Catalytic performance of $Ce_{1-x}Ln_xO_y$ of nanocrystalline Ln (III-IV)-substituted ceria

Poggio-Fraccari E[1*], **Mariño F**[1], **Sorbello C**[2], **Jobbagy M**[2]

[1] ITHES (UBA-CONICET), Facultad de Ingeniería, Universidad de Buenos Aires, Pabellón de Industrias, Ciudad Universitaria, C1428EHA,, Ciudad Autónoma de Buenos Aires, Argentina

[2] INQUIMAE (UBA-CONICET), Facultad de Ciencias Exactas y Naturales,, Universidad de Buenos Aires, Pabellón II, Ciudad Universitaria,, C1428EHA, Ciudad Autónoma de Buenos Aires, Argentina

Abstract: The activity of several lanthanide promoted Ceria in CO oxidation was studied. Samples were obtained by a high yield and sustainable method by urea thermal decomposition. Precursors basic carbonates, $Ce_{1-x}Ln_x(OH)CO_3$, being Ln = La (III), Sm(III), Gd(III), Pr(III) were prepared in the range of compositions 0 to 30 at.%. These precursors were annealed to moderate temperature obtain Ln-Ce mixed oxides, at 450ºC. These exhibit large surface areas up to 120 m^2/g. Their catalytic performance revealed good activity towards CO oxidation (COOX) for all samples. However, a different behavior may be observed for Ln content higher than 20 at.%. By the reactor operation in differential conditions, the activation energy for COOX were obtained for all samples. The rise of activation energy as a function of Ln(III-IV) content is analyzed in the frame of phase stability and surface segregation.

Keywords: Ce; Lanthanides; COOX

1. Introduction

Ceria is one of the most employed lanthanides oxides, due to its unique redox chemistry related to the Ce(III)/Ce(IV) redox pair [1]. In fact, this property was exploited for applications in catalysis for the last decades. The cerium oxide has been widely employed at industrial scale from the early '70 as support for Three Ways Catalysts (TWC), which are present in all vehicles catalytic converter, by taking benefit of the Oxygen Storage Capacity (OSC) of solids [2]. More recently, the ceria was utilized extensively in several redox reactions, as soot combustion, CO preferential oxidation, Water Gas Shif, partial methane oxidation, autothermal steam reforming, and CO oxidation [4-6].

In order to improve the ceria activity, some authors proposed to use transitions metals as promoters, most used are Zr, Y, Cu, and Mn. These samples showed an enhanced redox and textural properties, including a better catalytic performance in redox reactions, such as Water Gas Shift and CO oxidation, [7,8]. However, the most promising promoters found in literature were lanthanides. La was usually employed to increase ceria thermal stability and OSC [9]. She *et al.* tested several ceria catalysts for Water Gas Shift reaction, with La, Sm, and Nd as promoters, and found a higher performance for Ce-La and Ce-Nd, in comparison with unpromoted ceria sample [8]. Pr is the other rare earth element, as same as Ce, with redox couple i.e.: Pr(III)/Pr(IV). This feature make Pr a very attractive as promoter, by enhancing OSC, and reducibility of Ce-Pr mixed oxides [10]. In fact, some authors reported an acceptable performance of these samples as catalyst's supports for CO oxidation or combustion catalysts [11]. In summary, one can be found in literature studies for pure- and promoted- ceria samples, which were submitted to several redox reactions, in order to understand their redox properties and activity. Nevertheless, a screening of lanthanide elements and content is not usually discussed.

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In order to make such study, a reproducible synthesis method must be employed. It was reported in literature several strategies to obtain cerium-lanthanides mixed oxides, but mostly based on sophisticated procedures based on molecular templates or microemulsions, involving non-green and costly solvents or surfactants [12]. Hydrothermal co-precipitation of precursors by urea decomposition arise as environmental friendly alternative with high mass yield and non-harmful byproducts [1]. In the present work, different promoted ceria families, Ce-Gd, Ce-Sm, Ce-La, and Ce-Pr, were submitted to CO oxidation as test reaction, in order to determine activity as a function of the promoter and their content.

