

Rare-earth doped ceria nanostructures with engineered morphology and systematic activity for the oxidation of different types of carbon soot

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Highlights

- Mixed nanocubes and nanorods form in doped CeO₂
- Ceria-lanthana is rich in reactive surface oxygen species and acid sites
- Soot oxidation temperature depends on both catalyst activity and particulate reactivity
- Ceria-lanthana shows outstanding performances with all the types of soot

1. Introduction

Particulate matter is an undesired combustion byproduct emitted by different anthropogenic sources, such as direct injection internal combustion engines, power plants, waste incineration, etc. Due to its detrimental impact on the environment and human health, soot emissions must be abated, e.g. by application of properly developed particulate filters for exhaust gas systems. For the periodic regeneration of particulate filters, the use of catalysts allows to reduce the required temperature. Ceria-based materials can be fruitfully employed, due to their good redox properties and high oxygen storage capacity [1]. Moreover, nanostructured ceria particles with well-defined shapes can be prepared, the morphology of which affects not only the intrinsic activity and the defect abundance, but also the catalyst-carbonaceous particle contact area [2 - 3]. Further improvements in the catalytic performances can be obtained by combining ceria with other rare-earth elements [4]. In this study, pure ceria was compared to equimolar ceria-lanthana and ceria-praseodymia oxides. The physico-chemical properties of these nanostructured catalysts were investigated, with a focus on their acidic/basic features. Finally, their catalytic activity was evaluated during the oxidation of different types of carbonaceous particles with variable origin.

2. Methods

Nanostructured CeO₂, ceria-lanthana (Ce50La50) and ceria-praseodymia (Ce50Pr50) catalysts were prepared through hydrothermal synthesis, with a procedure reported elsewhere [4]. Briefly, nitrate precursors were coprecipitated in 8M NaOH, aged at 180 °C for 24 h, washed, dried, and calcined at 650 °C. The materials were comprehensively characterized through different techniques, such as XRD, N₂ physisorption, FESEM, TEM, H₂-TPR, NH₃- and CO₂-TPD, XPS, Raman spectroscopy, and in situ FTIR with different probe molecules. The catalytic activity was assessed by employing several kinds of carbonaceous particles with variable origin and reactivity, including commercial carbon black (CB), soot generated by a toluene-isooctane flame (TIO), and soot coming from a C₂H₂ flame (Ac), eventually extracted with CH₂Cl₂ to remove the soluble fraction (Ac-ext). Catalytic activity tests were carried out by heating a 9:1 catalyst:soot mixture (in tight or loose contact) from 100 to 700 °C with a 5 °C/min ramp under a flow of 10% O₂ in N₂, while measuring the CO and CO₂ concentration profiles at the reactor outlet.

3. Results and discussion

La and Pr ions can be well incorporated into the ceria structure, but the final morphology is significantly altered in the mixed oxides, consisting of smaller nanocubes together with nanorods (Fig 1A). Doping was also associated with the formation of smaller crystallites and with increased defectiveness and specific surface area (see Table 1). At the same time, the surface chemistry was affected: more reactive capping oxygen species were detected via XPS over doped ceria, as well as a higher fraction of reduced Ce^{3+} in Ce50La50 (Table 1). These findings can be related to enhanced oxygen spillover and Mars-van Krevelen mechanism. Moreover, doping fostered the formation of more surface acidic sites, able to stabilize carbocation intermediates. As a result, Ce50La50 outperforms the soot oxidation activity of Ce50Pr50 and CeO_2 with all the types of particulates (Fig 1B and 1C). No significant changes in the reactivity trend of the different carbonaceous particles were observed when changing the catalyst; similarly, the activity trend of the catalysts did not vary with the type of particles.

Table 1. Textural and chemical properties of ceria-based catalysts

| Sample | $S_{BET} / m^2 g^{-1}$ | Crystallite size / nm | Capping O / % | $Ce^{3+} / \%$ |
|----------|------------------------|-----------------------|---------------|----------------|
| CeO_2 | 6.3 | 169 | 32 | 22 |
| Ce50Pr50 | 7.9 | 50 | 42 | 19 |
| Ce50La50 | 10.8 | 15-32 | 67 | 25 |

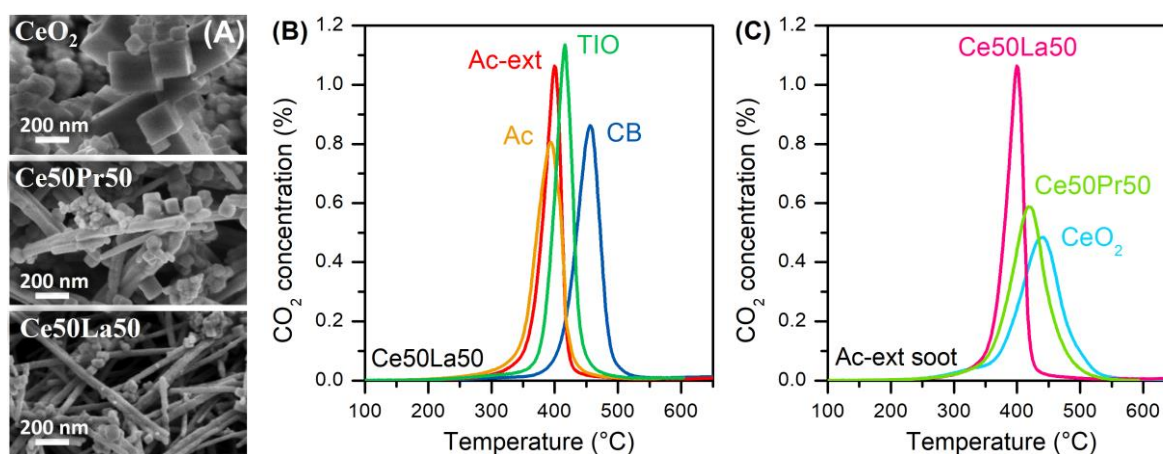


Figure 1. FESEM images of the three catalysts (A); CO₂ concentration at the reactor outlet as a function of the temperature during soot oxidation tests in tight contact: Ce50La50 catalyst with different soot samples (B) and Ac-ext soot with different catalysts (C).

4. Conclusions

The soot combustion temperature over ceria-based nanostructures depends on both catalyst activity and particulate reactivity. Ceria-lanthana mixed oxide shows outstanding performances, due to its optimized morphology, surface acidity and abundant reactive surface oxygen species.

References

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Keywords

soot oxidation; ceria-based catalysts; morphology; acidity