CeO$_2$ catalysts with fibrous morphology for soot oxidation: the importance of the soot-catalyst contact

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Abstract
Ceria nanofibers were synthesized as soot oxidation catalysts. In fact, the morphology of the catalyst was tailored to maximize the contact between the soot particles and the catalyst itself, at increasing degrees of soot-catalyst contact. Among the synthesized catalysts, the fibrous shape demonstrated to be most active towards soot oxidation: it reduced the peak combustion temperature from 600°C (non-catalytic combustion) to 375°C in tight contact, 428°C in prolonged loose contact (see detailed definition in the text), and 553°C in loose contact. These results were compared to a very active Ceria catalyst obtained with the Solution Combustion Synthesis method, characterized by much higher porosity and SSA surface. It emerged that the nanofibers, although they have one fifth of the BET of the nanopowders obtained with SCS, they show almost the same activity in tight conditions, and a considerably better one in prolonged loose contact: hence, their peak temperature is 31°C lower than the one of SCS-obtained nanopowders at the latter condition.

This encourages to deeply investigate the interaction between the morphology and the real contact-conditions between the catalyst and soot in Diesel Particulate Filters (DPF), and to tailor the DPF catalytic support to enhance this contact, still maintaining low the pressure drop associated to the catalytic layer.

Introduction
Pollution from diesel engines contributes a significant share of planetary air-quality problems due to the emission of nitrogen oxides and particulates. Diesel particulates belong to the family of particulates under 2 microns, the so-called “lung-damaging dust” family, and can easily be inhaled by humans. Modern diesel engines emit soot particles with an average diameter of 100 nm: a way to overcome the problem of diesel particulates is to combine a trap for filtration purposes with an oxidation catalyst, which is deposited in the trap for regeneration purposes, through catalytic combustion of the trapped soot.

The phenomena involved in soot catalytic combustion are multi-scale and complex. At the micro-scale ($10^{-8}$-$10^{-9}$ m), the catalyst cluster size, crystalline structure [1-3] and composition are decisive in soot oxidation activity. In this regard, catalyst formulations that are able to undergo redox cycles are developed by increasing their defective crystalline structure or by exposing crystalline planes that are
particularly active towards these redox cycles [4], as well as by enhancing the oxygen storage capacity of catalyst formulations to rapidly restore the oxidation state of the active metal. In this work, attention was dedicated to the soot-catalyst interaction: the morphology of the catalyst itself was investigated, in the attempt to maximize the number of contact points between the soot particle and the catalyst.

**Experimental procedure**

**Synthesis**

The CeO$_2$ nanofibers were synthesized by the precipitation/ripening method [5-7]. A 1 M solution of Cerium precursor was prepared by dissolving Ce(NO$_3$)$_3$·6H$_2$O (Aldrich, 99%) in distilled water. A second solution, with different mole ratios of NaOH/citric acid (from 0.6 to 1) (Aldrich), was prepared in another beaker. Both solutions were mixed together in a separate beaker (i.e. 0.1M of Ce(NO$_3$)$_3$, 0.375M of citric acid and 0.3M of NaOH to have a NaOH/citric acid ratio of 0.8) and put in a rotary evaporator kept at constant temperature, with the condensation of the vapors to maintain the same concentration of the precursors before nanofiber formation. In particular, the residence time and the temperature of the bath lead to the formation of different morphologies of the catalysts. Three conditions were investigated, which lead to the following morphologies:

1. **Fibers**: NaOH/citric acid of 0.8, temperature of 60°C, precipitation time of 6 h.
2. **Sticks**: NaOH/citric acid of 1, temperature of 60°C, precipitation time of 6 h.
3. **Flakes**: NaOH/citric acid of 1, temperature of 25°C, precipitation time of 24 h.

The precipitates were filtered and washed with distilled water, followed by 1h drying at 110°C and calcination at 600°C for 5h in air. The solution combustion synthesis (SCS) procedure was also used for catalyst preparation, to compare the foamy and highly porous catalysts obtained with this technique with the above-mentioned fibrous ones. For the synthesis of CeO$_2$ nanopowders with SCS, glycine was added to a 0.08M Ce(NO$_3$)$_3$·6H$_2$O aqueous solution in a two-fold molar ratio with respect to the stoichiometric conditions [8], and a temperature of 600°C was employed, which ensures the formation of the desired foamy and highly porous morphology.

