Accepted Manuscript

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PII: S0926-3373(14)00411-1
DOI: <http://dx.doi.org/doi:10.1016/j.apcatb.2014.07.013>
Reference: APCATB 13444

To appear in: *Applied Catalysis B: Environmental*

Received date: 21-5-2014
Revised date: 3-7-2014
Accepted date: 5-7-2014

Please cite this article as: L.P.S. Xavier, V. Rico-Pérez, A.M. Hernández-Giménez, D. Lozano-Castelló, A. Bueno-López, Simultaneous catalytic oxidation of carbon monoxide, hydrocarbons and soot with Ce-Zr-Nd mixed oxides in simulated Diesel exhaust conditions, *Applied Catalysis B, Environmental* (2014), <http://dx.doi.org/10.1016/j.apcatb.2014.07.013>

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Simultaneous catalytic oxidation of carbon monoxide, hydrocarbons and soot with Ce-Zr-Nd mixed oxides in simulated Diesel exhaust conditions.

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Abstract

$\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides ($x \leq 0.3$) were prepared, characterized by XRD, Raman spectroscopy, N_2 adsorption isotherms and H_2 -TPR, and tested for simultaneous CO, propylene, benzene and soot oxidation in a gas mixture containing O_2 , NO_x , H_2O , CO_2 , CO, propylene (model aliphatic hydrocarbon) and benzene (model aromatic hydrocarbon) that simulates a Diesel exhaust. Ce-Zr mixed oxide doping with a low atomic fraction of neodymium ($0.01 \leq x \leq 0.09$) promotes the creation of oxygen vacancies, has a minor effect in the BET specific surface areas of the oxides, increases the surface ceria reducibility and has a positive effect in the catalytic activity. On the contrary, higher neodymium atomic fractions ($x = 0.2$ and 0.3) promote sintering, with a drastic decrease of the BET specific surface area, surface reducibility and catalytic activity. The $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ catalysts with $x \leq 0.09$ are able to accelerate simultaneously soot, propylene and benzene combustion, and as a general trend, the catalytic behavior of $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$ is improved by low atomic fraction neodymium doping ($0.01 \leq x \leq 0.09$). These $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides with $0.01 \leq x \leq 0.09$ are also able to accelerate CO oxidation in a certain extent, but there is a net production of CO during soot combustion because the oxidation capacity of these oxides is not high enough to oxidize all CO released as soot combustion product.

Keywords: Diesel soot; carbon monoxide; hydrocarbons; ceria-zirconia catalyst; neodymium-ceria catalyst.

36

37 **1.- Introduction.**

38 Cerium-based oxides are part of the active phases used in Three Way
39 Catalysts (TWC) for gas pollution control in gasoline vehicles [1-4]. Cerium
40 oxides improve noble metals dispersion and stabilization, store and release
41 oxygen buffering the fluctuations of the O_2 concentration in the gas mixture and
42 catalyze (together with noble metals) some reactions like CO and hydrocarbons
43 oxidation.

44 Cerium oxide-based catalysts have been also proposed for soot
45 combustion in Diesel vehicles, where the gas exhaust is highly oxidizing [5-9].
46 Diesel engines also emit CO and hydrocarbons, but in much lower
47 concentration than gasoline engines [10-13]. Usually, a platinum-containing
48 Diesel Oxidation Catalyst (DOC) is used in Diesel vehicles for simultaneous
49 CO, hydrocarbons and NO oxidation. The NO_2 produced, which is much more
50 oxidizing than NO and O_2 , starts the combustion of soot collected downstream
51 in a Diesel Particulate Filter (DPF).

52 Noble metal-free catalysts are being investigated for soot combustion in
53 Diesel exhausts in order to lower the cost of the after-treatment devices. Ceria-
54 based oxides are promising candidates, and the role of O_2 and NO_x in the
55 ceria-catalyzed combustion of soot is well understood. One of the ceria-
56 catalyzed soot-combustion mechanisms consists of the oxidation of NO to NO_2
57 (as described for platinum-containing DOC), and other consists of the
58 production of active oxygen by oxygen exchange between the ceria-based
59 catalyst and the oxygen-containing gas molecules, mainly O_2 . Depending on the

60 ceria catalyst features and on the reaction conditions (temperature, gas
61 composition, etc.) either both mechanisms progress synergically together or
62 one of them prevails.

