



## Improving ceria-zirconia soot combustion catalysts by neodymium doping

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### ABSTRACT

The effect of Nd doping on the physicochemical and catalytic properties for soot combustion of  $\text{CeO}_2$  and  $\text{CeO}_2\text{-ZrO}_2$  oxides has been studied. Four oxides with composition  $\text{CeO}_2$ ,  $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_2$ ,  $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$  and  $\text{Ce}_{0.64}\text{Zr}_{0.27}\text{Nd}_{0.09}\text{O}_2$  have been prepared by co-precipitation and calcination at  $800^\circ\text{C}$ , characterized by XRD, Raman Spectroscopy,  $\text{N}_2$  adsorption and temperature programmed reduction by  $\text{H}_2$ , and tested for soot combustion with  $\text{NO}_x/\text{O}_2$ . The catalytic activity for soot combustion of  $\text{CeO}_2$  and  $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_2$  was null due to thermal sintering ( $1$  and  $5\text{ m}^2/\text{g}$ , respectively), and Zr-doping is mandatory to prevent such sintering. The best catalytic activity for soot combustion was obtained with  $\text{Ce}_{0.64}\text{Zr}_{0.27}\text{Nd}_{0.09}\text{O}_2$  ( $37\text{ m}^2/\text{g}$ ), and as far as we know, it is the first time that this improvement on Ce-Zr soot combustion capacity by Nd doping is reported.  $\text{Ce}_{0.64}\text{Zr}_{0.27}\text{Nd}_{0.09}\text{O}_2$  combines the beneficial effect of both Zr doping (improved thermal stability and redox properties) and Nd doping (additional benefit on redox properties by oxygen vacancies creation due to  $3+$  cations doping into the lattice). The highest activity for soot combustion of  $\text{Ce}_{0.64}\text{Zr}_{0.27}\text{Nd}_{0.09}\text{O}_2$  is related with its highest NO oxidation capacity. As deduced by in situ DRIFTS experiments, Nd-doping into the Ce-Zr oxide favors the formation of less stable surface nitrogen species (nitrates and nitrites were detected) in comparison to those formed on  $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$  (only nitrates were detected) providing alternative and faster  $\text{NO}_2$  production pathways.

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### 1. Introduction

Ceria-based oxides are suitable soot combustion catalysts for diesel exhausts purification. Diesel Particulate Filters (DPFs) are used for soot filtering [1–3] and ceria catalysts promote DPFs regeneration by lowering the required temperature to combust soot. The commercially available PSA (Peugeot-Citroën Société d'Automobiles) system, which is running on more than 1,000,000 cars, uses a cerium-fuel additive to lower the ignition temperature of soot [4], and it has been also demonstrated that DPFs regeneration is improved by loading ceria nanofibers on the filter [5].

This has motivated an intense research activity at laboratory scale in order to improve the features of soot combustion ceria catalysts. One of the critical aspects of the ceria-catalyzed soot combustion is the poor solid–solid contact between catalyst and soot particles [6], and some promising 3D-ordered ceria catalysts have been recently prepared to solve this problem. This kind of catalysts allows the soot particles to enter into the open structure of ceria, improving the soot-catalyst contact [7–9].

Thermal stability is also a mandatory requirement for soot combustion catalysts because, in spite of diesel exhaust temperature

is usually lower than  $400^\circ\text{C}$ , the temperature inside the DPF can increase significantly as a consequence of the highly exothermic soot combustion process. Thermal gradients of  $100^\circ\text{C}/\text{cm}$  have been measured during DPFs regeneration along both radial and longitudinal directions of the filters [10]. Pure cerium oxide has poor thermal resistance and sinters rapidly above  $600^\circ\text{C}$  [11], and ceria doping with certain alien cations can partially prevent thermal sintering. In addition, it is well known that doping ceria with proper foreign cations has different benefits on the catalytic activity of this material, improving surface reducibility, oxygen storage capacity and oxygen mobility within the framework [12]. The dopants that have been studied more often are Zr [7,9,11,13–21], Pr [8,14,22–24] and La [13,14,17,22–25].

