

Article

# Influence of Nanoscale Surface Arrangements on the Oxygen Transfer Ability of Ceria–Zirconia Mixed Oxide

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**Abstract:** Ceria-based materials, and particularly CeO<sub>2</sub>–ZrO<sub>2</sub> (CZ) solid solutions are key ingredient in catalyst formulations for several applications due to the ability of ceria to easily cycling its oxidation state between Ce<sup>4+</sup> and Ce<sup>3+</sup>. Ceria-based catalysts have a great soot oxidation potential and the mechanism deeply relies on the degree of contact between CeO<sub>2</sub> and carbon. In this study, carbon soot has been used as solid reductant to better understand the oxygen transfer ability of ceria–zirconia at low temperatures; the effect of different atmosphere and contact conditions has been investigated. The difference in the contact morphology between carbon soot and CZ particles is shown to strongly affect the oxygen transfer ability of ceria; in particular, increasing the carbon–ceria interfacial area, the reactivity of CZ lattice oxygen is significantly improved. In addition, with a higher degree of contact, the soot oxidation is less affected by the presence of NO<sub>x</sub>. The NO oxidation over CZ in the presence of soot has also been analyzed. The existence of a core/shell structure strongly enhances reactivity of interfacial oxygen species while affecting negatively NO oxidation characteristics. These findings are significant in the understanding of the redox chemistry of substituted ceria and help determining the role of active species in soot oxidation reaction as a function of the degree of contact between ceria and carbon.

**Keywords:** ceria–zirconia; redox activity; soot oxidation; ball milling

## 1. Introduction

Ceria-based materials, and particularly CeO<sub>2</sub>–ZrO<sub>2</sub> (CZ) solid solutions are key ingredient in catalyst formulations for several applications due to the ability of ceria to easily cycling its oxidation state between Ce<sup>4+</sup> and Ce<sup>3+</sup> [1–3]. Undoubtedly, its major technological application is the depollution of noxious compounds from internal combustion engines [4,5]. The wide success of ceria-based materials is strictly correlated to its oxygen storage capacity (OSC). Ceria based catalysts are able to modulate the available oxygen releasing it under reducing conditions and taking up oxygen under oxidizing conditions [1,2,5–7]. The removal/uptake of oxygen from the fluorite lattice is of fundamental importance in several catalytic applications. The redox/oxygen storage properties of ceria are at the origin for its widely application in formulations for diesel soot oxidation [8,9] and many studies investigate the role of ceria-based catalyst in carbon soot oxidation [10–20]. Specifically, the production of “active oxygen species” is believed to be among the most important features and several authors focused on the reaction mechanism in order to better elucidate the formation and the role of “active oxygen” [21–26]. We pointed out that two different mechanisms coexist during soot oxidation [21], one related to the amount of surface available oxygen and one associated to the amount of bulk oxygen; their relative significance on the overall reaction is dependent over ceria-soot interface and to the

accessibility of O<sub>2</sub> gas phase. Machida et al. [27] focused on the generation of “active oxygen” in the form of superoxide (O<sub>2</sub><sup>−</sup>) ions upon interaction of the O<sub>2</sub> gas phase with surface oxygen vacancies of reduced ceria. The mechanism is associated to the availability of adsorbed active oxygen species (peroxide and superoxide), which spill over onto the soot surface resulting in the formation of vacant sites, which are then filled with gas-phase O<sub>2</sub>. The mechanism is strictly affected by the degree of contact between soot and the ceria-based catalyst [28] and the temperature of soot oxidation dramatically decreases when an intimate contact is used. Recently, we observed that the interface between soot and ceria at a nanoscale level could dramatically influence the transfer of active oxygen from ceria to carbon boosting soot oxidation activity [28–30].

In this study carbon soot has been used as reductant to investigate the oxygen transfer of ceria at low temperature and obtain further insight on its oxygen storage properties and on the role of the carbon–ceria interface in oxygen exchange. For this purpose, a sample of ceria–zirconia particles of composition Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> was mixed with carbon soot to obtain different degrees of contact between carbon and catalyst. In addition to loose and tight contact carbon and ceria–zirconia were mixed in a high-energy mill to promote the formation of a core of oxide particles wrapped in a thin carbon envelope, which strongly improves contact (supertight contact) and contributes to lower soot oxidation temperatures [28]. Here, the effect of various oxidation atmospheres (O<sub>2</sub>, NO+O<sub>2</sub> and NO<sub>2</sub>+O<sub>2</sub>) has been investigated at different contact conditions. The presence of a core/shell carbon/ceria structure strongly enhances the reactivity of interfacial oxygen species while affecting negatively NO oxidation characteristics. This is due to the carbon envelope, which hinders NO interaction with ceria–zirconia while promoting vacancy formation at the interface with successive generation of active oxygen species. These findings are significant in the understanding of the redox chemistry of ceria and doped ceria based materials.