63 Platinum catalysts are much more active for NO oxidation to NO₂ than
64 ceria catalysts, but the latter are able to approach the activity of platinum for
65 soot combustion if the active oxygen mechanism gets involved. The main
66 handicap of the active oxygen mechanism is that the contact between soot and
67 ceria catalyst particles must allow the active oxygen species to be transferred
68 from catalyst to soot, otherwise they recombine to each other and yield O₂ [14].
69 Therefore, ceria catalysts must be impregnated into the DPF instead of being
70 loaded in a DOC located upstream the DPF, as usually done with platinum.

71 The substitution of the Pt-DOC + DPF soot removal device by a Ceria-
72 DPF configuration seems promising, but it must be analyzed whether ceria-
73 catalysts are able to remove simultaneously soot, hydrocarbons and CO, as
74 platinum catalyst does, or if further improvements are required.

75 We have recently analyzed the effect of H₂O, CO₂ and SO₂ in the
76 catalytic activity for soot combustion of Ce_{0.73}Zr_{0.27}O₂ and Ce_{0.64}Zr_{0.27}Nd_{0.09}O₂ in
77 simulated Diesel exhaust conditions, concluding that all these three gases lower
78 the activity of both catalysts and that the inhibiting effect follows the trend SO₂
79 >>> H₂O > CO₂ [15]. The poisoning effect of SO₂ was already reported by other
80 authors [16-19], but less attention was paid in the literature to the effect of H₂O
81 and CO₂. In situ DRIFTS experiments showed that CO₂, H₂O and SO₂ compete
82 with NO_x for the adsorption sites on the catalysts' surface [15]. CO₂ and H₂O
83 partially hinder the catalytic oxidation of NO to NO₂ while SO₂ chemisorption

84 inhibits almost all the activity due to sulfate formation. The catalytic activity for
 85 soot combustion of $\text{Ce}_{0.64}\text{Zr}_{0.27}\text{Nd}_{0.09}\text{O}_2$ was equal or higher to that of
 86 $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$ in the presence of NO_x , O_2 , H_2O and/or CO_2 , because Nd^{3+}
 87 doping promotes the participation of the active oxygen mechanism, which
 88 seems to resist the presence of H_2O and CO_2 better than the NO_2 -assisted
 89 soot combustion mechanism [15]. For this reason, the $\text{Ce}_{0.64}\text{Zr}_{0.27}\text{Nd}_{0.09}\text{O}_2$
 90 mixed oxide was identified as a potential catalyst with practical relevance for
 91 Diesel vehicles running with sulfur-free fuel, since it maintained significant
 92 activity for soot combustion even in the presence of H_2O and CO_2 .

93 As far as we know, the simultaneous ceria-catalyzed combustion of soot,
 94 CO, and hydrocarbons has not been studied and reported in the literature, and
 95 this is one of the goals of the current study. In addition, the positive effect of
 96 Nd^{3+} doping in the catalytic activity of the Ce-Zr mixed oxide for soot combustion,
 97 which was first reported in [20], has led us to focus the current study on ternary
 98 Ce-Zr-Nd mixed oxides. A series of $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides were
 99 prepared with different neodymium content, and were characterized and tested
 100 for the simultaneous oxidation of CO and hydrocarbons, both in the absence
 101 and presence of soot. A complex gas mixture that mimics a Diesel engine
 102 exhaust containing NO_x , O_2 , H_2O , CO_2 , CO, propylene and benzene was used.
 103 Propylene and benzene were selected as model aliphatic and aromatic
 104 hydrocarbons, respectively.

105 **2.- Experimental details.**

106 *2.1. Catalysts preparation.*

107 Six $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides were prepared, with $x = 0, 0.01,$
 108 $0.05, 0.09, 0.2$ and 0.3 . Formally, the stoichiometric coefficient of oxygen in the
 109 neodymium-containing catalysts should be lower than 2, since the tetravalent
 110 cation " Ce^{4+} " is replaced by a trivalent one (Nd^{3+}). However, the subscript 2 has
 111 been maintained in the nomenclature for the sake of simplicity.

112 The required amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, 99%),
 113 $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99.9%) and/or $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Fluka, $x \approx 6$) were
 114 dissolved in water and an ammonia solution was dropped to keep the pH at
 115 about 9, leading to the precipitation of the cations. After filtering, the precipitates
 116 were firstly dried at 110°C in air overnight and then calcined in air at 800°C for
 117 90 min to ensure thermal stability and practical meaning.

118 The synthesis method and the amount of zirconium on the mixed oxides
 119 were selected based on our previous studies on soot combustion, where
 120 catalysts with different Ce-Zr ratios were prepared by different methods [21, 22].

121 2.2. Catalysts characterization.

