

Soot combustion over ceria-praseodymia nanocatalysts

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Abstract

Recent legislation has introduced more stringent NO_x and particulate limits for light and heavy-duty vehicles as well as for passenger cars, and has imposed the use of catalytic devices to satisfy the required standards [1-2]. The solid carbon (soot) that forms Diesel Exhaust Particulates can be burnt off above 600 °C, although typical diesel engine exhaust temperatures fall within the 200 to 500 °C range [3]. Therefore, oxidation catalysts can be used to increase the oxidation rate of filter traps at lower temperatures. In this scenario, ceria-based materials are among the most active soot oxidation catalysts under either O₂ or in a NO_x/O₂ atmosphere. Ceria alone, or in combination with other metal oxides, may exhibit promising soot oxidation activity [3,4]. The redox behaviour, as well as the availability of chemisorbed oxygens, are the most important factors that play a role on the oxidation activity of CeO₂-based materials. However, the number of soot-catalyst contact points also affects the catalytic activity of ceria for soot oxidation and it is therefore necessary to maximize the interaction between the soot particles and the catalyst surface [1-4].

Ceria nanomaterials with well-defined reactive (100) and (110) planes are usually more active than conventional polycrystalline ceria NPs with preferred exposure of (111) planes [5,6]. Moreover, inserting aliovalent cations, like Pr³⁺/Pr⁴⁺ into ceria framework gives more surface oxygen vacancies (structural defects) as well as redox active sites.

The present work investigates the catalytic activity of a series of nanostructured ceria-praseodymia with various molar compositions, as well as their morphologies, in soot oxidation. Tailoring the morphology of nanoscale ceria confers interesting surface properties in terms of reactivity, as previously discussed in the literature [1]. Thus, a set of ceria-praseodymia catalysts with different Pr loadings (0, 10%, 25%, and 50%-mol, denoted further as Ce100, Ce90Pr10, Ce75Pr25, and Ce50Pr50 respectively) were synthesized through a hydrothermal process using nitrate metal salt precursors and concentrated sodium hydroxide. For comparison, a set of ceria-praseodymia catalysts, and a pure CeO₂, were also synthesized through the solution combustion synthesis (SCS).

The physico-chemical properties of the prepared catalysts have been investigated using complementary techniques.

The diffraction peaks for mixed Ce-Pr oxide catalysts, reported in Figure 1 (left), show that all samples refer to pure CeO_2 despite varying in praseodymium contents.

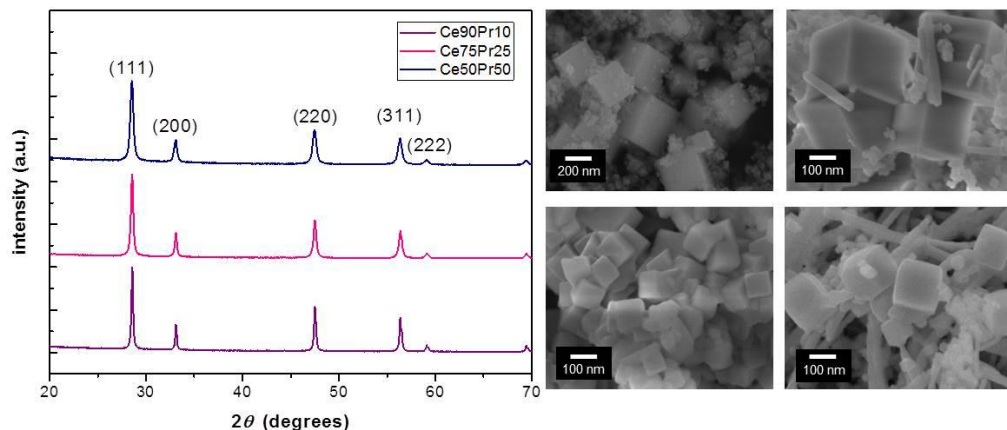


Figure 1. Powder XRD patterns of the prepared samples (left) and their corresponding FESEM images (right)

