates of fumes emitted by a real diesel engine (approximately 2 m^3 min^{-1}). From the TPO experiments performed on samples of catalytic ceramic papers taken from the test bench and in tight contact with the soot retained, it was possible to obtain a maximum soot combustion temperature equal to 428 °C. It was also found that the presence of ceria aggregates caused the papers to deactivate to a lesser degree after being treated at 900 °C.

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1. Introduction

Diesel engines are widely employed both in light and heavy vehicles due to their durability, reliability and fuel economy. Today, 60% of the vehicles sold in Europe are driven by diesel engines and they are also extensively used all over the world. However, the exhaust gases emitted by these engines have very high concentrations of particulate material (soot) and nitrogen oxides, which are harmful to human health [1,2].

Both particulate matter and nitrogen oxides are also harmful to the environment, acid rain and photochemical smog being among the adverse effects they provoke. For this reason, the legislation related to polluting emission control includes increasingly stricter standards. Standard Euro 6, which is to be implemented in 2014, maintains the values of particulate matter emitted by light vehicles up to 0.0045 g/km and the maximum number of particles emitted per km to 6.10^{11} but reduces the amount of nitrogen oxides (from 0.18 to 0.08 g NOx/km) [3].

The values mentioned above imposed by the EU directives cannot be achieved only by modifying the engines or by adding promoters to the fuel. Post-combustion treatments of exhaust fumes are also mandatory. So far, the most adequate treatment to abate particulate matter consists in employing filters capable of retaining the soot particles. These filters should be chemically, thermally and mechanically resistant to adequately endure the operating conditions, especially during the regeneration step that could originate high temperature peaks [4]. Besides, they should have a good filtering capacity to efficiently retain the soot particles present in the exhaust gases from diesel engines [5].

Different types of structures have been considered for the development of filters, monoliths and foams being the most widely studied ones [6–8]. Today's commercial filters are flow-through type SiC monoliths. As an attractive alternative, the use of flexible substrates would allow the filtering element to adapt to any geometry or shell, providing a more versatile filter. The paper-type structure, composed of a network of fibers interconnected through pore-type spaces provides a beneficial reaction environment which favors the gas diffusion through the catalytic bed [9]. Employing ceramic and cellulosic fibers during paper preparation produces ceramic papers resistant to severe thermal conditions after calcination (temperatures above 900–1000 °C).

In this context, the aim of this work is to employ the above described structures to develop filters for the treatment of diesel engine exhaust gases. The addition of catalysts to these structures allows obtaining catalytic filters with which self-regenerating systems could be obtained. Different catalysts have proved to be active in the temperature range of diesel engines exhaust gases, which varies upon speed, type of motion and the vehicle itself. However, at present, it is possible to heat the exhaust gases slightly without implying a significant demand of energy. Therefore, active catalysts at temperatures slightly above 350 °C can be considered suitable to be incorporated to the filters in order to achieve their continuous regeneration.

In a previous work, we studied the addition of KNO_3 to ceramic papers [10] and found that the catalytic activity of this system was acceptable (maximum soot combustion temperature = 395 °C). But, even though the addition of potassium improves the soot-catalyst contact and allows obtaining catalytically active systems, its volatility is high and therefore its use is not advisable.

Cobalt and cerium oxides were selected as active materials for filter regeneration. Studies of the Co_3O_4–CeO_2 mixed system [11–13] for soot combustion report a maximum combustion rate temperature of 500 °C for mixtures Co_3O_4 (20% molar) – CeO_2, working with a soot/catalyst ratio = 1/20, soot/catalyst mixtures with loose contact and an oxygen concentration in the feed stream of 15% [12]. In this vein, Banús et al. [14] studied the behavior of Co_3O_4–CeO_2 catalysts supported on metallic foams. The combustion activity of these structured catalysts was higher than the one corresponding to the powder catalysts for soot/catalyst mixtures in loose contact and slightly lower than that of the powder catalysts in tight contact.

In this work, CeO_2 nanoparticles were added during the preparation of ceramic papers in order to improve their mechanical properties. Cobalt was added as active component by impregnation of the ceramic paper disks with a cobalt nitrate solution. The systems thus developed were tested for the diesel soot combustion through TPO experiments carried out under laboratory conditions. Besides, in order to collect real soot particles, the catalytic ceramic papers were introduced into a metallic housing and tested in test bench with a Corsa 1.7 diesel engine.

2. Experimental

2.1. Ceramic paper preparation

The preparation method of the ceramic paper was based on a procedure similar to that used in the production of conventional paper from cellulose fibers. The ceramic fibers (50 wt.% SiO_2, 48 wt.% Al_2O_3, 2 wt.% impurities), obtained from CARBO ceramic material by elutriation, were dispersed in the aqueous medium in which a binder was added (commercial nanoparticles of CeO_2, NYACOL) to give mechanical resistance to the final ceramic paper. Cellulose fibers were also needed in order to properly form the paper matrix because they have an average length of about 3000 μm and are longer than the ceramic ones, of about 660 μm in length. Their length and ribbon shape helped retain the ceramic fibers during the formation stage. They were obtained by repulping an industrial blotting paper produced from virgin softwood Kraft slightly-refined fibers. The method required the addition of both cationic and anionic polyelectrolytes in order to form a double layer over the ceramic fibers and catalytic particles so as to favor the formation of the catalytic paper structure. The cationic polymer used was polyvinyl amine (PVAm) (Luredur PR 8095) from BASF and the anionic polymer was anionic polyacrylamide (A-PAM) from AQUATEC.

A two-step method was employed for the preparation of catalytic ceramic papers. In the first step, 1000 ml NaCl solution 0.01 N were stirred into a vessel. Several ingredients were incorporated every 3 min under constant moderate stirring (66 ml of cationic polyelectrolyte, 10 g of ceramic fibers, the CeO_2 colloidal suspension in different percentages with respect to the amount of ceramic fiber – 10 or 20 wt./wt.% as CeO_2 – 42 ml of anionic polyelectrolyte and, finally, 1.5 g of cellulosic fiber). With this suspension, a sheet was structured using the SCAN standard method (SCAN-C 26:76 and SCAN-M 5:76), applying a pressing pressure greater than the one established by the above mentioned standards for the preparation of cellulosic papers (37.5 kPa). The sheet (16.5 cm in diameter) was dried under controlled atmosphere (23 °C, 50%RH) for 24 h and finally calcined in air at 600 °C for 2 h.

The second step corresponded to the incorporation of the catalytic ingredients by impregnation of the ceramic paper discs with solutions of $Ce(NO_3)_3$ and $Co(NO_3)_2$, both with a 0.25 M concentration. Although Ce was already present as a binder, we found that the addition of the Ce salt was beneficial to improve the catalytic activity. The total amount of cerium coming from both the CeO_2 Nyacol suspension and the $Ce(NO_3)_3$ solution was intended to be kept constant in ca. 30 wt.% of atomic cerium. The calcined paper was uniformly impregnated by dripping a solution with the desired component and then calcined again at 600 °C for 2 h. In the case of papers containing both cobalt and cerium, each one