## 2. Results and Discussion

### 2.1. Textural and Structural Characterization

A sample of ceria–zirconia particles of nominal composition Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> was mixed with soot using different approaches in order to obtain a carbon/catalyst composite with varying degrees of contact between the two components. Conventional catalyst/soot mixtures were obtained in tight and loose contact mode by mixing the appropriate amount of ceria–zirconia with soot (Printex U by Degussa) in an agate mortar for 10 min or mixing with a spatula for 2 min, respectively. Improved contact (supertight contact) was achieved in a high-energy Spex mill equipped with zirconia balls and jar. In a typical experiment ceria–zirconia particles were milled with soot for 8 h [28].

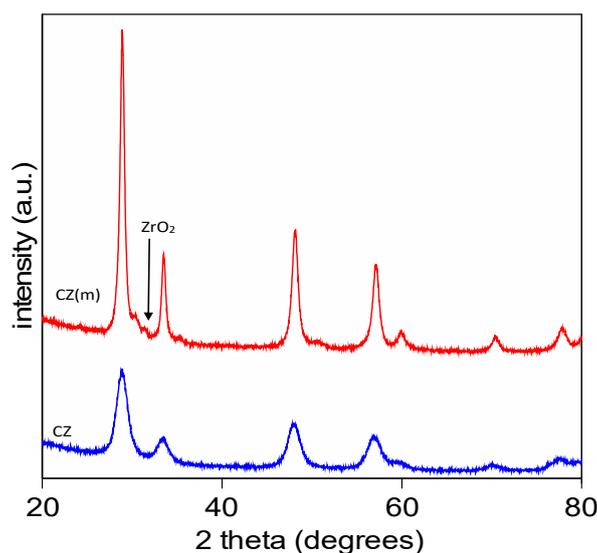
Composition, BET surface area and apparent density of materials are reported in Table 1. While mixing soot in the loose and tight mode did not affect surface area, the high energy milling process induced a significant surface area loss (from 79 to 29 m<sup>2</sup>/g) that was typically observed upon milling of a high-surface-area powder that is presumably due to adhesion of fine particles on the surfaces of larger agglomerates [5,31]. Similarly, an increase in the apparent density of the powder was observed due to the milling process (from 1.45 to 1.65 g/mL).

XRD peaks for CZ, CZ(l) and CZ(t) were broad and the values of the crystallite size obtained according to the Scherrer equation [32] was about 6 nm; after milling, peaks became more intense, clear and well defined (Figure 1), with an increase of crystallite size to 14 nm together with a drop in surface area. The milling process induces contamination of the CZ sample with a small amount of free ZrO<sub>2</sub> originating from the milling media, as evidenced by XRD profiles (Figure 1), while no reaction between CZ and carbon was highlighted. Rietveld refinement of XRD profiles revealed also a zirconia enrichment of ceria–zirconia solid solution with a decrease of cell parameter in agreement with the introduction of the smaller Zr<sup>4+</sup> in the lattice.

**Table 1.** Characteristics of the materials.

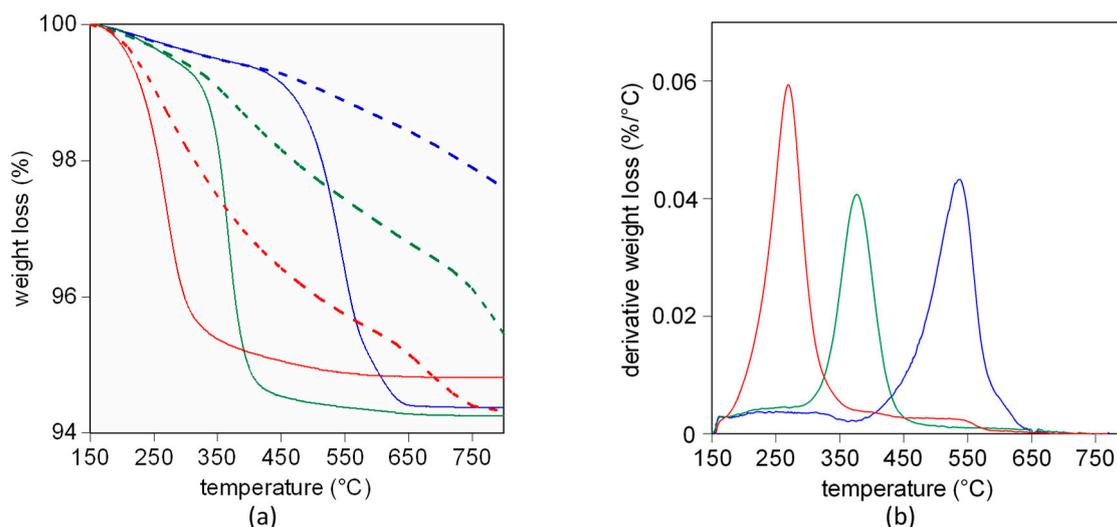
Sample	Name	SA (m <sup>2</sup> /g)	Apparent Density (g/mL)	Crystallite Size (nm) <sup>a</sup>	Cell Parameter <sup>b</sup> (nm)	Molar Composition <sup>b</sup>	Free ZrO <sub>2</sub> <sup>c</sup> (%)
Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub>	CZ	79	1.45	6	5.3590(4)	Ce <sub>0.82</sub> Zr <sub>0.18</sub> O <sub>2</sub>	/
Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub> /C loose	CZ(l)	79	1.44	6	5.3586(4)	Ce <sub>0.82</sub> Zr <sub>0.18</sub> O <sub>2</sub>	/
Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub> /C tight	CZ(t)	78	1.45	6	5.3588(4)	Ce <sub>0.82</sub> Zr <sub>0.18</sub> O <sub>2</sub>	/
Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub> /C milled	CZ(m)	29	1.65	14	5.3487(2)	Ce <sub>0.78</sub> Zr <sub>0.22</sub> O <sub>2</sub>	10

