



Contact dynamics for a solid–solid reaction mediated by gas-phase oxygen: Study on the soot oxidation over ceria-based catalysts



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ABSTRACT

Ceria-based catalysts with different topological and textural properties have been prepared to study the role of the soot–catalyst contact on the soot oxidation reaction. The physico-chemical features of the catalysts have been investigated by means of complementary techniques, such as powder XRD, N₂ physisorption at –196 °C, optical microscopy at variable temperature, FESEM, TEM, and thermogravimetric analysis.

As a whole, the best catalytic activity has been obtained with the CeO₂–nanocubes (denoted to as “Ce-NC”) because of their higher intrinsic reactivity. On the other hand, high-surface area materials prepared by the cerium nitrate decomposition (denoted to as “Ce-ND”) or hydrothermal route (CeO₂–stars, referred to as “Ce-SAS”) resulted less effective toward the soot combustion, confirming the surface-sensitivity for this reaction.

Moreover, it has been proven a higher dependence of the oxidation activity on the catalyst-to-soot ratio (wt./wt.) for the nanostructured catalyst (Ce-NC) exhibiting the lowest BET specific surface area ($S_{\text{BET}} = 4 \text{ m}^2 \text{ g}^{-1}$). On the other hand, the accessible (real) surface area, at variance of the BET surface area, seems to play a relevant role for this solid–solid reaction mediated by gas-phase oxygen.

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1. Introduction

Recent legislation has introduced stringent particulate matter (PM) limits for vehicles, thus promoting the improvement of current technologies to satisfy the stated standards [1–4]. Among the different alternatives, the entrapment of particulates from exhaust gases by Diesel particulate filters (DPFs) has received much interest since its application by PSA in years 2000s, and has become widely applied in EU since 2008 with the introduction of Euro 4 standards [5–10].

The solid carbon (soot) that forms Diesel exhaust particulate can be burnt above 500 °C [9], whereas typical Diesel engine exhaust temperatures fall within the 200–500 °C range [10]. Therefore, solid catalysts are necessary to increase the oxidation rate of filter traps at low temperatures. Among the many oxidation catalysts designed since the 1980s, ceria-based catalysts appear to be the most promising candidates for DPFs due to their excellent redox behavior and high oxygen storage capacity (OSC) [11]. Moreover, the low cost

of ceria (as compared to noble metals) made CeO₂–based materials particularly attractive for Diesel exhaust aftertreatment devices [1].

The feasibility of soot combustion depends to a great extent on the catalyst–soot contact conditions and it is, therefore, necessary to maximize the interactions between the catalyst surface and soot particles, both of which are solid components [12,13]. However, “tight” contact conditions are usually difficult to be obtained in real exhaust conditions because of the different orders of magnitude between soot and catalyst particle sizes. In order to consider the soot oxidation activity of various catalytic materials, two kinds of catalyst–soot contact conditions are mostly used for laboratory-scale studies [14,15]:

- “Loose” contact is usually obtained by gently shaking the catalyst–soot mixture with a spatula. Although the procedure is very short (it takes about 1–2 min), the established contact leads to reproducible results. The method, in fact, consents to homogenize the solid mixture, but still allows the two solid phases to be put in contact loosely. Neeft et al. [16] have shown that the soot–catalyst contact in a DPF is as loose as that of materials mixed roughly with a spatula.

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- “Tight” contact is achieved through a ball-milling (or a mortar) to obtain an intimate contact between the catalyst and soot. When soot is mixed with a catalyst by a ball-milling procedure, the oxidation rate is much higher than when soot and catalyst are mixed in “loose” contact. Moreover, this procedure maximizes the soot-catalyst contact points and then it is able to discriminate the surface reactivity better. On the other hand, it is less representative of the “real” contact conditions occurring in a catalytic trap.

As it is known, the contact between soot and catalyst particles is of great importance in the estimation of the soot oxidation kinetics and, nowadays, there is still a need to study soot-catalyst contact dynamics more realistically for designing highly effective materials, such as the nanostructured ceria-based catalysts. Thus, in order to increase the soot-catalyst interactions, different structures of ceria have been developed, such as nanofibers, stars, nanorods and, more recently, nanocubes [17–21].

In the present work, ceria-based materials with different topological and textural properties (CeO₂-nanocubes, CeO₂-stars and “classical” CeO₂, referred to as Ce-NC, Ce-SAS and Ce-ND, respectively) have been prepared to investigate the soot-catalyst contact conditions and their role toward the soot oxidation reaction. The physico-chemical features of the prepared catalysts have been investigated by complementary techniques.

2. Experimental

2.1. Preparation of the samples

A detailed description of the procedures used for the preparation of the three catalysts is reported elsewhere [19,20]. Briefly, ceria nanocubes (denoted as “Ce-NC”) were prepared via the hydrothermal method: proper amounts of NaOH (24 g) and Ce(NO₃)₃·6H₂O (2.2 g) were dissolved in 35 mL and 5 mL of bi-distilled water, respectively. The two solutions were then mixed together and stirred for 1 h to obtain a milky slurry. The final mixture was transferred to an autoclave (150 mL) and then aged at 165 °C for 24 h. The fresh precipitate was washed and dried at 60 °C overnight. Finally, the powder was calcined at 550 °C for 4 h.

