

Improved Ceria Zirconia Coated Diesel Particulate Filter

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ABSTRACT

Ceria nanofibers were prepared and deposited on SiC diesel particulate filters (DPFs), aiming at improving the soot-catalyst contact conditions and promote soot combustion at lower temperatures than in the noncatalytic case. In particular, the nanofibers have been found to be very active with respect to other ceria catalyst morphologies, due to their arrangement in a network which enhances the number of soot-fiber contact points. This effect was initially elucidated in a series of tests of soot temperature programmed combustion, which were carried out on the catalysts powders mixed with soot in loose contact conditions: a specific sub-set of nanofibers exhibited a 112 °C anticipation of the onset oxidation temperature (10% of total soot combustion) with respect to the non-catalytic test, and 38 °C with respect to ceria nanopowders obtained with the so-called Solution Combustion Synthesis (SCS). The nanofibers were then supported on Alumina washcoated DPFs, which were loaded with soot for 1 h, and subsequently subjected to a progressive temperature increase to induce soot ignition. Both CO₂ concentration in the outlet gas, and the pressure drop, were recorded during these tests. The main advantage given by the nanofiber catalyzed DPF, with respect to the other investigated morphologies, was not related to the maximum rate of soot oxidation, which was similar for all ceria catalysts, but again to the onset temperature. In fact, the pressure drop curve started to decrease more than 50 °C before the DPF catalyzed with ceria through in situ SCS

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I. INTRODUCTION

Diesel Particulate Matter (PM) is a very complex aerosol system [1,2], which has been the focus of a number of studies regarding its effects on human health [3]. PM is mainly constituted by carbonaceous particles (often called soot), originated from the incomplete in-cylinder combustion of the fuel, with diameters ranging from few nanometers (10–20 nm)

to up to hundreds of nanometers (the particles exceeding few μm are a negligible fraction), and the most common ones are around 100–200 nm [1]. However, the carbonaceous fraction is only a component of PM [1,2]: the nucleation and aggregation of soot particles is also accompanied by the adsorption of gases and the condensation of vapors (condensed volatile hydrocarbons). Moreover sulfur compounds and metallic ashes are also part of

PM. PM emission reduction is a challenging technological step for diesel engines, and is being tackled in the framework of a strict regulation worldwide. Diesel particulate filters (DPFs) are the most common devices for the collection of particulate matter for on-board diesel exhaust after-treatment. The capture of the solid fraction present in the diesel engine emissions, is carried out through a physical entrapment, thus preventing its release into the atmosphere. The filtration occurs in monolith shaped reactors having a wall-flow structure. The filter cannot accumulate particles indefinitely, and needs to be thermally regenerated, which involves the in situ combustion of the trapped PM. Particle removal can be continuous (passive regeneration), during the normal DPF filtration activity, or periodical (active regeneration), through a temperature increase inside the DPF. This temperature rise is induced by the post-injection of a specific amount of fuel, which burns in a catalytic converter upstream of the DPF itself and heats up the flue gases entering the filter, until the trapped soot starts to ignite and is converted to oxidized gaseous products. Active regeneration is mandatory if gas thermal levels are not sufficient to ensure a passive regeneration.

The drawback of the DPF catalytic coating is the increased pressure drop as compared to the bare filter, due to the additional resistance to the gas flow opposed by the washcoat layer. The catalytic coating is located on the porous walls of the filter, and is normally constituted by a washcoat on the top of which noble metals are deposited. Alternative catalysts, such as mixed oxides of transition metals, have also been the object of several studies [4,5]: in fact, despite their lower activity compared to noble metals, they are characterized by a considerably lower cost. The latter phenomenon explains the CeO₂ catalyst activity even in the absence of O₂ in the gas phase, at least until the oxide integrity is preserved [12]. The bulk oxygen uptake/release cycle can be fostered by doping CeO₂ with rare earth, alkali or transition metal oxides, in order to promote bulk oxygen mobility, therefore speeding-up the soot