<sup>a</sup> calculated with Scherrer formula from X-ray diffraction patterns. <sup>b</sup> from Rietveld refinement. <sup>c</sup> amount of free ZrO<sub>2</sub> originating from abrasion during milling obtained from Rietveld refinement.

**Figure 1.** XRD profile for ceria–zirconia before and after high energy milling.

## 2.2. Catalytic Activity

In the present study the effect of a different atmosphere and contact conditions on soot combustion over the Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst was studied to better understand the oxygen transfer ability of ceria–zirconia at low temperatures. Soot combustion at different contact conditions in oxidizing (air) and in inert (N<sub>2</sub>) atmosphere was investigated by means of thermogravimetry experiments (Figure 2). Under oxidizing conditions, a complete soot combustion was achieved for all samples independent of the degree of contact. However, the type of contact dramatically affected the activity and increasing the soot/catalyst contact, a large decrease in the temperature of 50% soot conversion (T<sub>50</sub>) was observed with CZ(m) already removing 50% of carbon at temperature lower than 268 °C, compared to 364 °C and 534 °C, for CZ(t) and CZ(l) respectively. This behavior originates from the different morphology of the ceria–zirconia/carbon interface that in the case of the loose and tight contact mode was characterized by the presence of carbon on ceria–zirconia surface in the form of large particle aggregates with a modest degree of contact, while after high energy milling, soot aggregates progressively disappeared and carbon could be observed prevalently as a thin shell over the CZ crystallites [28–30]. This morphology favors the redox mechanism and activates the transfer of the surface/bulk oxygen of ceria–zirconia to carbon, strongly affecting soot oxidation activity. As previously reported, this enhancement is observed only by milling simultaneously ceria–zirconia and carbon soot [28]; the individual and separate milling of ceria–zirconia and carbon did not affect the material and did not change/promote the redox/oxidation behavior. A similar promotion of the soot oxidation behavior was found when combustion was carried out without gas phase oxygen, as reported in Figure 2 (dotted lines), which shows the weight loss of CZ/soot mixture against temperature in nitrogen atmosphere. In this case oxidation was driven exclusively by oxygen originating from ceria–zirconia and weight-loss accounted not only for the removal of carbon due to oxidation but also from oxygen loss from the lattice to give CO/CO<sub>2</sub>.



**Figure 2.** (a) Weight loss profile analysis of CZ/carbon mixtures in air (solid line) and in  $N_2$  (dashed line) under different contact conditions and (b) derivative weight loss profile in air: CZ(l) (blue), CZ(t) (green) and CZ(m) (red).