122 X-ray diffractograms of the catalysts were recorded in a Rigaku Miniflex II
 123 diffractometer, using CuK_α radiation ($\lambda = 0.15418\text{ nm}$). The diffractograms were
 124 recorded between 10 and 80° (2θ) with a step of 0.025° .

125 Raman spectra were recorded in a Bruker RFS 100/S Fourier Transform
 126 Raman Spectrometer with a variable power Nd-YAg laser source (1064 nm).
 127 The laser beam was focused on the sample in a 180° backscattering
 128 configuration and 128 scans at 100 mW laser power were recorded.

129 The BET specific surface area of the oxides was determined by physical
 130 adsorption of N₂ at -196 °C in an automatic volumetric system (Autosorb-6,
 131 Quantachrome). The samples were outgassed at 150 °C for 4 hours before the
 132 N₂ adsorption measurements.

133 Temperature programmed reduction (H₂-TPR) experiments were carried
 134 out with 15 mg of fresh mixed oxide, which were pre-treated *in situ* at 500 °C for
 135 1 hour in a 35 mL/min flow of 5 vol.% O₂ in He. Once cold, the flow gas was
 136 switched to 35 mL/min of 5 vol.% H₂ in Ar and the temperature was increased at
 137 10 °C/min up to 1050 °C.

138 2.3. Catalytic tests.

139 Catalytic tests were performed at atmospheric pressure in a cylindrical
 140 reactor coupled simultaneously to a HP 6890 gas chromatograph equipped with
 141 a TCD and two columns (Porapak Q, for CO₂ and Molecular Sieve 13X, for O₂,
 142 N₂ and CO) and a Pfeiffer Vacuum mass spectrometer (model OmniStar) to
 143 monitor NO, propylene, NO₂ and benzene concentrations following the m/z =
 144 30, 39, 46 and 78 signals, respectively. The total flow rate was 100 ml/min
 145 (GHSV = 42000 h⁻¹) and the gas composition was 300 ppm CO / 120 ppm
 146 propylene / 3% CO₂/ 180 ppm benzene / 1000 ppm NO_x (~ 0 ppm NO₂) / 5%O₂
 147 / 2%H₂O and He as balance gas. Gas flow controllers were used to feed the
 148 required amount of each individual gas, and the O₂ flow was bubbled in water at
 149 72 °C before mixing with the remaining flows to add steam into the gas mixture.
 150 This complex composition simulates a real Diesel engine exhaust and allows
 151 evaluating the simultaneous catalytic oxidation of CO, propylene, benzene and
 152 soot in quite realistic conditions.

Catalytic tests were performed with and without soot. Experiments performed without soot consisted of the simultaneous CO, propylene and benzene catalytic oxidation studied at selected temperatures from room temperature up to 550 °C. 100 mg of each mixed oxide catalyst were used for these experiments, which were diluted with 300 mg of SiC to avoid pressure drop and favor heat transfer. The experiments were extended until steady-state at each temperature, typically for 30 minutes.

Experiments were also performed with 100 mg of catalyst mixed with 25 mg of soot and 300 mg of SiC. Soot and catalyst were mixed with a spatula in the so-called loose contact conditions to simulate the contact in a real DPF filter [23]. The model soot used was a carbon black supplied by Evonik–Degussa GmbH (Printex U). The soot-catalyst-SiC mixture was heated at 530 °C in 13 mL/min He. Then, the inert gas was replaced by the reactive gas mixture and the gas composition was monitored as a function of time.

Propylene and benzene conversions were determined following the m/z 39 and 78 signals, respectively, by mass spectrometry and CO conversions were determined from gas chromatography measurements. The conversions of CO, propylene and benzene were calculated as follows:

$$\text{Conversion (\%)} = 100 \cdot ([\text{pollutant}]_{\text{in}} - [\text{pollutant}]_{\text{out}}) / [\text{pollutant}]_{\text{in}}$$

where $[\text{pollutant}]_{\text{in}}$ and $[\text{pollutant}]_{\text{out}}$ are the inlet and outlet concentrations, respectively, of each gas pollutant (CO, propylene and benzene).

Soot conversion was determined from CO₂ and CO evolved (both followed by gas chromatography) after subtracting the stoichiometric amounts

176 of CO₂ corresponding to the propylene, benzene and CO conversions assuming
 177 oxidation of these gases to CO₂ and H₂O.