oxidation rate, and to increase the oxide stability [7–9,11,12]. In fact, it is established that when soot is mixed with a catalysts in a ball mill (tight contact), the oxidation rate is much higher than when soot and the same catalyst are mixed by a spatula (loose contact). The increased number of contact points in tight conditions is responsible for this higher activity. In situ microscopy studies of catalytic soot oxidation, carried out under realistic conditions of temperature and oxygen partial pressure, confirmed the relationship between the oxidation rate and the nature of the soot-catalyst contact [13]. However, under practical conditions occurring in a catalytic DPF, loose contact rather than tight contact is encountered [4]. In fact, good contact conditions are very difficult to be reached due to the different orders of magnitude of the soot particle and the catalyst cluster sizes, which clearly hinders the overall activity of the catalyst. In this work, in order to improve the soot-catalyst interaction, the morphology of the catalyst itself was designed in the attempt to maximize the number of contact points. CeO₂ catalysts in the form of nanofibers were synthesized to this end: instead of having a foamy morphology, peculiar of the Solution Combustion Synthesis (SCS) technique [10], with inner porosities hardly accessible to soot particles [11], nanofibers are characterized by a high surface to volume ratio, typical of nearly mono-dimensional geometrical structures. Nanofibers are randomly arranged in a network which enhances the number of soot-fiber contact points, still having a high open porosity and thus a low associated pressured drop.

II. EXPERIMENTAL PROCEDURE

2.1 Powder catalyst synthesis, characterization and testing

The CeO₂ nanofibers were synthesized by the coprecipitation/ ripening method [14,15]. A 1 M solution of Cerium precursor was prepared by dissolving Ce(NO₃)₃·6H₂O (Aldrich, 99%) in distilled water. A second solution, with different mole ratios of NaOH/citric acid (0.3, 0.6, 0.8 and 1.0) (Aldrich), was

prepared in another beaker. Both solutions were mixed together in a separate beaker and then kept at 90 °C for 24 h until the fibrous precipitates were obtained. The morphology of the precipitates was influenced by the NaOH/citric acid ratio: either bundle of sticks, or elongated individual fibers, or even flakes, were produced by controlling this parameter. After the precipitates were aged, the supernatant solution was analyzed by means of AAS (atomic absorption spectroscopy) to confirm the complete precipitation of Ce³⁺. The precipitates were finally filtered and washed with distilled water, followed by drying and calcination at different temperatures, between 300 and 600 °C, for 3 h in air. An aging test at 800 °C, in air for 12 h, was also performed to check the morphology stability. The fibrous powder catalysts were then characterized: X-ray diffraction (PW1710 Philips diffractometer equipped with a monochromator, Cu K α radiation) was used to check the achievement of the cerium oxide structure. A field emission scanning electron microscope (FESEM, Leo 50/50 VP Gemini column) was employed to analyze the morphology of the CeO₂ nanofibers, and to correlate it to the activity towards soot oxidation. Finally, the specific surface areas of the prepared catalysts were evaluated through BET analysis, using a Micromeritics ASAP 2010 analyzer. The activity of the oxidation catalysts towards soot combustion was analyzed by means of temperature programmed combustion (TPC), which was carried out in a fixed-bed micro-reactor (a quartz tube, i.d. 5 mm, placed in an electric oven), according to the standard operating procedure described in [16]: an N₂ flow containing 10% of O₂, was fed at a constant rate of 100 Nml min⁻¹, to the fixed bed which was constituted by 50 mg of a mixture of carbon (Prin-tex U) and powdered catalyst (1:9 on a mass basis), diluted with 150 mg of inert silica. The resulting amounts of each species were the following: 45 mg of catalyst, 5 mg of soot and 150 mg of silica. The loose contact catalyst-carbon mixture was prepared by gently shaking it in a polyethylene vessel for at least 15 min: in fact, as previously mentioned, loose

contact is representative of the real contact conditions that occur in a catalytic trap for diesel particulate removal [4]. The reaction temperature was controlled through a PID-regulated oven and varied from 200 to 700 °C at a 5 °C/min rate. The CO/CO₂ concentration in the outlet gas was measured via NDIR analyzers (ABB)

