

SOOT COMBUSTION IMPROVEMENT IN DIESEL PARTICULATE FILTERS CATALYZED WITH CERIA NANOFIBERS

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Abstract

Ceria nanofibers were prepared, aiming at improving the soot-catalyst contact conditions and promote soot combustion at lower temperatures than in the non catalytic case. In this work, in order to improve the soot-catalyst interaction, CeO₂ catalysts in the form of nanofibers were synthesized: instead of having a foamy morphology, peculiar of the *Solution Combustion Synthesis* (SCS) technique, with inner porosities hardly accessible to soot particles, nanofibers are randomly arranged in a network which enhances the number of soot-fiber contact points. CeO₂ nanofibers were tested for soot oxidation in the form of powders and coated on lab-scale DPFs, in order to discriminate the effect of the fibrous morphology with respect to the one obtained with SCS, in particular at low temperatures, which are relevant for passive regeneration purposes.

Introduction

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 (DPF) are the most common devices for the collection of particulate matter for on-board diesel exhaust after-treatment. Most DPFs perform a catalytically assisted regeneration; however, good contact conditions are difficult to be reached between soot particles and the catalytic coating of the DPF, which clearly hinders the overall activity of the catalyst itself. Ceria-based catalysts for soot oxidation were investigated in this paper, with a specific focus on their morphology.

CeO₂ has been widely investigated as a catalyst for soot combustion: the Ce⁴⁺/Ce³⁺ redox cycle confers the ability to adsorb gaseous O₂, thus forming active oxygen at the catalyst surface (O_{ads}), which can be transferred to the soot-catalyst interface [1]. In fact, soot combustion rate can be limited either by the oxygen availability at the soot-catalyst interface [1], which depends on the intrinsic activity of the catalyst in delivering active oxygen, or by the extension of the soot-catalyst interface itself [2]. 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. In this work, in order to improve the soot-catalyst interaction, the

morphology of the catalyst was designed in the attempt to maximize the number of contact points: CeO₂ in the form of nanofibers were synthesized to this end.

Synthesis and Characterization

The CeO₂ nanofibers were synthesized by the precipitation method [3]: starting from a 1M aqueous solution of Cerium nitrate precursor, several CeO₂ nanofibers were synthesized by varying the NaOH/citric acid molar ratio: ratios of 0.3, 0.6, 0.8 and 1 were used to select the most appropriate morphology to our purpose. For CeO₂ nanofibers synthesized with a ratio equal to 0.8, hereafter denoted as CeO₂ (0.8), a clear fibrous structure was obtained, as depicted in Figure 1: 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. 3-hour 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.

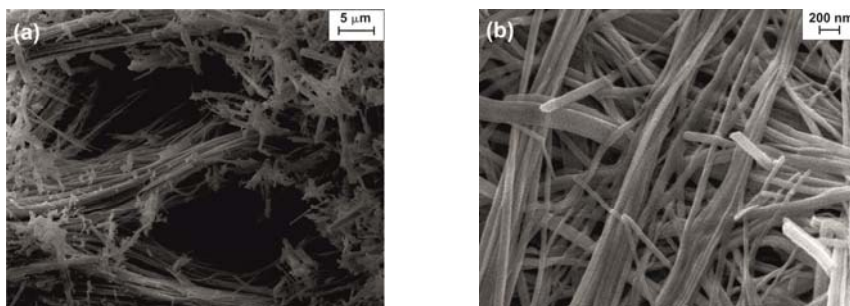


Figure 1. FESEM images of CeO₂ (0.8) fibers calcined at (a) 300°C and (b) 600°C.

Catalytic 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: 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 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 (°C)	T _p (°C)	T _{10%} (°C)	T _{10%} (°C)
	tight contact	loose contact	tight contact	loose contact
No-catalyst	600		470	
CeO ₂ (0.3)	400	440	341	376
CeO ₂ (0.6)	399	445	346	373
CeO ₂ (0.8)	401	447	349	354
CeO ₂ (1)	397	438	353	358
CeO ₂ with SCS	408	465	365	388