**Characterization**

The powder catalysts were characterized with: X-ray diffraction (PW1710Philips diffractometer) to check the achievement of the cerium oxide structure, and to estimate the average crystallite size via peak broadening; field emission scanning electron microscope (FESEM, Leo 50/50 VP Gemini column) to analyze the morphology of the CeO$_2$ nanofibers; BET analysis (Micromeritics ASAP 2010 analyzer) to evaluate the specific surface areas of the prepared catalysts.

**Activity**

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, inner diameter of 5 mm, placed in an electric oven): an N\textsubscript{2} flow containing 10% of O\textsubscript{2}, was fed at a constant rate of 100 Nml min\textsuperscript{-1}, to the fixed bed which was constituted by 50 mg of a mixture of carbon (Printex U) and powdered catalyst (1:9 on a mass basis), diluted with \(\approx 150\) mg of inert silica. Three kinds of contact conditions were explored:

1. **loose contact**: the catalyst–carbon mixture was prepared by gently shaking it with a spatula in a polyethylene vessel for around 1-2 min. This was sufficient to homogenize the soot-catalyst mixture, still loosely putting in contact the two solid phases.

2. **prolonged loose contact**: the catalyst–carbon mixture was prepared by extending the mixing time to 30 min, still with the same technique described for the loose contact. In this case, a better contact was established between the soot particles and the catalyst, without exerting any mechanical force.

3. **tight contact**: the catalyst–carbon mixture was obtained through a 15 min ball milling at 240 rpm, to reach an intimate contact between the catalyst and soot.

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/CO\textsubscript{2} concentration in the outlet gas was measured via NDIR analyzers (ABB).

**Results and discussion**

**Characterization**

Figure 1 shows the effects of the NaOH/citric acid molar ratio, the synthesis temperature and the reaction time on the complexity of the catalyst morphology. In particular, as similarly reported in [7], a NaOH/citric acid molar ratio of 0.8, a reaction temperature of 60°C, and a residence time of 6 h in the reactor, lead to the formation of nanofibers, characterized a filamentous shape with lengths ranging from some \(\mu\)m to tens of \(\mu\)m, and a fiber diameter from \(\approx 100\) nm to few hundreds of nm. A higher NaOH/citric acid molar ratio of 1 generated two different morphologies according to the temperature and residence time in the rotary evaporator: at 6 h and 60°C, i.e. the same reaction conditions which formed the nanofibers but different pH, a stick-wise morphology was obtained. These appear as thicker nanofibers, whose network is characterized by an open porosity lower than the one of the nanofibers. Presumably, the intrusion capacity of soot in these structure is rather low. If the reaction temperature is lowered to 25°C, and the time extended to 24h, a flake-like shape of the CeO\textsubscript{2} catalysts appears, with the presence of platelets instead of mono-dimensional structures.

The XRD confirmed in all cases the formation of the fluorite structure of CeO\textsubscript{2} (JCPDS card no. 34-0394); the XRD of the CeO\textsubscript{2} obtained with the SCS technique clarified that a much less crystalline structure was achieved in this case, due to the fast procedure typical of the SCS technique able to reach foamy and highly porous morphology. Through the Peak Broadening technique, the average crystallite size
of the synthesized catalysts was 66 nm for the fibers, 68 nm for sticks, and 105 nm flakes; on the other hand, the CeO$_2$ nanomaterials obtained with the SCS technique have an average crystallite size of 13 nm, for the above-mentioned reasons connected to the SCS procedure, which impacts on the final crystallinity and morphology of the catalyst.

This peculiarity affects also the specific surface area (SSA): the SCS nanopowders had a BET of 52.4 m$^2$/g; whereas, the precipitated fibers showed a BET of 9.8 m$^2$/g, the sticks of 3.4 m$^2$/g, and the flakes of 3.9 m$^2$/g. The catalyst obtained with SCS had therefore a much higher SSA than the ones synthesized with the ripening method, and especially as compared to the latter two morphologies, which reflects the bigger size of these structures than nanofibers’ ones. The following catalytic activity tests enlighten the relationship between the catalyst morphological characteristics and their performances.

Activity

All prepared CeO$_2$ 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.