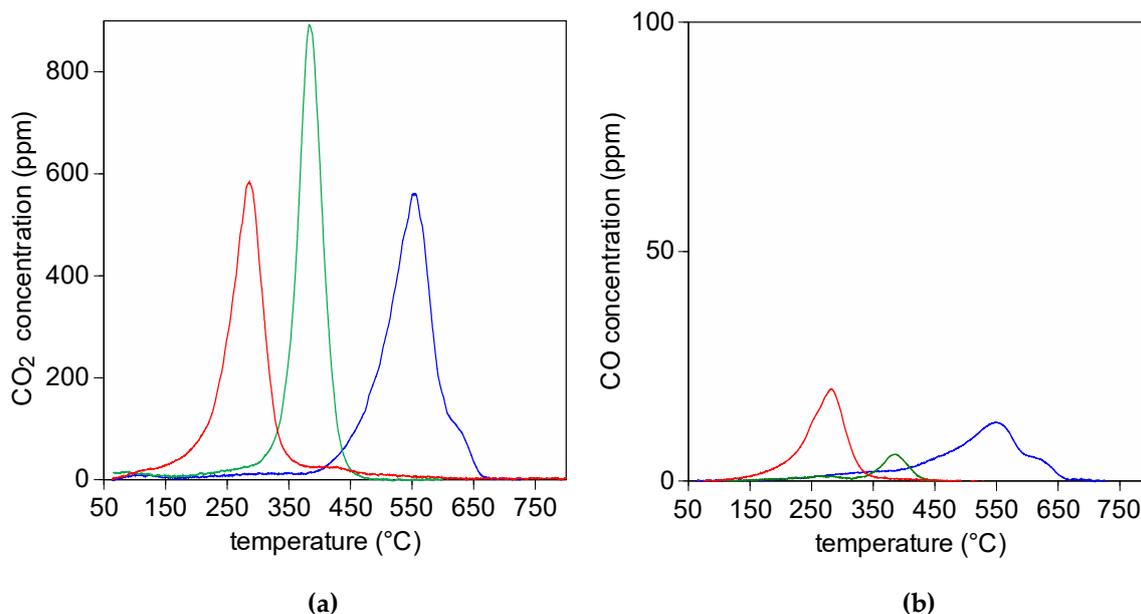
Selectivity to  $CO_2$  for each kind of contact could be obtained by a separate temperature programmed experiment carried out in  $N_2$  atmosphere and monitoring  $CO/CO_2$  evolution. As a first approximation  $CO_2$  selectivity obtained can be used for estimating the amount of soot oxidized in TGA (Table 2). The results reported in Figure 2 and Table 2 indicate that the degree of contact strongly influenced oxidation also under inert atmosphere. In loose contact, due to the poorer distribution of soot over ceria, soot was oxidized more slowly (compare slope of the weight loss curves in Figure 2) and in smaller quantities. As the degree of contact increased, the exchange of the lattice oxygen of CZ with carbon was facilitated and much faster, leading to an overall calculated weight loss of 1.65% due to carbon and 3.95% due to oxygen for CZ(m). Although this value was lower than that observed under air (where complete carbon removal was observed with ca. 5.1% weight loss due to carbon), it indicates that transfer of oxygen from ceria to carbon played a key role in soot oxidation and was a strong function of the contact conditions.

**Table 2.** Summary of results for soot oxidation under inert conditions.

Sample	Total Weight Loss <sup>a</sup> (%)	Selectivity from TP Experiment <sup>b</sup> CO/ $CO_2$	Calculated Weight Loss % (Carbon) <sup>c</sup>	Calculated Weight Loss % (Oxygen) <sup>c</sup>
CZ(l)	2.4	5/95	0.67	1.73
CZ(t)	4.6	10/90	1.32	3.28
CZ(m)	5.6	14/86	1.65	3.95

<sup>a</sup> total weight loss under inert atmosphere as measured from TGA experiment from 150 to 800 °C. <sup>b</sup>  $CO/CO_2$  selectivity as measured in a temperature programmed oxidation experiment carried out from 150 to 800 °C under nitrogen atmosphere. <sup>c</sup> contribution of carbon and oxygen in total TGA weight loss calculated assuming selectivity measured in a TP experiment.

To further investigate the mechanism of oxygen transfer over different type of contact, the soot oxidation activity has been measured by running temperature programmed oxidation (TPO) experiments and using peak temperatures ( $T_p$ ) as a measure of activity. As shown in Figure 3, by increasing the soot ceria contact, the oxidation temperature in  $O_2/N_2$  significantly decreased (from 554 to 285 °C for loose and milled sample respectively), in agreement with  $T_{50}$  obtained from TGA.



**Figure 3.** Temperature programmed oxidation (TPO) profiles of (a) CO<sub>2</sub> and (b) CO evolved from CZ/C mixtures at different mixing condition: CZ(l) (blue), CZ(t) (green) and CZ(m) (red).