CeO₂ self-assembled stars (denoted as “Ce-SAS”) were prepared via a hydrothermal route in a batch stirred-tank reactor [19]. The first step consists in dropping CeCl₃·7H₂O (0.2 M) in cetyl trimethylammonium bromide (CTAB) aqueous solution (0.01 M); subsequently, urea (80 mmol) was added to the mixture to get a 4:1 ratio between urea and cerium salt. The obtained solution was stirred for 30 min at room temperature. Next, the final solution must stay in the stirred tank for 24 h at 120 °C, and then cooling for 24 h to get a white precipitate. The latter was dried at 60 °C for 24 h and calcined at 600 °C for 4 h.

“Classical” CeO₂ (denoted as “Ce-ND”) was obtained through the thermal decomposition of Ce(NO₃)₃·6H₂O (dried initially at 100 °C for 5 h) by calcination at 500 °C for 5 h. All calcinations have been carried out in static air.

2.2. Characterization of the catalysts

The powder X-ray diffraction patterns were collected on a X’Pert Philips PW3040 diffractometer using Cu K α radiation (2 θ range = 20°–70°). The diffraction peaks were indexed according to the Powder Data File database (PDF 2000, International Centre of Diffraction Data, Pennsylvania).

The BET specific surface area (S_{BET}) and total pore volume (V_{p}) were determined by N₂ physisorption at –196 °C on a Micrometrics ASAP 2020 instrument. Prior to the analyses, the samples were

outgassed at 200 °C for 2 h to remove water and other atmospheric contaminants. The specific surface area of the samples was calculated using the BET method.

Sample morphology was investigated by means of a field emission scanning electron microscope (FESEM Zeiss MERLIN, Gemini-II column) and Transmission Electron Microscopy (TEM, Jeol JEM 3010 operating at 200 kV).

Thermogravimetric analyses (TGA) were performed through a Mettler-Toledo instrument (TGA/SDTA851e). Printex-U was used as model soot. The ceria+soot (3 wt.%) mixture was obtained by shaking the container for 1 min. Samples were heated to 800 °C at 10 °C min^{–1} flowing air (100 mL min^{–1}). The weight loss was recorded versus temperature. Optical microscopy analyses at variable temperature were performed with a ZEISS SteREO Discovery.V8 microscope using an objective of 80x linear magnification. The image generated (250x, 2080 x 1540 pixels) by the microscope was recorded by AxioCam ICc3 camera and transferred to a computer using the AXIOVision software. The sample was placed on a 7 mm diameter quartz disc and placed in a high temperature Linkam Stage TS1500 *in-situ* cell sample holder, as schematized in Fig. 1-top. Air flow rate was 10 mL min^{–1}. A temperature controller Linkam TMS 93 was used to carry out temperature programmed experiments. Image observations were done with the optical microscope (Fig. 1-bottom) at the increase of temperature up to 1000 °C. The heating rate was approximately 30 °C min^{–1}.

The comparison between TGA and Linkam stage tests is not direct, since the soot oxidation temperatures recorded by the microscope camera do not match with the weight loss curves shown in the corresponding TGA plots. The shift in temperature, around 250 °C for each catalyst sample, can be explained by: i) the design of the Linkam stage, entailing that the heating element temperature differs from the one of the soot-catalyst sample; ii) the difference in heating rate.

2.3. Catalytic activity tests

The soot combustion activity of the catalysts was measured by means of temperature programmed oxidation (TPO). Tests were carried out in a fixed-bed micro-reactor (a quartz U-tube, with an inner diameter of 4 mm, heated by an electric, PID-regulated furnace). An oxidizing atmosphere containing 50% air and 50% N₂ was fed at a constant rate of 100 mL min^{–1} to the reactor. The catalytic bed was prepared by mixing 5 mg of carbon soot, 45 mg of powdered catalyst, and 150 mg of inert silica (soot/catalyst = 5/45 wt./wt.). The mixtures were prepared using two different methods to simulate the “loose” and “tight” contact conditions, as described elsewhere (*vide supra*) [11]. In order to evaluate the activities for various soot-to-catalyst ratios in “loose” contact conditions, further soot-catalyst mixtures were prepared with the following ratios: 9/41, 15/35, 20/30 wt./wt. (soot-catalyst mixture = 50 mg). The reaction temperature was measured with a thermocouple placed 5 mm above the catalytic bed, while the oven temperature was controlled by means of a PID-regulated system and varied from 200 to 700 °C at a 5 °C min^{–1} rate. The CO_x concentrations in the outlet gas were measured via NDIR analyzers (ABB).

3. Results and discussion

3.1. Textural and morphological properties of the catalysts

Table 1 summarizes the main textural properties of the prepared samples, derived from both N₂ physisorption at –196 °C and X-ray diffraction patterns.

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