**Surface and redox properties of cobalt-ceria binary oxides: on the effect of Co
content and pretreatment conditions**

Michalis Konsolakis^{1*}, Michalis Sgourakis¹, Sónia A.C. Carabineiro²

¹School of Production Engineering and Management, Technical University of Crete,
GR-73100, Chania, Crete, Greece

²Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM,
Faculdade de Engenharia, Universidade do Porto, 4200-465 Porto, Portugal

***Corresponding author (M. Konsolakis): E-mail: mkonsol@science.tuc.gr;**

Tel.: +30 28210 37682; Web: www.tuc.gr/konsolakis.html

Abstract

Ceria-based transition metal catalysts have recently received considerable attention both in heterogeneous catalysis and electro-catalysis fields, due to their unique physicochemical characteristics. Their catalytic performance is greatly affected by the surface local chemistry and oxygen vacancies. The present study aims at investigating the impact of Co/Ce ratio and pretreatment conditions on the surface and redox properties of cobalt-ceria binary oxides. Co-ceria mixed oxides with different Co content (0, 20, 30, 60, 100 wt.%) were prepared by impregnation method and characterized by means of N₂ adsorption at -196 °C, X-ray diffraction (XRD), H₂ temperature-programmed reduction (H₂-TPR) and X-ray photoelectron spectroscopy (XPS). The results shown the improved reducibility of Co/CeO₂ mixed oxides compared to single oxides, due to a synergistic interaction between cobalt and cerium. Oxidation pretreatment results in a preferential localization of cerium species on the outer surface. In contrast, a uniform distribution of cobalt and cerium species over the entire catalyst surface is obtained by the reduction process, which facilitates the formation of oxygen vacancies through Co³⁺/Co²⁺ and Ce³⁺/Ce⁴⁺ redox cycles. Fundamental insights toward tuning the surface chemistry of cobalt-ceria binary oxides are provided, paving the way for real-life industrial applications.

Keywords: cobalt-ceria mixed oxides; surface science; oxygen vacancies; XPS; TPR

1. Introduction

Ceria-based transition metal catalysts have recently received considerable attention both in heterogeneous catalysis and electro-catalysis fields, as a result of their unique physicochemical properties and lower cost, compared to noble metals (NMs)-based catalysts [1-3]. Ceria is also an excellent co-catalyst for noble metal materials [4,5]. The combination of ceria with transition metals, results in materials with excellent redox properties and surface oxygen mobility, reflected then on their catalytic activity. In this regard, cobalt-ceria mixed oxides have shown great potential in heterogeneous catalysis field as alternative to NMs-based catalysts, for several applications, such as: oxidation of volatile organic compounds (VOCs) [1,6,7], low temperature CO oxidation [8], soot oxidation [9], hydrocarbons (HCs) oxidation [10-12], NO oxidation [13], preferential oxidation of CO in the presence of H₂ excess (PROX) [14,15], ethanol steam reforming [16,17], iso-octane steam reforming [18], ammonia synthesis [19], among others.

Furthermore, cobalt-ceria materials have been extensively applied in the field of solid oxide fuel cells (SOFCs) as alternatives to the well established Ni/YSZ anodes. Co-Ce oxides offer an interesting combination of electronic conductivity and electro-catalytic activity, which render them as suitable anodes in direct hydrocarbon fed SOFCs [20].

Recent studies have shown that the catalytic behavior of Co-Ce binary systems can be notably altered by adopting several strategies, involving among others, the employment of advanced synthesis procedure [7,15,17], the establishment of a certain Co/Ce atomic ratio [10,11,14] etc. For instance, Liotta *et al.* [10,11] found that the best catalytic activity for methane oxidation can be attained for a Co/Ce atomic ratio

close to 1, due to the well contact of Co_3O_4 particles with ceria. In a similar manner, in our recent study related to the steam reforming of iso-octane over mono- and bi-metallic Cu-Co/ CeO_2 catalysts, it is shown that Co/ceria composites with a Co content of about 20 wt.% exhibit the optimum characteristics in terms of catalytic activity and carbon tolerance [18]. The high concentration of surface oxygen species was considered to be responsible for the enhanced performance of Co/ CeO_2 catalysts [18]. Carabineiro *et al.* [7] examined the impact of preparation procedure on the VOCs oxidation performance of Ce-Co mixed oxides at a constant Ce/Co ratio of 0.5. The best performance was obtained with Ce-Co samples prepared by exotemplating, which resulted to a fine dispersion of oxide phases [7].