As far as we know, the study of Nd-containing ceria-based soot combustion catalysts has never been reported in the open literature. Actually, there are only few articles devoted to study catalytic properties of Nd-doped cerium oxides. Wang et al. [26] studied the effect of neodymium doping on the properties of ceria-zirconia solid solutions and on the catalytic performance of its supported Pd-only three-way catalysts for gasoline engine exhaust reduction. They demonstrated that the addition of Nd results in the formation of ceria-zirconia-neodymia ternary solid solution with better textural and structural properties than a similar undoped ceria-zirconia mixed oxide, as well as improved reducibility and redox behavior, leading to the promoted three way catalytic

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activity and enlarged air/fuel operation window. These benefits were more relevant on aged catalysts than on fresh catalysts.

These results lead us to think that Nd could be able to improve the catalytic performance of ceria-zirconia soot combustion catalysts and the goal of the current study is to prepare and characterize Nd-doped ceria and ceria-zirconia mixed oxides and test these materials as soot combustion catalysts.

## 2. Experimental

### 2.1. Oxides preparation

Four oxides with the following nominal composition have been prepared: CeO<sub>2</sub>, Ce<sub>0.9</sub>Nd<sub>0.1</sub>O<sub>2</sub>, Ce<sub>0.73</sub>Zr<sub>0.27</sub>O<sub>2</sub> and Ce<sub>0.64</sub>Zr<sub>0.27</sub>Nd<sub>0.09</sub>O<sub>2</sub>.

Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Sigma–Aldrich, 99%), ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O (Fluka, x ≈ 6) and Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Aldrich, 99.9%) were used. The required amounts of the metal precursors were dissolved in water and co-precipitation was carried out by dropping an ammonia solution to keep the pH at about 9. After filtering, the precipitate was dried at 110 °C in air overnight and calcined in air at 800 °C for 90 min to ensure thermal stability. This synthesis method has been selected taking into account our previous studies, where soot combustion Ce–Zr mixed oxide catalysts prepared by different methods were compared (nitrates calcination, co-precipitation, carbon template, solid combustion synthesis (SCS), microemulsion, formation of citrate complexes... ) [27]. The co-precipitation method is one of the simplest and environmental-friendly (no dissolvent, no surfactants, etc. are required) methods, and among catalysts calcined at 800 °C, the catalytic results obtained with the Ce–Zr mixed oxide prepared by co-precipitation were only outperformed by home-made catalysts prepared by the microemulsion and citrate-complexes methods. For these reasons, the co-precipitation method has been selected for the current study.

### 2.2. Oxides characterization

X-ray diffractograms of the ceria-based oxides were recorded in a diffractometer Rigaku Miniflex II, using Cu K<sub>α</sub> radiation (λ = 0.15418 nm). The diffractograms were recorded between 10 and 80° (2θ) with a step of 0.025°. The average crystallite size (*D*) of the oxides was determined using the Scherrer's and Williamson–Hall's equations. In the Scherrer's equation

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$$

(Scherrer's equation)

λ is the X-ray wavelength, *K* is the particle shape factor, taken as 0.94 for ceria-based materials [28], β was defined as the width at half maximum of the peak and θ is the position (angle) of the (1 1 1) peak.

The Williamson–Hall's equation (W–H) separates the effects of size and strain in the nanocrystals:

$$\beta_{\text{Total}} = \beta_{\text{Size}} + \beta_{\text{Strain}} = \frac{0.9 \cdot \lambda}{D \cdot \cos \theta} + \frac{4 \cdot (\Delta d) \cdot \sin \theta}{d \cdot \cos \theta}$$

(Williamson–Hall's equation)

where β<sub>Total</sub> is the full width half maximum of the XRD peak, λ is the incident x-ray wave length, θ is the position of the peaks, *D* is the crystallite size, and Δ*d* is the difference of the *d* spacing corresponding to a typical peak. A plot of β<sub>Total</sub>·cosθ versus 4·sinθ yields the crystal size from the intercept value.