2. Materials and Methods

Precursors were prepared by the urea method, by aging several Cerium(III) nitrate (0.1 mol/dm^3) and Ln(III) nitrate (0.1 mol/dm^3) solutions with urea. Pr(III)-Ce(III) samples were prepared with chlorides instead, in order to prevent partial oxidation driven by nitrate observed on certain binary samples. The ratio [urea] / ([Ce(III)]$_o$ + [Ln(III)]$_o$) was kept constant at 5 in all preparations, and the value $X_{Ln(III)}$ expressed as [Ln(III)] / ([Ln(III)] + [Ce(III)]) was explored in the range, 0 to 50 at.%. Solutions were aged at 200ºC for 10 days in Teflon lined autoclaves. Further details can be found elsewhere [1]. Mixed oxides were obtained by heating precursors under an airflow (50 cm^3/min) at 5 ºC/min from room temperature to 450 ºC and holding this temperature for 5 h.

Catalytic activity of the present samples were evaluated by CO oxidation reaction (hereafter called COOX). The reaction was performed in a fixed bed reactor using 100 mg of solid, diluted with a ceramic inert. The total inlet flow was equal to 100 cm^3/min, with a CO concentration of 5% and O_2 equal to 5% (with N_2 as balance). Prior to catalytic test, the solid was cleaned at 400 ºC with airflow during 30 min and purged with N_2. Finally, the temperature was raised to 450 ºC under the reactant flow. The analysis of CO converted and the concentration of other gaseous products was performed in a Hewlett Packard gas chromatograph equipped with a Thermal Conductivity Detector (TCD). The CO reported conversion corresponds to steady state values. CO conversion was calculated by equation (1), where F_{CO}^{out} and F_{CO}^{in} are the molar flows of CO ant reactor outlet and inlet respectively.

$$\text{conversion} = \frac{F_{CO}^{out} - F_{CO}^{in}}{F_{CO}^{out}} \quad (1)$$

Ethics Statement

No ethics conflicts are presented.

3. Results and discussion

All families of $Ce_{1-x}Ln_xO_{2-\delta}$ compounds decomposed at 450ºC were concluded to be mixed oxides according a previous study [1]. These samples were evaluated as oxidation catalysts, explored in 100-450 ºC range. The CO oxidation reaction was chosen due to the inherent simplicity, in which poisoning effects and/or simultaneous reactions can be neglected, see Figures 1 to 4.

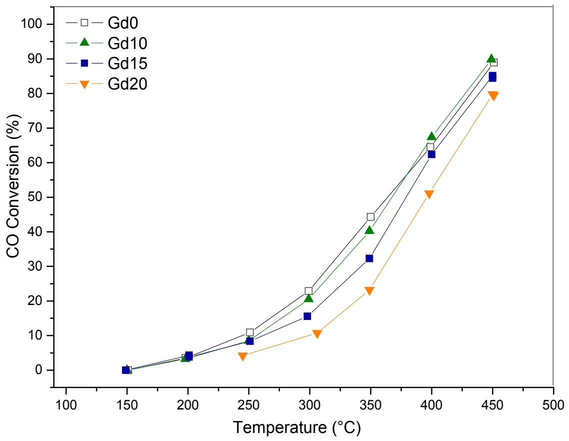

Figure 1: Conversion versus temperature in COOX reaction test for CeGd samples.

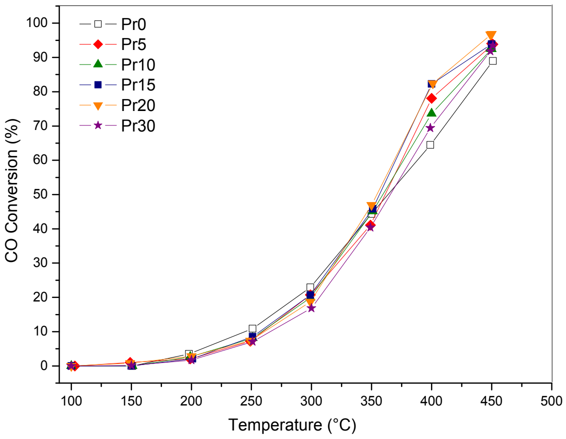

Figure 2: Conversion versus temperature in COOX reaction test for CePr samples.

