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CeO_2 catalysts with fibrous morphology for soot oxidation: The importance of the soot–catalyst contact conditions

S. Bensaid*, N. Russo, D. Fino

Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

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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 (DPFs), and to tailor the DPF catalytic support to enhance this contact, still maintaining low the pressure drop associated to the catalytic layer.

1. Introduction

Pollution from diesel engines contributes a significant share of planetary air-quality problems due to the emission of nitrogen oxides and particulates. With the growing concern over health effects associated with diesel soot, the reduction in diesel particulate emissions from stationary and mobile sources has become a requirement in urban areas [1,2]. Diesel particulates belong to the family of particulates under 2 μm, 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 [3], which are widely recognized as carriers for a number of harmful substances, and many authors suggest that long-term exposure to this fine particulate matter is a risk factor for cardiovascular disease mortality [4].

A way to overcome the problem of diesel particulates is to combine a trap for filtration purposes with an oxidation catalyst [5,6], 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 filter scale (10^{-2}–10^{-3} m), the composition [7] and distribution of soot in the filter channels [8,9] plays a significant role in the propagation of the thermal front in the axial and radial directions during regeneration. At the meso-scale (10^{-5}–10^{-7} m), the boundary between the deposited soot cake and the catalytic layer defines the contact points at which effective soot oxidation occurs [10], which could be enhanced by catalyst morphology optimization (e.g. [11]). At the micro-scale (10^{-8}–10^{-9} m), the catalyst cluster size, crystalline structure [12–14] 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 [15], as well as by enhancing the oxygen storage capacity of catalyst formulations to rapidly restore the oxidation state of the active metal following soot oxidation.

In this work, particular 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.

CeO_2-based catalysts were selected for this investigation, since their mechanism for soot combustion [16,17] is in tight relationship with the soot–catalyst contact nature: the Ce^{4+}/Ce^{3+} redox cycle confers the ability to adsorb gaseous O_2, thus forming active oxygen at the catalyst surface (O_{ads}), which can be transferred to the soot–catalyst interface by superficial diffusion. This mechanism

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* Corresponding author. Tel.: +39 011 0904662; fax: +39 011 0904699.
E-mail address: samir.bensaid@polito.it (S. Bensaid).

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coexists with a temporary storage of the adsorbed oxygen as bulk lattice oxygen, which is then delivered as active O_{ads} at the catalyst surface. As a result, the overall activity of the catalyst towards soot oxidation is directly correlated to both the availability of active O_{ads} at the catalyst surface and, especially, the number of soot–catalyst contact points [18].

However, 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. CeO_2 catalysts with several morphologies (fibers, sticks and flakes) were synthesized to this end: the purpose of obtaining fibrous morphologies was to form networks of randomly arranged fibers which enhance the number of soot-fiber contact points, still having a high open porosity and thus a low associated pressured drop when deposited on the DPF surface. The effect on the catalytic activity of the obtained CeO_2 morphologies was assessed through soot oxidation tests; the results were compared to the ones of foamy catalysts obtained with the *solution combustion synthesis* (SCS) technique [19].

2. Experimental procedure

2.1. Synthesis

The CeO_2 nanofibers were synthesized by the precipitation/ripening method [11,20,21]. A 1 M solution of Cerium precursor was prepared by dissolving $Ce(NO_3)_3{\cdot}6H_2O$ (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. 0.1 M of $Ce(NO_3)_3$, 0.375 M of citric acid and 0.3 M 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 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 the bath of 60 °C, precipitation time of 6 h.
2 *Sticks*: NaOH/citric acid of 1, temperature of the bath of 60 °C, precipitation time of 6 h.
3 *Flakes*: NaOH/citric acid of 1, temperature of the bath of 25 °C, precipitation time of 24 h.

The precipitates were filtered and washed with distilled water, followed by 1 h drying at 110 °C and calcination at 600 °C for 5 h in air. The supernatant solution was analyzed by means of AAS (atomic absorption spectroscopy) to confirm the complete precipitation of Ce^{3+}.

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. The SCS involves different phenomena and reactions that allow the process to be self-sustaining from an energetic viewpoint [19]. A homogeneous aqueous solution of metal nitrates and urea or glycine is placed into an oven at a constant temperature of between 400 °C and 800 °C; it quickly begins to boil and froth until ignition takes place. The exothermic reaction, due to urea or glycine combustion, provides the heat necessary for the endothermic transformation of nitrates into the desired oxide. The whole process is over in a few minutes and the result is an inorganic foam that crumbles easily, with a very high specific volume and surface area. For the synthesis of CeO_2 nano-powders with SCS, glycine was added to a 0.08 M $Ce(NO_3)_3{\cdot}6H_2O$ aqueous solution in a two-fold molar ratio with respect to the stoichiometric conditions [19], and a temperature of 600 °C was employed, which ensures the formation of the desired foamy and highly porous morphology.

2.2. Characterization

The powder catalysts were characterized with: X-ray diffraction (PW1710Philips diffractometer equipped with a monochromator, Cu Kα radiation) to check the achievement of the cerium oxide structure, and to estimate the average crystallite size via the peak broadening technique; field emission scanning electron microscope (FESEM, Leo 50/50 VP Gemini column) to analyze the morphology of the CeO_2 nanofibers, and to correlate it to the activity towards soot oxidation; BET analysis (Micromeritics ASAP 2010 analyzer) to evaluate the specific surface areas of the prepared catalysts.

2.3. 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), according to the standard operating procedure described in [21]: an N_2 flow containing 10% of O_2, was fed at a constant rate of 100 N ml min^{-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 ≈150 mg of inert silica. The resulting amounts of each species were the following: 45 mg of catalyst, 5 mg of soot, 150 mg of 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. Although the procedure lasted a very short time, the established contact lead to reproducible results for each tested catalyst.
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, but without exerting any mechanical force to enhance the contact between the two solid phases.
3. *Tight contact*: the catalyst–carbon mixture was obtained through a 15 min ball milling at 240 rpm (IG/W2/E, Giuliani Tecnologie), to reach an intimate contact between the catalyst and soot. This technique maximizes the number of contact points and, even if it is less representative of the real contact conditions that occur in a catalytic trap for diesel particulate removal [22], it better discriminates among the different morphologies.

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_2 concentration in the outlet gas was measured via NDIR analyzers (ABB). Each test was repeated three times to ensure the reproducibility of the obtained results: the maximum deviation from the mean value over the three tests was ±4 °C, therefore being around 1% of the measured temperature.

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 onset ($T_{10\%}$) combustion temperature, defined as the temperature at which 10% of the initial soot is converted, was also considered in order to better discriminate the intrinsic catalytic activity of the prepared catalysts. This is particularly important in order to