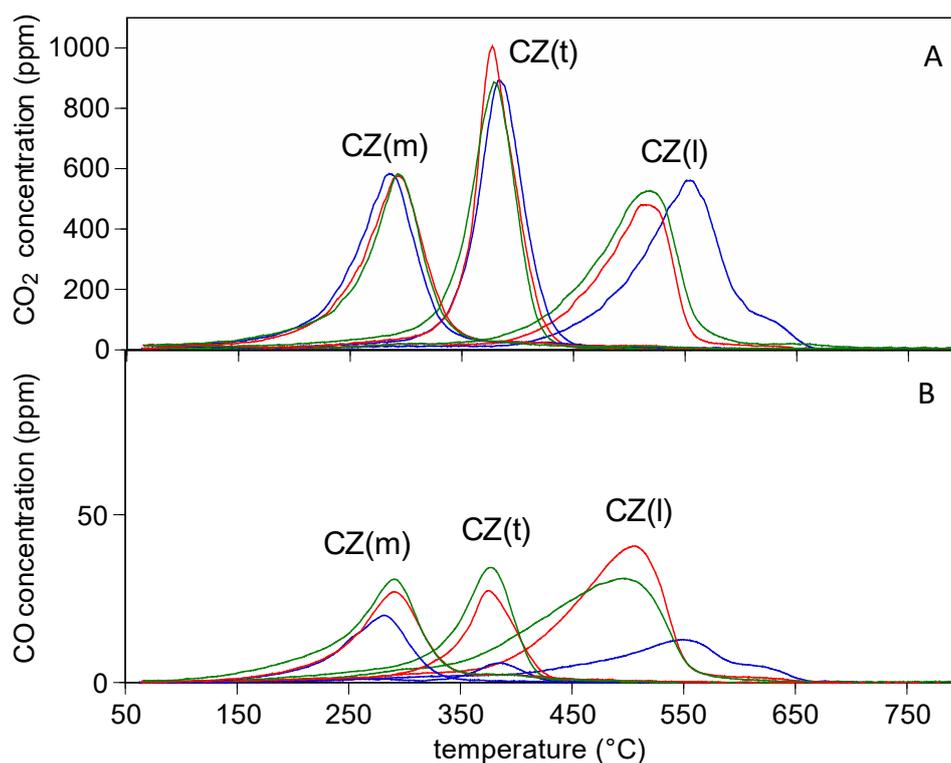
Figure 3b shows the concentration of CO evolved during soot combustion. CO concentration was very low compared to CO<sub>2</sub>, indicating higher selectivity for carbon dioxide, mainly due to the capability of ceria-zirconia catalyst to oxidize CO to CO<sub>2</sub> [17]. Contact conditions had a minor influence on the selectivity to CO<sub>2</sub>, which changed from 99% under tight conditions to 97% for the loose and supertight contact mode.

The effect of the oxidation atmosphere (O<sub>2</sub>/N<sub>2</sub>, NO/O<sub>2</sub>/N<sub>2</sub> and NO<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub>) in soot oxidation over the different catalyst/soot morphologies was investigated using TPO. The results are summarized in Table 3 and Figure 4. When the catalyst was in the loose contact mode, the use of a more oxidant mixture containing NO<sub>x</sub> contributes to lower soot oxidation temperature by several degrees (from 554 to 515/516 °C) while, when CZ/soot was mixed in tight contact, less significant differences were found, in the range 378–383 °C. As expected, the presence of NO<sub>x</sub> contributes to lower soot oxidation temperature by several degrees when the catalyst is in loose contact [18–20]. This is due to the oxidation of NO to NO<sub>2</sub> catalyzed by CZ and the subsequent carbon oxidation due to gas-phase NO<sub>2</sub>, which is a more efficient oxidant than gas-phase O<sub>2</sub> [9]. With tight contact a very small positive contribution of NO<sub>x</sub> atmosphere can be observed and the temperature of oxidation of carbon over NO<sub>x</sub>/N<sub>2</sub> is only a few degrees lower compared to reaction in O<sub>2</sub>/N<sub>2</sub> (378 vs. 383 °C). On the contrary, the presence of NO does not induce any promotion when more efficient contact is achieved using milled samples. The increased interfacial area between CZ and soot promotes active oxygen species formation at temperatures lower than that of the transformation of NO to NO<sub>2</sub> operated by ceria-zirconia. This does not allow formation of NO<sub>2</sub> before soot is already oxidized by oxygen, thus making ineffective the addition of NO. Looking at the details of peak temperatures, in the milled sample, the presence of NO<sub>x</sub> in the gas phase slightly lowers the soot oxidation activity with a T<sub>p</sub> increasing from 285 °C in O<sub>2</sub>/N<sub>2</sub> to 294 °C in NO/N<sub>2</sub>, indicating a general behavior in which soot oxidation for CZ(m) is favored under O<sub>2</sub>/N<sub>2</sub>. The creation of a thin layer of soot distributed on the catalyst with a high degree of contact at the nanoscale overcomes the limitation due to the poor mobility of active oxygen and boosts its oxidation potential.

**Table 3.** Activity and selectivity results from TGA and TPO experiments.

Sample	$O_2/N_2$ <sup>a</sup>			$NO/O_2/N_2$		$NO_2/O_2/N_2$	
	T50 (°C)	Tp (°C)	S <sub>CO2</sub> (%)	Tp (°C)	S <sub>CO2</sub> (%)	Tp (°C)	S <sub>CO2</sub> (%)
CZ(l)	534	554	97	515	91	516	92
CZ(t)	364	383	99	378	95	377	96
CZ(m)	268	285	97	294	95	293	94

<sup>a</sup> TGA 21% O<sub>2</sub> in N<sub>2</sub>; TPO 10% O<sub>2</sub> in N<sub>2</sub>. 500 ppm NO/10% O<sub>2</sub> in N<sub>2</sub>. 250 ppm NO<sub>2</sub>/10% O<sub>2</sub> in N<sub>2</sub>.