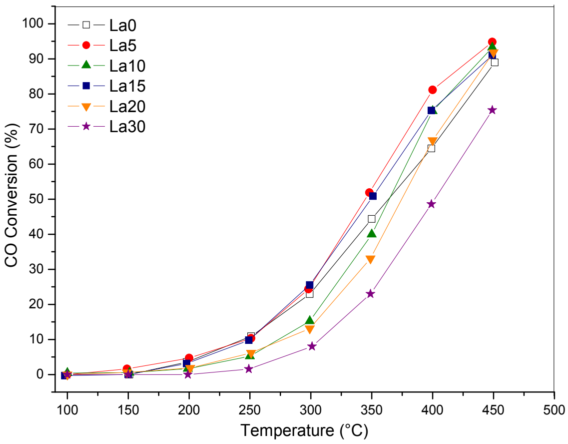

Figure 3: Conversion versus temperature in COOX reaction test for CeLa samples.

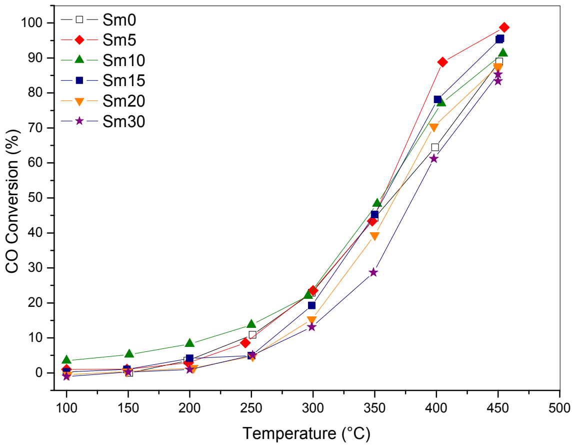

Figure 4: Conversion versus temperature in COOX reaction test for CeSm samples.

As can be seen, all samples probed to active in 100-450 ºC range with this moderate contact time (see Materials and Method section), suggesting an acceptable oxidation activity for CO. In case of CePr family samples, two main regions must be observed, below and above 350 ºC. For temperatures below 350 ºC, it is seems that reaction performance is almost unchanged with Pr addition to ceria, however, for temperatures higher to 350ºC all promoted samples showed a better activity. In fact, the optimal Pr content can be found in 15-20 at.% range. CeGd samples showed a tendency to decrease performance in reaction with Gd addition, which is more markedly for CeGd20 sample. This is an interesting feature because no structure changes were observed by XRD or TGA for 20 at.% of promoter [1], but CO oxidation has proved to be a sensitive reaction. CeLa and CeSm families showed a very similar behavior, solids with promoter content lower than 15 at.%, presented an improved performance in reaction in comparison with bare ceria. Otherwise, samples with highest promoter content showed less activity. This might be due to the lower surface area observed in comparison with the remaining samples, see Table 1.

Promoter	Langmuir surface area (m2/g) for promoter contents					
	0%	5%	10%	15%	20%	30%
Pr	90	111	116	118	73	100
Sm	90	129	105	91	80	58
Gd	90	-	111	116	110	-

Table 1: Specific surface area (m^2/g) obtained from N_2 isotherms recorded at 77 k for CeSm, CePr, and CeGd samples families taken from [1].

In summary, the screening of Ln content suggested that samples were quite different for high promoter content, i.e.: >20 at.%. Nevertheless, in case of Ln addition in range 5-15 at.% it was a generalized improvement of catalytic activity for CO oxidation, and therefore might be involve an enhancement of redox properties of solids. In order to achieve a better comparison between samples, it was employed the temperature at which the CO conversion, calculates as Equation (1), reaches the 50%, hereafter called T_{50}. For samples bearing Ln(III) substitution degrees of 15%, the T_{50} were found in the range 350-375 ºC, irrespective of Ln(III) nature, in agreement with other authors, **Figure 5** [9].