Raman spectra were recorded in a Bruker RFS 100/S Fourier Transform Raman Spectrometer with a variable power Nd-YAG laser source (1064 nm). The laser beam was focused on the sample

in a 180° backscattering configuration and 128 scans at 100 mW laser power were recorded.

The BET surface area of the oxides was determined by physical adsorption of N<sub>2</sub> at –196 °C in an automatic volumetric system (Autosorb-6, Quantachrome). The samples were outgassed at 150 °C for 4 h before the N<sub>2</sub> adsorption measurements.

Experiments of temperature programmed reduction by H<sub>2</sub> (H<sub>2</sub>-TPR) were carried out in a Micromeritics Pulse ChemiSorb 2705 device, consisting of a tubular quartz reactor (inner diameter 5 mm) coupled to a thermal conductivity detector (TCD). The experiments were conducted with 15 mg of fresh catalyst, which was heated at 10 °C/min from room temperature to 1050 °C in 40 ml/min flow of 5 vol.% H<sub>2</sub> in Ar. A cold trap was placed before the TCD, consisting of a mixture of isopropyl alcohol and liquid nitrogen (temperature –89 °C).

### 2.3. Catalytic tests

Catalytic tests were performed in a tubular quartz reactor coupled to specific NDIR-UV gas analyzers for CO, CO<sub>2</sub>, NO, NO<sub>2</sub> and O<sub>2</sub> monitoring (Fisher–Rosemount, models BINOS 100, 1001 and 1004). 20 mg of soot, 80 mg of catalyst, or 20 mg of soot +80 mg of catalyst mixed in the so-called loose contact conditions [6] were used in these experiments (and also an empty reactor). In all cases, the samples were diluted with 300 mg of SiC to avoid pressure drop and favor heat transfer. The model soot used in this study is a carbon black by Evonik–Degussa GmbH (Printex U). The gas mixture composition was 500 ppm NO/5% O<sub>2</sub>/N<sub>2</sub> and the gas flow was fixed at 500 ml/min (GHSV = 30,000 h<sup>–1</sup>). The experiments consisted of heating the reactor from room temperature until 700 °C at 10 °C/min.

### 2.4. In situ DRIFTS experiments

A FTIR spectrometer (Jasco, model FT/IR-4100) was used for in situ DRIFTS experiments, with a reaction cell that allows temperature and gas flow composition control. The reactor is designated to allow the gas to flow through the catalytic bed. The individual gases (NO/He, O<sub>2</sub>/He and pure He) were mixed by using a set of mass flow controllers, and a mixture of 500 ppm NO/5%O<sub>2</sub>/He was used to perform the experiments.

The experiments consisted of heating the oxides until 460 °C under He flow, and a background spectrum was recorded in these conditions for each oxide. Then, the inert gas was replaced by the NOx/O<sub>2</sub> gas mixture and spectra were recorded after different times. The background spectrum has been subtracted in all spectra shown in this article, and therefore, only bands attributed to adsorbed species are observed.

## 3. Results and discussion

### 3.1. Structural characterization by XRD, N<sub>2</sub> adsorption and Raman spectroscopy

XRD and Raman spectroscopy provide complementary information about the structure of the ceria-based materials. X-Ray diffraction takes place on the ceria lattice cations, giving information of more than 1 μm thickness if particles of this size are analyzed. On the contrary, Raman spectra of cerium oxides are caused by oxygen breathing around the Ce<sup>4+</sup> cations [29,30] and a surface thickness of about 10–100 nm is usually analyzed.

Fig. 1 shows the XRD patterns of the four ceria-based oxides, all of them with the typical peaks of the cubic structure of ceria. All the diffractograms show the main reflections of a fluorite-structured material, corresponding to the (1 1 1), (2 0 0), (2 2 0),

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