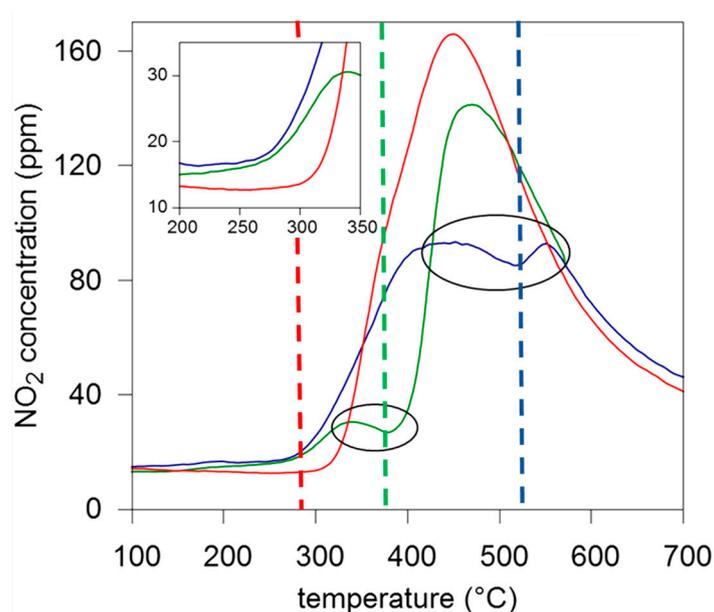


**Figure 4.** (A) CO<sub>2</sub> evolution and (B) CO evolution from temperature programmed oxidation (TPO) profiles for CZ/C mixtures at different mixing condition and different atmosphere: O<sub>2</sub> (blue), NO+O<sub>2</sub> (red) and NO<sub>2</sub>+O<sub>2</sub> (green).

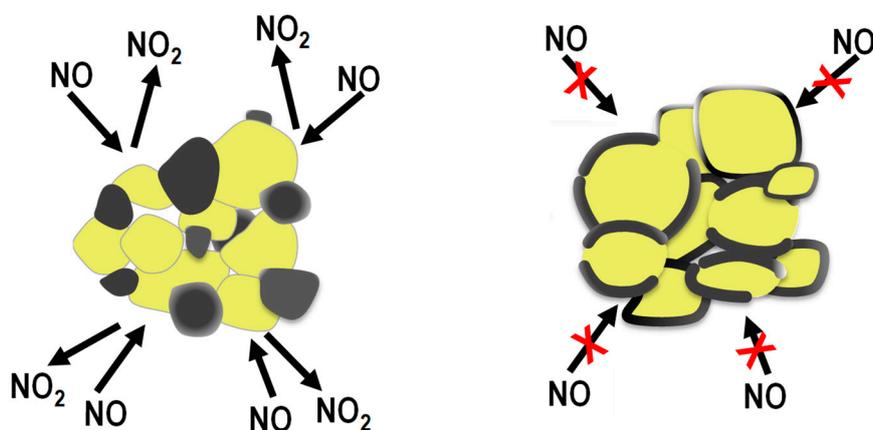
Selectivity to CO<sub>2</sub> was always higher than 90% and slightly dependent on the composition of the gas stream (Table 3), with values close to 100% when only O<sub>2</sub> was present as an oxidant in the gas phase, independently on the type of contact. When NO<sub>x</sub> species were added to the gas stream a lowering in CO<sub>2</sub> selectivity was observed, which is in agreement with data reported by García-García et al. [33,34]. Soot oxidation over ceria-based catalyst was connected with the formation of surface oxygenated species C(O) that act as intermediates in the formation of CO and CO<sub>2</sub> from thermal decomposition and/or reaction of C(O) with “active oxygen” species [7,8,10,12,26,35]. When NO<sub>x</sub> is present in the gas stream, two different reactions, NO adsorption and C(O) oxidation, compete over ceria active sites, both contributing to soot oxidation, but with NO adsorption competing with CO oxidation to CO<sub>2</sub> and consequently increasing CO production.