178

179 **3.- Results and discussion.**

180 *3.1. Catalysts characterization.*

181 Figure 1 shows the X-ray diffractograms of the Ce_{0.73-x}Zr_{0.27}Nd_xO₂
 182 catalysts. The main peaks observed in this figure correspond to the typical cubic
 183 structure of ceria. A shoulder is also distinguished in all diffractograms at high
 184 angles of the (111) cubic peak, which evidences the formation of a tetragonal
 185 segregated phase. The cations sublattice is similar in the cubic and tetragonal
 186 structures, corresponding to a face-centered cubic (fcc) framework with cations
 187 placed in the corners and faces center of a cubic unit cell. The difference
 188 between the cubic and tetragonal frameworks is the position of the oxygen
 189 anions. Oxygen anions are placed in the octahedral positions in the cubic
 190 structure while they are out these positions (four above and four below the
 191 equilibrium positions) in the tetragonal structure [24-27]. Tetragonalization of
 192 the cubic structure of pure ceria typically occurs upon partial substitution of the
 193 Ce⁴⁺ cations (0.097 nm) by smaller Zr⁴⁺ cations (0.084 nm), because the
 194 oxygen anions are displaced from the octahedral position to relax the tensions
 195 created by different size cations. The segregation of a cerium-rich cubic
 196 structure and a zirconium-rich tetragonal structure was already observed for
 197 Ce_{0.73}Zr_{0.27}O₂ and Ce_{0.64}Zr_{0.27}Nd_{0.09}O₂ oxides [20], and this conclusion is now
 198 extended to a wider range of neodymium atomic fractions.

199 The XRD peaks positions, intensity and broadening strongly depends on
 200 the neodymium atomic fraction (see inset in Figure 1), because the introduction
 201 of large trivalent Nd^{3+} cations (0.112 nm) distorts the lattices. The crystal sizes
 202 have not been estimated from XRD because the presence of the segregated
 203 tetragonal zirconium-rich phase hinders the proper estimation of the cubic
 204 peaks broadening. It is also difficult to quantify the amount of dopants actually
 205 loaded into the ceria lattice for ternary Ce-Zr-Nd mixed oxides, because the cell
 206 expansion produced by Nd^{3+} doping faces the cell contraction produced by
 207 Zr^{4+} doping. However, some information can be obtained from the cell
 208 parameters determined from the (111) peak position, which can be properly
 209 determined for all oxides in spite of the tetragonal peak shoulder. The
 210 experimentally measured cell parameters are plotted in Figure 2 together with
 211 the theoretical values estimated for pure Ce-Zr-Nd solid solutions using the
 212 Kim's equation [28, 29]:

$$213 \quad \text{Cell parameter (nm)} = 0.5411 - 0.000286 \cdot m_{\text{Zr}} + 0.00018 \cdot m_{\text{Nd}}$$

214 where m_{Zr} and m_{Nd} are the atomic % of zirconium and neodymium in the Ce-Zr-
 215 Nd solid solution, respectively. This empirical equation is based on the Vegard's
 216 rule, which predicts a linear relationship between the lattice parameter and the
 217 concentration of dopants in a solid solution.

218 The experimental cell parameters of all samples are well above the
 219 theoretical trend predicted for a pure solid solution, in agreement with the
 220 segregation of part of the zirconium in a tetragonal phase. For $\text{Ce}_{0.73-}$
 221 $\text{xZr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides with $x \leq 0.09$, the slope of the linear trend followed by
 222 the experimental values with regard to the neodymium concentration is quite

223 similar to that predicted by the Kim's equation, suggesting that the insertion of
224 neodymium cations into the cubic lattice of ceria is quite good and better to that
225 of zirconium. This slope decreases for higher neodymium concentrations, which
226 suggests that Nd^{3+} loading into the parent ceria lattice becomes more difficult
227 for 0.2 and 0.3 neodymium atomic fractions.

228 The better insertion of neodymium cations into the ceria lattice in
229 comparison with those of zirconium can be explained taking into account the
230 charge of the cations precursors used for the preparation of the mixed oxides,
231 being +3 for cerium and neodymium while +4 for zirconium. The coprecipitation
232 of cations upon ammonia adding is much more homogeneous for cations with
233 the same charge and similar size (0.114 nm for Ce^{3+} and 0.112 nm for Nd^{3+}),
234 because their acid strength is similar, than for cations of different charge and
235 size. That is why, in the current study, cerium and neodymium formed better
236 solid solutions than cerium and zirconium. It must be taken into account that
237 cerium precursors with both +3 and +4 charges exist, while not for zirconium
238 and neodymium which are only available in the +4 and +3 oxidation states,
239 respectively. Our choice for the current study was to use a Ce^{3+} precursor
240 because the study is focused on the effect of neodymium loading, but in a
241 previous article the effect of the cerium precursor in the features of binary Ce-Zr
242 oxides was discussed in detail [30]. It is known that much better insertion of Zr^{4+}
243 into the ceria framework would be obtained with the selection of a Ce^{4+}
244 precursor, but this would be hindered Nd^{3+} doping.