Starting from the tight condition (Figure 2-left), one can observe that all catalysts considerably reduce the onset temperature of soot combustion, with a reactivity in the following increasing order: sticks (101°C T$_{10\%}$ reduction with respect to non-catalytic combustion), flakes (118°C T$_{10\%}$ reduction), fibers (157°C T$_{10\%}$ reduction) and SCS-derived nanopowders (164°C T$_{10\%}$ reduction). The tight contact maximizes the soot-catalyst contact, and is able to discriminate between the intrinsic activity of the various catalysts. The fact that a catalyst with low BET surface, such as the nanofibers, exhibited an onset temperature almost comparable to the one achieved with the nanopowders from SCS, is a confirmation of the concept behind the exploration of nanofibers as suitable morphology for soot catalysts. If one focuses on the soot conversion peak temperature, the same behavior occurs, with a slight advantage of SCS nanopowders over the fiber morphology. The small peaks occurring at around 530°C pertain to a small amount of soot poorly mixed with the catalyst, since they correspond to the peaks later showed for the loose contact condition.

One important feature of the nanopowders obtained with SCS is their better selectivity towards CO$_2$ than all other morphologies: hence, the high BET surface
confers a greater reactivity towards gaseous species, namely CO. In any case, all catalysts reach five to ten-fold reduction in CO emissions with respect to the non-catalytic case.

When the contact obtained in the so-called prolonged loose conditions is considered (Figure 2-middle), the nanofibers are even more proficient than SCS nanopowders is total soot oxidation: an improvement of 130°C in the onset temperature, and of 172°C in the peak temperature was achieved compared to soot non-catalytic oxidation, which represented a 25°C and 29°C improvement with respect to the SCS-nanopowders, respectively. This is perfectly in line with the results first obtained in [7]. More specifically, this so-called prolonged loose contact was adopted because the fibers, sticks and flakes are harder than the SCS nanopowders, which instead are very soft. The latter are very easily and rapidly mixed up with the soot particles, while the fibers require a longer time to be fully covered by the soot particles. This should not be a disadvantage in practical applications, where the soot cake adheres to the catalytic layer of the DPF, but in lab-scale tests it showed to be relevant. In these conditions, even the selectivity to CO$_2$ of the nanofibers is satisfactory and not much different from the SCS nanopowders' one, as showed by the CO curves.

Figure 2 CO$_2$ concentration, CO concentration and total soot conversion obtained in (from left to right): "tight", "prolonged loose", and "loose" contact conditions.
Finally, in loose conditions (i.e. a condition which brings out the easier mixing of SCS nanoparticles with soot, due to their softness), no clear preeminence of either the powders or fibers is observed (Figure 2-right): the total soot conversion onset temperatures are both around 393-395°C, while the peak temperature is slightly lower for the nanopowders. Even sticks and flakes approach the SCS nanopowders activity, especially at peak temperatures: even low BET surfaces are able to equal the activity of a much more nanoporous catalyst obtained with SCS, because they better match the soot particle size distribution. In order to improve the selectivity of the catalyst, one has to consider that a network of CeO$_2$ nanofibers could represent a framework with very high open porosity, thus with high permeability in the DPF: techniques for their deposition on DPFs were successfully implemented in [7], involving alumina-washcoated filter dipping in the suspension containing the uncalcined fibers, with successive calcination of the fiber-impregnated filter at 600°C for 3 h. Thus, the deposited CeO$_2$ nanofibers might be used as a reactive support for nanosized catalysts, for direct [7] or NO$_2$-mediated soot oxidation [5].

Conclusions
Different morphologies of Ceria catalysts were synthesized through the precipitation/ripening method. According to the NaOH/Citric acid, reaction time and temperature, several morphologies were obtained, among which three kinds were shown and tested in this work: fibers, sticks and flakes. Since the morphology exhibits its effect with relation to the nature of soot-catalyst contact, three soot-catalyst mixing procedures were performed: tight contact (with mechanical means) and loose contact, for short or long times, the latter called "prolonged loose contact". It emerged that the fibers are the best morphology for soot oxidation, probably due to the network of fibers which surround the soot particles, and maximize the number of contact points. Nanofibers are even more active than nanopowders synthesized with the SCS method, although they are characterized by much lower BET areas, in particular at prolonged loose contact conditions (31°C peak temperature difference between the two catalysts, in the soot conversion curve). The Authors believe that these nanofiber morphologies could be interestingly investigated as DPF coatings if used as supports for active metals.

References