This means good praseodymium dispersion in CeO_2 lattice, forming a homogeneous solid solution. Samples with higher praseodymium content show broader peaks, indicating smaller particle sizes according to Scherrer equation. These data are in agreement with findings from FESEM analysis on Figure 1 (right). Pure CeO_2 sample (Ce100) takes form in nanocubes with average size of 200-300 nm. Samples with praseodymium experienced reduction of particle size to 100 nm. Both Ce90Pr10 and Ce75Pr25 still maintain the dominance of nanocubes, while in Ce50Pr50 sample a mixed phase of nanocubes and nanorods is observed. The addition of praseodymium, since it modifies the morphology, slightly increases the surface area of the catalysts, as reported on Table 1.

Table 1. BET surface area of the catalysts.

Samples	BET surface area ($\text{m}^2 \text{g}^{-1}$)
Ce100	6
Ce90Pr10	9
Ce75Pr25	12
Ce50Pr50	20

Catalytic tests in a fixed bed micro reactor were performed to gain initial insights

into the effect of praseodymium doping and morphology on soot combustion activity. A typical “tight contact” condition between soot and catalyst in the reactor bed was preferred since it allows better discrimination of the activity of each catalyst. The results of catalytic tests in the fixed bed reactor are summarized in Figure 2. It appears that the morphology of the catalyst plays a relevant role: hence, the nanocube morphology of pure Ceria (Ce100) is more active than the corresponding Ce-SCS, at high conversion degrees. Moreover, increasing praseodymium contents in the nanocube structure entailed lower soot combustion temperatures.

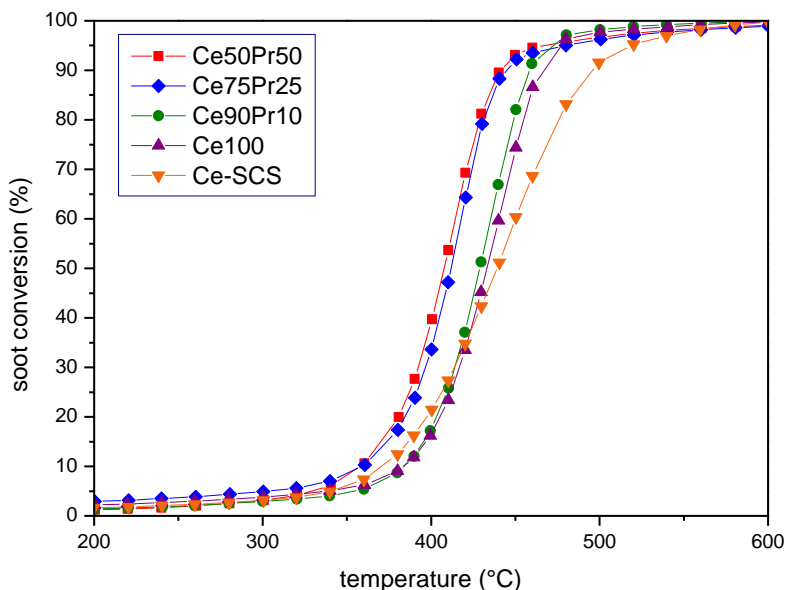


Figure 2. Soot conversion values as a function of temperature over ceria-praseodymia and pure ceria catalysts using “tight” soot-catalyst contact condition.

Therefore, the best catalytic activity was found in the sample with the highest praseodymium loading (Ce50Pr50), whose temperature at which soot is half burnt ($T_{50\%}$) is the lowest (408 °C). This result is due the doping effect of Pr coupled to the presence of crystalline planes with enhanced reactivity towards soot combustion. It is worth noticing that, as obtained with pure Ceria in [6], the nanostructured catalysts possess a strong thermal stability over repeated cycles of soot oxidation.

Moreover, a series of structured catalysts was eventually prepared by impregnating SiC monoliths into suspensions of the readily-made catalysts. The tests with

structured catalysts are currently under investigation; preliminary results confirm the same powder catalyst activity ranking, under real soot-catalyst contact conditions, and reveal the potential of such nanostructured morphologies, and Pr doping, for soot combustion.

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