2.2 Supported catalyst preparation and testing

The CeO₂ nanofibers showing the best catalytic activity towards soot oxidation were supported on a lab-scale DPF. The SiC wall-flow filter, which was used for this purpose, had the following geometrical characteristics: 3 cm in length, 1.2 cm in side (square section), 180 cpsi, and average porosity of 42%. The deposition of CeO₂ nanofibers on the surface of the filter inner channels has been performed through the two following methods:

Method 1: the CeO₂ nanofibers prepared by coprecipitation/ripening (NaOH/citric acid molar ratio equal to 0.8, calcination temperature of 300 °C for 2 h in air) were dispersed in a 5% HNO₃ solution, acting as a binder between CeO₂ and the SiC surface. This slurry solution was then ball-milled for 4 h. Grinding was used to obtain small enough particles to facilitate deposition on the monolith. The DPF was successively dipped into the resulting slurry, which adhered to the inner channel surface of the channels.

Method 2: the prepared CeO₂ nanofibers were deposited on Alumina washcoated DPF. First, a thin layer of γ -Alumina (Al₂O₃) was deposited at 10% of the total weight of the monolith, in order to improve the subsequent adhesion of the catalytic powder to the monolith, and to increase the specific surface area on which the active CeO₂ fiber catalyst was deposited. Alumina powder was ground in a ball mill for 24 h at room temperature after adding 3.5 % of HNO₃ to obtain a slurry, in order to create an acidic environment and thus facilitate the dispersion of the particles. The monolith samples were immersed in the slurry, after which they were withdrawn slowly and then dried at 200 °C. On the top of this layer, the

CeO₂ was deposited by dipping the washcoated filter into a water solution containing the uncalcined fibers.

III. RESULTS AND DISCUSSION

3.1 Powder catalyst characterization

Several CeO₂ nanofibers were synthesized by varying the NaOH/citric acid molar ratio: in particular, ratios of 0.3, 0.6, 0.8 and 1 were used to select the most appropriate morphology to our purpose. As has been reported in [15], a NaOH/citric acid molar ratio below 0.6 lead to the formation of sticks, characterized by an elongated structure but collected in thick bundles which makes inaccessible most of the available surface. Conversely, a NaOH/citric acid molar ratio around one generates a morphology closer to a flake than a filament, still having elongated stick-wise sub-structures. In-between, i.e. for a ratio equal to 0.8, a clear

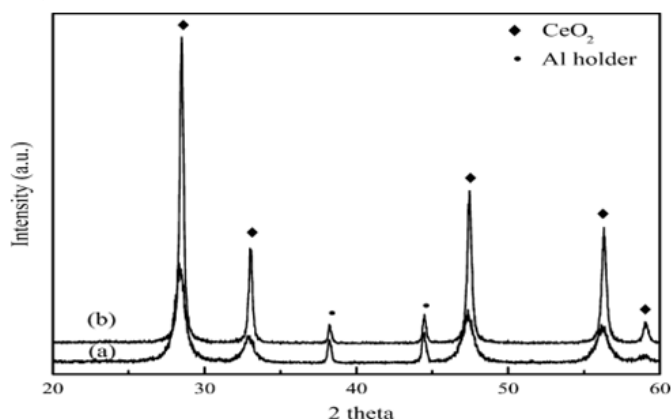


Fig. 1. FESEM images of CeO₂ (0.8) fibers calcined at different temperatures: (a) 300 °C and (b) 600 °C.