If one focuses on the onset temperatures, in our case fixed as 10% of the total soot conversion to CO₂, it is clear that a remarkable advantage is obtained with the nanofibers as compared to the non-catalytic case or to other morphologies, such as the nanopowders obtained with Solution Combustion Synthesis (SCS) [4]: in loose contact conditions, CeO₂ (0.8) and (1) nanofibers are much more reactive than the other morphologies, as demonstrated by a $\approx 20^\circ\text{C}$ decrease in T_{10%} with respect to CeO₂ (0.3) and (0.6). This is probably due to the better accessibility of the catalyst surface to the soot particle; in other words, CeO₂ (0.8) reached an optimal match between the soot particle and catalyst fiber sizes, among the obtained morphologies. This result is certainly not ascribed to the SSA, since all CeO₂ fibers were characterized by almost the same values.

The CeO₂ (0.8) nanofibers were also calcined at 600°C: no considerable T_p increase was observed with respect to the results shown in Table 1. A further aging of the CeO₂ (0.8) nanofibers at 800°C in air, for 12h, proved that the stability of the fibers was compatible with the temperatures occurring during soot oxidation, and no considerable activity loss was recorded.

DPF Performance

The CeO₂ nanofibers showing the best catalytic activity towards soot oxidation were supported on a lab-scale DPF. The deposition of CeO₂ nanofibers on the surface of the filter inner channels has been performed through the following method: the prepared CeO₂ nanofibers were deposited on Alumina washcoated (10%wt) DPF, until 14 %wt referred to the monolith weight was attained (Figure 2-left). The as-prepared catalyzed monoliths were canistered with vermiculite in a stainless steel reactor, and then loaded with soot through a synthetic soot generator (Aerosol Generator GFG-1000-PALAS), at an Argon flow rate of 6 Nl/min, as described in [5]. The soot mass flow rate was 5 mg/h and the loading time was fixed to 1 h for all investigated DPF samples (Figure 2-right).

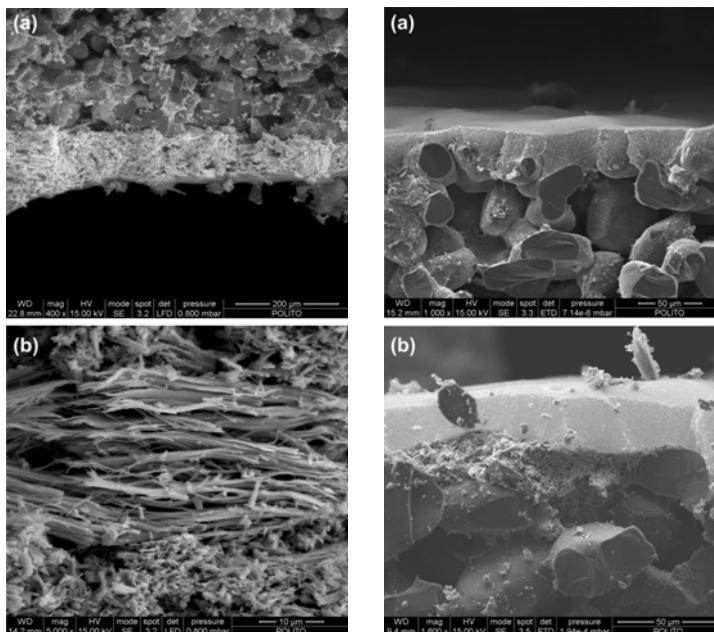


Figure 2. Left: CeO₂ (0.8) fibers deposited on Alumina washcoat and *in-situ* calcined on the DPF channel surface - magnification (a) 400X (b) 5000X; Right: soot cake build-up on the top of (a) the bare DPF channel surface and (b) the CeO₂ (0.8) fiber layer.

In Figure 3-a, the normalized pressure drop is plotted against the temperature: it can be seen that, at increasing temperature, all monolith samples exhibit the same pressure drop profile in the first part of the curve. The pressure drops were characterized by exactly the same slope for all samples, which is simply due to the viscosity increase of the gas, and its higher velocity inside the filter. Then, the profiles start to differentiate, due to the individual features of soot combustion inside the DPFs. The analysis of the curve referred to the CeO₂ (0.8) nanofibers, suggests the occurrence of a substantially different phenomenon: the pressure drop curve bends well before all the other curves, and becomes almost flat for a quite large temperature interval (between 230°C and 350°C). This signifies that the soot oxidation rate generates a virtual pressure drop decrease, which is balanced by the increasing velocity of the flow, and thus its friction losses inside the filter.