To further investigate the NO/NO<sub>2</sub> interaction with ceria–zirconia/soot mixtures, the NO oxidation profile over the CeZrO<sub>2</sub> oxide in the presence of soot was analyzed. Figure 5 shows the NO<sub>2</sub> concentration profile resulting from oxidation of NO. In general, formation of NO<sub>2</sub> started at a low temperature and was kinetically controlled. On increasing temperature (T > 500 °C) the opposite reaction predominated and the concentration of NO<sub>2</sub> decreased at values close to equilibrium. For samples in loose and tight contact, the onset of NO oxidation was at lower temperatures compared to milled samples (270 °C vs. 300 °C) indicating a higher NO oxidation rate and the overall NO<sub>2</sub> profile

strongly differed from that observed in the CZ(m) sample. A decrease in  $\text{NO}_2$  concentration (see circles in Figure 5) could be found in the range 490–560 °C and 340–390 °C, respectively for CZ(l) and CZ(t) mixtures. The decrease of NO conversion to  $\text{NO}_2$  in these two samples was correlated to the decrease of oxygen concentration in these temperature ranges, as  $\text{O}_2$  was consumed in carbon oxidation that peaks in the above temperature range, as indicated in Figure 5. This behavior was not observed in the case of CZ(m) because soot oxidation occurred at a temperature much lower to that of  $\text{NO}_2$  production and  $\text{NO}_2$  production occurred only after carbon was removed. This explains the onset of NO oxidation at higher temperatures for CZ(m); the presence of a thin carbon shell around ceria–zirconia particles, hindered NO oxidation to  $\text{NO}_2$ , delaying  $\text{NO}_2$  formation at higher temperatures, when the carbon envelope was completely oxidized by active oxygen species making accessible the ceria–zirconia catalyst surface to gas phase NO (Figure 6).



**Figure 5.** Temperature programmed oxidation (TPO) profiles of  $\text{NO}_2$  evolved from CZ/C mixtures at different mixing condition under  $\text{NO}+\text{O}_2$  gas flow: CZ(l) (blue), CZ(t) (green) and CZ(m) (red). Dotted lines indicate  $T_p$  of carbon oxidation (from red line in Figure 4).



**Figure 6.** Scheme of  $\text{NO}_x$  interaction over CZ(t) and CZ(l) (left) and CZ(m) (right). Ceria–zirconia particles are indicated in yellow, while carbon agglomerates and carbon layers are indicated in black.

Summarizing, this study investigated the influence of nanoscale surface arrangements of the soot/catalyst mixture on the redox behavior of ceria–zirconia mixed oxide and on the reactivity of active surface oxygen species. The difference in the contact morphology between carbon soot and CZ

particles strongly affected the oxygen transfer ability of ceria; in particular, increasing the carbon–ceria interfacial area, the reactivity of CZ lattice oxygen significantly improved. In addition, with a higher degree of contact, the soot oxidation was not affected by the presence of  $\text{NO}_x$ . Moreover, the existence of a core/shell structure strongly enhanced reactivity of interfacial oxygen species while affecting negatively NO oxidation characteristics.

### 3. Materials and Methods

Ceria–zirconia sample was prepared by coprecipitation of appropriate amount of ceria and zirconia precursors (cerium nitrate,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and zirconium nitrate,  $\text{Zr}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ , Treibacher Industrie AG, Althofen, Austria) with  $\text{NH}_4\text{OH}$  in the presence of  $\text{H}_2\text{O}_2$ . The precipitate was dried overnight at  $100\text{ }^\circ\text{C}$  and calcined in air at  $500\text{ }^\circ\text{C}$  for 3 h. Ceria–zirconia composition in the solid solution was checked by XRD using the Rietveld refinement analysis (Table 1). Catalyst/soot mixtures were prepared by mixing a synthetic soot (Printex U by Degussa, Essen, Germany) with ceria–zirconia solid solution in a weight ratio 1:20. Printex U was selected as model soot due to its extensive use in literature; it is characterized by a C content of 96% and a surface area of  $100\text{ m}^2/\text{g}$ . Loose contact was obtained by mixing the mixture in a vial for 2 min, while tight contact conditions were realized by grinding CZ and soot in an agate mortar for 10 min. Supertight contact was achieved milling ceria–zirconia particles and soot for 8 h in a high-energy Spex mill equipped with zirconia balls and a jar. Surface area measurements were carried out by means of a Tristar 3000 gas adsorption analyzer (Micromeritics, Norcross, GA, USA). X-ray diffraction patterns were recorded using a step size of  $0.02^\circ$  and a counting time of 40 s per angular abscissa in the range  $20\text{--}145^\circ$  on a Philips X'Pert diffractometer (40 kV and 40 mA, Ni-filtered  $\text{Cu-K}\alpha$  radiation, (PANalytical B.V., Almelo, The Netherlands). Phase identification was processed by Philips X'Pert HighScore software (Version 1.0b, PANalytical B.V., Almelo, The Netherlands), while mean crystalline size was estimated by the Scherrer [32] equation from the full width at the half maximum (FWHM) of the X-ray diffraction peak. The GSAS-EXPGUI program [36,37] was used for Rietveld refinement [38] of the XRD pattern.