fibrous structure was obtained, as depicted in Fig. 1. If one focuses on this specific case, the length of the fibers ranges from some μm to tens of μm , while the fiber diameter goes from 100 nm to few hundreds of nm. Fig. 1 shows the morphology of the CeO₂ nanofibers synthesized with a NaOH/citric acid molar ratio equal to 0.8, hereafter denoted as CeO₂ (0.8), which seems not to be considerably affected by the calcination temperature: in particular, 3 h lasting calcinations in air at 300 °C and 600 °C were performed, the latter being more adequate to the

temperatures normally encountered inside the DPF. It is therefore encouraging that the fibrous structure does not collapse after this thermal treatment

3.2 Powder catalyst activity

All prepared CeO₂ morphologies were tested towards the oxidation of soot in TPC runs, in order to select the structure which maximized the contact between soot and the catalyst itself. Both tight contact and loose contact conditions were investigated. As previously mentioned in the introduction, tight contact forces the soot particle and the catalyst to be in intimate contact; generally, this analysis is used to discriminate the catalysts in terms of intrinsic activity, because soot oxidation is not rate-limited by a poor soot-catalyst contact. Loose contact conditions were also evaluated: in this case, the morphology of the catalyst plays a relevant role in determining the nature of the soot-catalyst contact. Table 1 gathers the results of the performed TPC runs with CeO₂ catalysts calcined at 300 °C: both the peak temperature (T_p) and the onset temperature (T_{10%}) are here reported. All values refer to the conversion of soot to CO₂, since the CO concentration was always almost negligible as compared to the one of CO₂.

Table 1 Soot combustion activity results, under loose and tight contact conditions, of CeO₂ nanofibers calcined at 300 °C and CeO₂ powders synthesized with SCS.

Catalyst	T _p tight contact (°C)	T _p loose contact (°C)	T _{10%} tight contact (°C)	T _{10%} loose contact (°C)
No-catalyst	600		470	
CeO ₂ nanofibers (0.3)	400	440	341	376
CeO ₂	399	445	346	373

nanofibers (0.6)				
CeO ₂ nanofibers (0.8)	401	447	353	354
CeO ₂ nanofibers (1)	397	438	353	358
CeO ₂ with SCS	408	465	365	338

IV. CONCLUSIONS

Ceria-based catalysts for soot oxidation were investigated in this paper, with a specific focus on their morphology. In fact, soot combustion rate can be limited either by the oxygen availability at the soot-catalyst interface, which depends on the intrinsic activity of the catalyst in delivering active oxygen, or by the extension of the soot-catalyst interface itself. Since soot particles and the catalyst grain sizes often have different orders of magnitude, this leads to a poor accessibility of the soot particles to the catalyst inner porosities. This aspect could be rate-limiting especially at low temperatures.

For these reasons, CeO₂ nanofibers were obtained through the coprecipitation/ripening method, by controlling the pH using different NaOH/citric acid mole ratios, which lead to the formation of several kinds of structures, such as stick in bundle, fibers and flakes, as confirmed by FESEM images. The fibrous morphology (NaOH/citric acid = 0.8) was sought in the attempt to maximize the number of contact points between soot and the catalyst, by allowing a better penetration of soot in the network of nanofibers, which is characterized by a very high open porosity. This concept was tested in soot oxidation tests. The most interesting finding was the following: while no major differences were noticed among all ceria catalysts in the tests performed in tight contact conditions, the catalyst morphology was quite relevant in loose contact ones. In particular,

nanofibers promoted soot combustion at lower temperatures than the other kinds of structures, especially as far as the onset temperature (T_{10%}) was concerned. CeO₂ nanofibers reduced by 112 °C the noncatalytic onset temperature, and by 38 °C the one of CeO₂ nanopowders obtained by Solution Combustion Synthesis (SCS). This proves that, when the ceria catalysts are intimately mixed to soot, they exhibit very close performances; whereas, if the soot-catalyst contact is limited, the morphology plays a relevant role, especially at low temperatures.

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