245 Raman spectra included in Figure 3 also provided information about the
246 structure of the oxides, and supported some conclusions of the XRD analysis.

247 All spectra show a Raman band centered at $460\text{--}465.8\text{ cm}^{-1}$, which is assigned
 248 to the F_{2g} mode of the fluorite-type cubic structure of cerium oxides [31, 32]. The
 249 presence of low-intensity bands in the range $120\text{--}300\text{ cm}^{-1}$ has been related to
 250 the tetragonal shift of the oxygen anions from the ideal octahedral positions that
 251 occupy in the fluorite cubic structure [33, 34], which typically occurs upon
 252 zirconium insertion into the CeO_2 lattice. The displacement of the F_{2g} band
 253 position towards low Raman shifts by increasing the neodymium atomic fraction
 254 (see Figure 3b) is an evidence of the introduction of large Nd^{3+} cations into the
 255 parent cubic structure of ceria. The creation of oxygen vacancies is related to
 256 the shoulder at 620 cm^{-1} [35], and the intensity of this shoulder suggests that
 257 the number of vacancies increases significantly for low neodymium atomic
 258 fractions ($x \leq 0.09$) but it is not so relevant for higher neodymium content ($x =$
 259 0.2 and 0.3). This is consistent with the cell parameter trend determined by
 260 XRD (see Figure 2), which suggested that the neodymium insertion becomes
 261 worse for mixed oxides with 0.2 and 0.3 neodymium atomic fractions.

262 The BET specific surface areas also showed important differences
 263 among $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides. The values plotted in Figure 4 show
 264 that the BET specific surface areas ranged from 0 to $31\text{ m}^2/\text{g}$. These low values
 265 were expected considering that the oxides were sintered at $800\text{ }^\circ\text{C}$ to provide
 266 practical meaning to the study. The BET surface area of the neodymium-free
 267 Ce-Zr mixed oxide ($26\text{ m}^2/\text{g}$) is in line with typical values previously obtained for
 268 similar materials with the same thermal history [20, 21], and slightly higher
 269 areas were obtained for $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ oxides with $0.01 \leq x \leq 0.09$.
 270 However, higher neodymium atomic fractions lead to an important sintering of
 271 the mixed oxides with a drastic decrease of the BET surface area down to 8 and

0 m²/g for $x = 0.2$ and 0.3 , respectively. The existence of an optimum dopant loading has been already reported for some other mixed oxides. Zhang et al. [36, 37] studied La³⁺-doped TiO₂ oxides and reported that the optimum lanthanum atomic fraction was 1% in order to avoid the phase transformation of titania. This amount of lanthanum was estimated to correspond to a monolayer of surface cations, and further increase of the dopant concentration above the monolayer coverage induced the segregation of lanthanum oxide and titanium oxide. This argument could also be applied to our Ce_{0.73-x}Zr_{0.27}Nd_xO₂ mixed oxides, that is, low neodymium atomic fractions ($x \leq 0.09$) seem to slightly stabilize the mixed oxide, while higher neodymium contents have the opposite effect, in spite of evidences of segregated neodymium phases were neither obtained by XRD nor by Raman spectroscopy.

Characterization of the mixed oxides was also carried out by Temperature Programed Reduction with H₂, and the obtained profiles were drawn in Figure 5. Note that the only reducible cations in the Ce_{0.73-x}Zr_{0.27}Nd_xO₂ mixed oxides are Ce⁴⁺, while both Zr⁴⁺ and Nd³⁺, which cannot be reduced in the experimental conditions of the H₂-TPR experiments, modify the redox behavior of the Ce⁴⁺/Ce³⁺ couple.

Most H₂-TPR profiles consist of a mild-temperature peak around 550 °C, which is attributed to surface reduction of the mixed oxides, and a high-temperature peak assigned to bulk reduction. The formation of two well-defined reduction peaks in most of the mixed oxides studied occurs because there is an energetic restriction for the bulk oxygen to move until the particles surface, and high temperature is required to promote such oxygen mobility.