Although these temperatures are representative of the gas temperature, and not of the real temperature inside of the DPF, it is a remarkable result since this happens 150°C before the uncatalyzed case, and more than 50°C before the CeO₂ deposited by *in-situ* SCS. This behavior is clearly attributed to the morphology of the catalyst, and to its capacity to entrap the soot particles in way that maximizes the number of contact points, at least in the proximity of the interface between the

catalytic and soot layer. This is a very interesting finding since the morphology alone is responsible for this behavior. Finally, when CeO_2 entered in its suitable temperature range to show the highest activity, the morphology ceased to be the discriminating aspect, and the pressure drop decreased following the same trend of the other catalyzed DPFs.

In Figure 3-b, the CO_2 evolution during soot combustion confirms that the pressure drop decrease is ascribed to soot consumption, since the maximum slopes of the pressure drop decrease correspond to the CO_2 concentration main peaks. The CO_2 profile is peculiar of the soot combustion inside catalyzed DPFs, where part of the deposited soot is in contact with the catalytic layer, while part of it is inaccessible to the catalytic surface, and it burns according to uncatalyzed combustion.

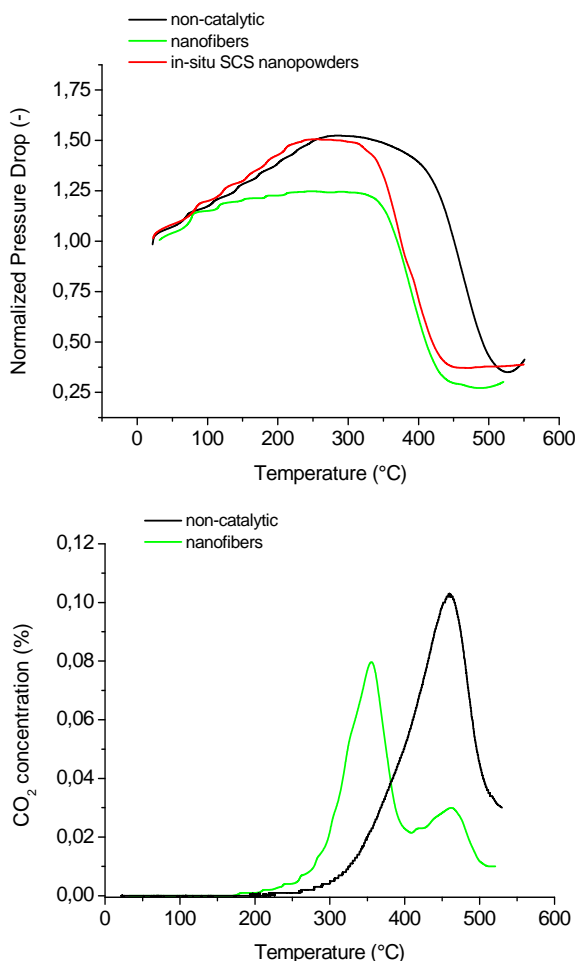


Figure 3. Pressure drop and CO_2 evolution across the DPF during soot oxidation, for a bare DPF (non-catalytic), a DPF with a catalytic layer of CeO_2 (0.8) nanofibers and a DPF coated with CeO_2 *in-situ* synthesized with SCS.

Conclusions

CeO₂ nanofibers were obtained through the coprecipitation/ripening method. 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: 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 (T10%) 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).

The CeO₂ nanofibers were then deposited on the channel surface of lab-scale DPFs, which were loaded with soot: in this way, the real contact conditions between the catalyst coating and the soot cake can be obtained, instead of resorting to the tight/loose concepts. The deposition method involved a 10 wt.% Alumina washcoating, after which the DPF was impregnated by the uncalcined nanofiber suspension (14wt%), and then a final thermal treatment in air at 600 °C for 2 h. The DPF coated with nanofibers anticipated by ≈50 °C the initial soot oxidation inside the filter with respect to the other morphologies (including the one obtained by *in-situ* SCS), likely due to the better soot-catalyst contact conditions occurring inside the filter.

References

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