The carbon soot oxidation activity was followed by running temperature programmed oxidation (TPO) and thermogravimetric (TGA) experiments. In TPO the samples (ca. 20 mg) were treated by a fixed gas flow of 500 mL/min ( $10\%\text{O}_2/\text{N}_2$ , 500 ppm  $\text{NO}_x/10\%\text{O}_2/\text{N}_2$  or 250 ppm  $\text{NO}_2/10\%\text{O}_2/\text{N}_2$ ) from room temperature to  $800\text{ }^\circ\text{C}$  (heating rate  $10\text{ }^\circ\text{C}/\text{min}$ ) with a GHSV ranging from 2.2 to  $2.5 \times 10^6\text{ h}^{-1}$ . A chromel–alumel thermocouple was used to measure the temperature of the catalyst and the outlet composition was monitored by FT-IR gas analyzers (MultiGas 2030, MKS Instruments, Inc., Andover, MA, USA).  $T_p$ , peak-top temperature was used to compare the activity. Selectivity to  $\text{CO}_2$  formation was determined by CO and  $\text{CO}_2$  concentration in the outlet gas using the expression:

$$\text{Selectivity to } \text{CO}_2 = 100 \times C_{\text{CO}_2} / C_{\text{CO}_2} + C_{\text{CO}} \quad (1)$$

TGA experiments were carried out in a Q500, TA Instruments. The samples (ca. 20 mg) were first pretreated under inert atmosphere at  $150\text{ }^\circ\text{C}$  for 60 min to eliminate adsorbed water and then heated at a constant rate ( $10\text{ }^\circ\text{C}/\text{min}$ ) in air or  $\text{N}_2$  (60 mL/min).  $T_{50}$ , the temperature at which 50% of weight loss was obtained was used to compare the activity. Reproducibility in term of  $T_{50}$  and/or  $T_p$  in TPO and TGA experiments was always within  $\pm 5\text{ }^\circ\text{C}$  and  $\pm 3\text{ }^\circ\text{C}$ , respectively. Reproducibility tests on weight loss were carried out and have shown that the total weight loss for each type of contact was close to the nominal value with reproducibility within  $\pm 3\%$  for CZ(m), and  $\pm 7\%$  for CZ(t) and CZ(l).

### 4. Conclusions

In this study the effect of different atmosphere and contact conditions on soot combustion over a ceria-based catalyst was investigated to better understand the oxygen transfer ability and redox behavior of ceria–zirconia at low temperatures promoted by the use of carbon soot as a solid reductant. To accomplish this aim three different contact models were used with varying degrees of interfacial

interaction between carbon and ceria–zirconia. The nanoscale carbon–ceria interface that we built using milling, although far from being representative of real conditions, can disclose information that are important in the understanding of oxidation properties of ceria. By increasing the numbers of contact points the temperature of soot oxidation in O<sub>2</sub> progressively decreased (from 550 to 280 °C). The effect of various oxidation atmospheres (O<sub>2</sub>, NO+O<sub>2</sub> and NO<sub>2</sub>+O<sub>2</sub>) was investigated at different contact conditions. It appeared for example that oxygen atmosphere was best utilized for oxidation of carbon at the interface in close contact with ceria in contrast to the well-known properties of NO/O<sub>2</sub> mixtures that surpass oxygen when contact conditions are less robust. Therefore when the interfacial ceria–zirconia/soot contact was strongly enhanced, gas phase O<sub>2</sub> promoted the formation of active oxygen through interfacial oxygen vacancies, resulting in a more powerful oxidant than NO<sub>2</sub>. The presence of a ceria–zirconia core/carbon shell architecture strongly enhanced the reactivity of interfacial oxygen species while at the same time affecting negatively NO oxidation characteristics, by establishing a sort of protective shield, which did not allow ceria–zirconia to act as an oxidant for NO, thus preventing its action toward carbon. Therefore, the active oxygen species formed through interaction of the gas-phase oxygen with interfacial ceria vacancies immediately reacted with soot enhancing the combustion at very low temperature and hindering NO oxidation that usually takes place in that temperature range. This indicates that, even under an oxidizing atmosphere, the close and extended interfacial contact between ceria and carbon, allows the formation of oxygen vacancies, which then activate oxygen through the formation of well-known active oxygen species. This did not occur with the same intensity over CZ/carbon mixture prepared using the tight mode and did not occur at all over CZ(l), thus explaining the different level of activity toward oxygen and NO/NO<sub>2</sub>. The above findings confirmed the key role of active oxygen species in soot oxidation with ceria-based materials and more importantly they disclosed the subtle but distinct redox chemistry of ceria with O<sub>2</sub> and NO/NO<sub>2</sub> mixtures at varying degree of interaction with carbon.

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