296 The surface and bulk reduction-peak temperatures are plotted in Figure 6
 297 versus the neodymium atomic fraction. The neodymium loading affected both
 298 the surface and bulk reduction. The bulk reduction peak shifted towards lower
 299 temperature with the neodymium content increase (see Figure 6), and the
 300 surface and bulk reduction peaks even merge for the highest neodymium-
 301 content mixed oxides (see Figure 5). This occurs because the introduction of
 302 large trivalent Nd^{3+} cations into the parent ceria-zirconia framework improves
 303 the mobility of oxygen into the lattice, and only 0.01 neodymium atomic fraction
 304 is enough to shift significantly the bulk reduction peak. The effect of neodymium
 305 on surface reduction was the opposite, and the surface reduction-peak
 306 temperature was delayed towards higher temperatures as the neodymium
 307 atomic fraction was increased. This delay was small for $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$
 308 mixed oxides with $x \leq 0.09$, but became much more relevant for $x = 0.2$ and 0.3 ,
 309 which is consistent with the very low surface area of these two mixed oxides (8
 310 and $0 \text{ m}^2/\text{g}$). However, the area under the surface reduction peak (see Figure 5)
 311 increased for $\text{Ce}_{0.72}\text{Zr}_{0.27}\text{Nd}_{0.01}\text{O}_2$ and $\text{Ce}_{0.68}\text{Zr}_{0.27}\text{Nd}_{0.05}\text{O}_2$ with respect to
 312 $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$, that is, few neodymium increased the amount of surface Ce^{4+}
 313 reduced.

314 As a summary, the characterization results have shown that the $\text{Ce}_{0.73-}$
 315 $x\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides prepared consist of two segregated ceria-rich and
 316 zirconium rich phases with proper neodymium doping for $x \leq 0.09$. This is a
 317 consequence of the preparation method used, where Ce^{3+} , Nd^{3+} and Zr^{4+}
 318 cations were precipitated. Doping the Ce-Zr mixed oxides with low atomic
 319 fractions of neodymium promoted the creation of oxygen vacancies, had a
 320 minor effect on the BET specific surface area of the oxides, increased the

amount of surface Ce^{4+} reduced and, as it will be discussed in the coming section, had a positive effect on the catalytic activity. On the contrary, higher neodymium atomic fractions ($x = 0.2$ and 0.3) had a negative effect on the mixed oxides features because promote sintering, with a drastic decrease of the BET specific surface area and of the surface reducibility. These worst features of $\text{Ce}_{0.53}\text{Zr}_{0.27}\text{Nd}_{0.2}\text{O}_2$ and $\text{Ce}_{0.43}\text{Zr}_{0.27}\text{Nd}_{0.3}\text{O}_2$ are also evidenced in the catalytic behavior in the next section.

3.2. Catalytic tests.

Catalytic tests were performed with the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ oxides in the absence and presence of soot under a complex gas mixture with O_2 , NO_x , H_2O , CO_2 , CO , propylene (model aliphatic hydrocarbon) and benzene (model aromatic hydrocarbon). The consumption of NO_x was negligible in all cases, and the discussion is focused on the removal of the remaining pollutants (CO , hydrocarbons and soot).

Figure 7 shows the conversion percentages and conversion rates of propylene, benzene and CO obtained in steady state at different temperatures. The catalytic activities for the conversion of these three pollutants of the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides with $x \leq 0.09$ were significantly higher than those of the mixed oxides with higher neodymium content. This behavior is consistent with the drastic decrease of the BET surface area and surface reducibility of $\text{Ce}_{0.53}\text{Zr}_{0.27}\text{Nd}_{0.2}\text{O}_2$ and $\text{Ce}_{0.43}\text{Zr}_{0.27}\text{Nd}_{0.3}\text{O}_2$ with regard to the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides with $x \leq 0.09$.

CO conversion started above 300°C for all catalysts and increased smoothly with temperature achieving 30 % conversion at 550°C for $\text{Ce}_{0.73-x}$

345 $x\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides with $x \leq 0.09$. Propylene and benzene conversions
 346 needed temperatures above 350 and 400 °C, respectively, to occur in
 347 measurable extents in the experiment performed with $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$, which is
 348 the most active catalyst at low temperature among those prepared in this study.
 349 The onset temperatures for propylene and benzene conversion were slightly
 350 higher for the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides with $x = 0.01, 0.05$ and 0.09 than
 351 for $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$. However, the conversions rose faster with temperature for
 352 these neodymium-containing mixed oxides and they were more active than
 353 $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$ at the highest temperatures tested. This change of the reaction
 354 order of neodymium-free and neodymium-containing Ce-Zr mixed oxides at
 355 different temperatures could be related with the surface reducibility of these
 356 oxides, as studied by H_2 -TPR (see Figures 5 and 6). The temperature for
 357 maximum signal in the surface reduction peak was the lowest for $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$
 358 (Figure 6), and the onset temperatures for propylene and benzene conversions
 359 were also the lowest for this catalyst (Figures 7a and 7b). The surface reduction
 360 peak temperature was slightly higher for the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides
 361 with $x = 0.01, 0.05$ and 0.09 than for $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$ (Figure 6), and so does the
 362 onset propylene and benzene conversion temperatures (Figures 7a and 7b,
 363 respectively), but once the temperature was high enough for these reactions to
 364 occur the conversions rose faster for the neodymium-containing catalysts. This
 365 could be tentatively attributed to the improved oxygen mobility upon neodymium
 366 doping, which would restore faster the oxygen balance on the catalyst surface
 367 after consumption in propylene and benzene oxidation. This agreement
 368 between the surface reduction behavior observed by H_2 -TPR experiments and
 369 the catalytic combustion of propylene and benzene suggest that redox