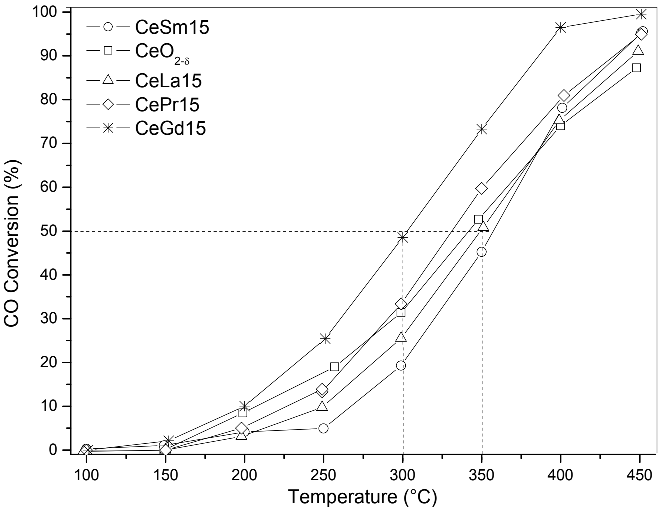

Figure 5: T_{50} for medium content promoted-ceria samples.

Interestingly, almost the same T_{50} were found despite the significant differences in specific surface area, reported elsewhere, see Table 1. On the other hand, for substitutions of 30%, the T_{50} were found to be close to 400 ºC, a slightly higher temperature, indicating a weaker redox catalytic properties, irrespective of Ln(III) nature. In order to analyze this feature, the low temperature zone was studied in more detail.

If conversion values were lower than 15%, differential reactor conditions can be assumed. Therefore, reaction rates were calculated, and activation energy for COOX reaction can obtained from Arrhenius Plots. Results are reported for all samples in **Figure 6.** Taking bare ceria as reference, samples behave similar for Ln substitution lower 20%, while the activation energy suddenly increases with lanthanide content of 30%, except for Pr-substituted sample. This feature are in agreement with specific surface area, which were slightly modified for CePr30 in comparison with other samples of CePr family, see Table 1. One can conclude that Pr incorporation in Ceria lattice are allowed in higher degrees without no appreciable structural changes. Otherwise, for CeGd, CeLa, and CeSm, families, The increase in activation energy with promoter may be related to a decrease in active sites available to oxidize the CO, when Ce^{4+} sites are replaced by 3+ ions by Ln(III) [13], and the low surface area of these samples.

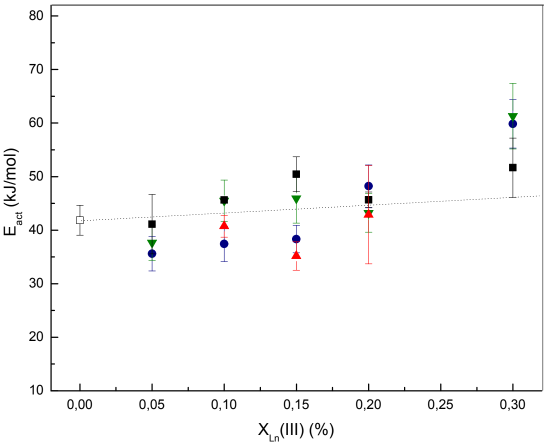

Figure 6: Activation energy of CO oxidation reaction over bare CeO$_{2-\delta}$ oxide (empty square) and as a function of substitution with Ln(III)=Sm(III) (blue filled circles), Gd(III) (red filled upwards triangles), Pr(III-IV) (black filled squares) and La(III) (green filled downwards triangles).

4. Conclusion

All samples have proven to be useful for CO oxidation reaction. The T$_{50}$ for samples was practically the same for solids with substitution contents lower than 15% irrespective of Ln nature. However, the T$_{50}$ increased for samples with Ln content of 20-30 at.%. The analysis of activation energy obtained from Arrhenius Plots, showed an suddenly increase in values for samples with Ln addition of 30 at.%, except for Pr substituted samples which was slight change. In summary, one can conclude that CO oxidation was a test reaction capable to shown differences between samples, which was not evidenced by other techniques sensitive to surface or structure, as XRD, adsorption isotherms, or TGA.

Acknowledgements

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