mechanisms are taking place, as typically occurs in oxidation reactions catalyzed by cerium-based oxides [3, 38].

Soot combustion experiments were also performed at 530 °C under the complex gas mixture with O₂, NO_x, H₂O, CO₂, CO, propylene and benzene that simulates a Diesel exhaust, and the soot conversion profiles were plotted in Figure 8 as a function of time. The most active soot combustion Ce_{0.73-x}Zr_{0.27}Nd_xO₂ catalysts are those with x = 0.01, 0.05 and 0.09. These low neodymium atomic fractions improved the Ce_{0.73}Zr_{0.27}O₂ catalytic activity, while the improvement in activity for soot combustion is null for the mixed oxides with higher neodymium atomic fraction (Ce_{0.53}Zr_{0.27}Nd_{0.2}O₂ and Ce_{0.43}Zr_{0.27}Nd_{0.3}O₂). This behavior is in line with the previously discussed conversions of CO, propylene and benzene obtained in experiments performed without soot (Figure 7). The improved catalytic activity for soot combustion of the Ce-Zr mixed oxide catalyst by 0.09 atomic fraction neodymium doping was already reported [20], but the current study analyzes the effect of neodymium in a wider range of concentrations and in a more complex gas mixture.

The removal of propylene, benzene and CO was analyzed during soot combustion, and the conversion profiles were plotted in Figure 9 with regard to soot conversion. The propylene conversion percentage was around 90% for the Ce_{0.73-x}Zr_{0.27}Nd_xO₂ mixed oxides with x ≤ 0.09, while remained much lower for Ce_{0.53}Zr_{0.27}Nd_{0.2}O₂ and Ce_{0.43}Zr_{0.27}Nd_{0.3}O₂. It was observed that the catalyst temperature (the thermocouple was placed inside the reactor facing the catalytic bed) increased few degrees (~3-5 °C) during the exothermal soot combustion, and this leads to think that the local increase of temperature could

394 be higher in local hot spots at the soot-catalyst particles interface. This could
 395 explain why propylene conversions obtained in the presence of soot (Figure 9)
 396 were slightly higher than those obtained in the absence of soot (Figure 7).

397 The conversions of benzene during soot combustion were lower than
 398 those of propylene (Figure 9), in accordance with the behavior in the absence of
 399 soot (Figure 7), and the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides with $x \leq 0.09$ were
 400 more active than $\text{Ce}_{0.53}\text{Zr}_{0.27}\text{Nd}_{0.2}\text{O}_2$ and $\text{Ce}_{0.43}\text{Zr}_{0.27}\text{Nd}_{0.3}\text{O}_2$, which showed
 401 almost null activity.

402 Finally, the CO conversion profiles obtained in catalytic combustion
 403 experiments performed with soot (Figure 9c) were very different to those
 404 obtained without soot (Figure 7c). Actually, most CO conversion values were
 405 negative during soot combustion, that is, CO was actually emitted in
 406 experiments with soot instead of being depleted. The $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed
 407 oxides with $x = 0.01, 0.05$ and 0.09 reached positive CO conversion values,
 408 once soot was consumed (see inset in Figure 9c), what means that there is a
 409 net production of CO during soot combustion because the catalytic CO
 410 oxidation rates seem to be lower than the CO emission rate by soot
 411 combustion. It was estimated in a previous study that 75 % of soot was oxidized
 412 to CO_2 in a $\text{Ce}_{0.64}\text{Zr}_{0.27}\text{Nd}_{0.09}\text{O}_2$ -catalysed combustion of soot, while the
 413 remaining 25% yielded CO. The emission of CO as soot combustion product
 414 could be positive if a deNO_x device (by Selective Catalytic Reduction-SRC or
 415 NO_x Storage and Reduction-NSR) is going to be located downstream the ceria-
 416 DPF, because CO would contribute to NO_x reduction and would save reductant.
 417 On the contrary, if the ceria-DPF is the last device in the after-treatment system

actions must be taken to avoid CO release, for instance, including into the DPF a transition metal like copper with high CO oxidation capacity.

As a summary, the catalytic tests performed in the current study evidenced that some $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ catalysts were able to accelerate simultaneously soot, propylene and benzene combustion. As a general trend, the catalytic behavior of $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$ was improved by low atomic fraction neodymium doping ($0.01 \leq x \leq 0.09$), while a very negative effect was obtained for higher loading ($x = 0.2$ and 0.3). The $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides were also able to accelerate CO oxidation in a certain extent, but there was a net production of CO during soot combustion because the oxidation capacity of these oxides was not high enough to oxidize all CO released as soot combustion product.

430

431 **4.- Conclusions.**

$\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides ($x = 0, 0.01, 0.05, 0.09, 0.2$ and 0.3) were prepared, characterized, and tested for simultaneous CO, propylene, benzene and soot combustion in simulated Diesel exhaust conditions, and the following conclusions can be summarized:

- 436 • The $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides consisted of two segregated ceria-rich and zirconium-rich phases with proper neodymium doping for
437 atomic fractions of $x \leq 0.09$. This was a consequence of the preparation
438 method used, where Ce^{3+} , Nd^{3+} and Zr^{4+} cations were precipitated.
439

440

- 441 • Doping of the Ce-Zr mixed oxides with low neodymium atomic fractions
 442 ($x \leq 0.09$) promoted the creation of oxygen vacancies, had a minor
 443 effect on the BET specific surface area of the oxides, increased the
 444 amount of surface Ce^{4+} reduced and had a positive effect on the
 445 catalytic activity. On the contrary, higher neodymium atomic fractions (x
 446 $= 0.2$ and 0.3) had a negative effect on the mixed oxides features
 447 because promoted sintering, with a drastic decrease of the BET specific
 448 surface area, surface reducibility, and catalytic activity.
- 449

450 • The $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ catalysts with $x \leq 0.09$ were able to accelerate
 451 simultaneously soot, propylene and benzene oxidation. As a general
 452 trend, the catalytic behavior of $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$ was improved by low
 453 atomic fraction neodymium doping ($0.01 \leq x \leq 0.09$), while a very
 454 negative effect was obtained for higher loading ($x = 0.2$ and 0.3).
- 455

456 • The $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ mixed oxides were also able to accelerate CO
 457 oxidation in a certain extent, but there was a net production of CO
 458 during soot combustion because the oxidation capacity of these oxides
 459 was not high enough to oxidize all CO released as soot combustion
 460 product.

461

462 Acknowledgments

463 The authors thank the financial support of CNPq – National Counsel of
464 Technological and Scientific Development (Brazil), of the Spanish Ministry of
465 Economy and Competitiveness (Project CTQ2012-30703) and of the UE
466 (FEDER funding).

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Accepted Manuscript

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538

539 **Figure captions**

540

541 **Figure 1.** X-Ray diffractograms of the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ oxides.542 **Figure 2.** Cell parameter of the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ oxides determined from
543 X-Ray diffractograms.544 **Figure 3.** Raman spectra of the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ oxides. (a) General view
545 of the $100\text{-}1600\text{ cm}^{-1}$ range and (b) detail of the F_{2g} ceria peak
546 centered at $460\text{-}465.8\text{ cm}^{-1}$.547 **Figure 4.** BET specific surface area of the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ oxides.548 **Figure 5.** TCD profiles obtained in temperature programmed reductions with
549 H_2 of the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ oxides.550 **Figure 6.** Temperature of the surface and bulk reduction peaks obtained in
551 H_2 -TPR experiments with the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ oxides.552 **Figure 7.** Catalytic tests performed at different temperatures with the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ oxides in the absence of soot. (a) Propylene, (b)
553 benzene and (c) CO.
554555 **Figure 8.** Soot conversion in catalytic tests performed at $530\text{ }^\circ\text{C}$ with the
556 $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ oxides mixed in loose contact with soot.557 **Figure 9.** Catalytic tests performed at $530\text{ }^\circ\text{C}$ with the $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$
558 oxides mixed in loose contact with soot. (a) Propylene, (b)
559 benzene and (c) CO.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Graphical abstract

Research highlights

- CeZrNd mixed oxides accelerate simultaneously soot, propylene and benzene oxidation
- Best $\text{Ce}_{0.73-x}\text{Zr}_{0.27}\text{Nd}_x\text{O}_2$ catalysts were obtained with $0.01 \leq x \leq 0.09$
- Nd improves surface reducibility and creation of oxygen vacancies