Despite the wide application range of cobalt-ceria binary oxides, there is no a systematic study on the impact of Co/Ce ratio and the pretreatment conditions (oxidation or reduction) on the local surface chemistry. To this end, the present study aims to shed some light into the surface chemistry modifications of cobalt-ceria mixed oxides that can be induced by altering the Co/Ce ratio and the pretreatment environment. More specifically, the physicochemical properties of cobalt-ceria mixed oxides of different Co content (0, 20, 30, 60, 100 wt.%) are determined by several complimentary techniques, such as BET, XRD, TPD and XPS. Special emphasis is paid to the impact of oxide composition and pretreatment conditions on elemental chemical states and surface oxygen vacancies, due to their pivotal role on catalytic activity. A direct motivation here it to answer how the oxides composition in conjunction with the pretreatment atmosphere affects the local surface structure (elemental chemical states, surface composition, oxygen vacancies), which finally determines the catalytic activity.

2. Experimental

2.1 Materials synthesis

Single CeO_2 and Co_3O_4 oxides as well as Co/CeO_2 composites with different cobalt loadings (20, 30 and 60 wt.%) were prepared by wet impregnation. Single oxides were synthesized by diluting the appropriate quantities of the corresponding precursor salts ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in double distilled water. The whole content was next heated under stirring until water evaporation. The resulting samples were dried at 120°C for 16 h and calcined at 600°C for 2 h, using a heating rate of $5^\circ\text{C}/\text{min}$. Following this procedure bare CeO_2 and Co_3O_4 oxides were obtained.

The Co/CeO_2 catalysts were synthesized by impregnation of the CeO_2 oxide in an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich) with appropriate concentration, so as to yield 20, 30, 60 wt.% nominal Co loading. The resulting suspensions were heated under stirring in order to remove the excess of water. The obtained samples were then dried overnight at 120°C and calcined at 600°C for 2 h. These samples are hereinafter denoted as $x\text{Co/Ce}$, where x stands on Co loading. To assess the impact of reduction pretreatment on the mixed oxides characteristics, the 30 wt.% Co/CeO_2 mixed oxide (30Co/Ce sample) is further subjected to a reduction pretreatment at 600°C for 1 h in a reducing atmosphere (10 vol.% H_2 in He, $100 \text{ cm}^3/\text{g}$). This sample is referred as 30Co/Ce-R.

For binary Co-Ce oxides the Co content was varied in the range of 20-60 wt.% loading. This specific range was carefully selected taking into account the composition of mixed oxides employed in several electro-catalytic applications. More specifically, a relatively high Co loading (usually higher than ca. 20 wt.%) is required

in fuel cell applications in order the required electronic conductivity to be accomplished [21]. In a similar manner, sufficient catalytic activity in various applications, such as VOCs oxidation [7,11], CO oxidation [8], etc., is achieved by Co loading higher than ca. 20 wt.%.

2.2 Characterization studies

Textural characterization

The surface area of bare CeO_2 , Co_3O_4 as well of $\text{Co}_3\text{O}_4\text{-CeO}_2$ mixed oxides was determined by N_2 adsorption/desorption isotherms at -196°C , using the multipoint BET analysis method, in a Tristar Micromeritics 3000 flow apparatus. BET surface area was determined according to the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.05 to 0.30. The total pore volume was calculated based on the adsorbed nitrogen volume at the highest relative pressure, while the average pore size diameter was determined by the Barrett, Joyner, and Halenda (BJH) method. Prior to the measurements, the samples were degassed at 250°C overnight.

XRD analysis

The crystalline structure of the catalysts was determined by X-ray powder diffraction (XRD) on a Siemens D 500 diffractometer using Cu K_α radiation ($\lambda=0.154\text{ nm}$) and operating at 40 kV and 30 mA. Diffractograms were recorded in the $2\theta=10\text{--}80^\circ$ range at a scanning rate of 0.04° over 2 s. The Scherrer equation was used to determine the crystal size of different phases based on the most intense diffraction peaks.

TPR analysis

Temperature programmed reduction (TPR) experiments were performed in a fully automated AMI-200 Catalyst Characterization Instrument (Altamira Instruments). In a typical TPR experiment, ~50 mg of sample was placed in a U-shaped quartz tube located inside an electrical furnace and heated to 1100°C at 10°C/min under He flow of 29 cm³/min and H₂ flow of 1.5 cm³/min.

SEM analysis

Surface analysis for morphological characterization was carried out by SEM, using a FEI Quanta 400 FEG ESEM (15 keV) electron microscope. The sample powders were mounted on a double-sided adhesive tape and observed at different magnifications under two different detection modes, secondary and back-scattered electrons. EDS confirmed the nature of the components.

XPS analysis

The XPS measurements were carried out in the analysis chamber of MAX200, at room temperature and $\sim 10^{-8}$ mbar pressure, using non-monochromatic MgK α X-rays and a Hemispherical Electron Energy Analyser (SPECS EA200) with Multi-Channel Detection properly calibrated according to ISO15472 and ISO24237. The analyser operated under conditions optimized for better signal intensity (constant pass energy of 100 eV, maximum lens aperture, analysis along the specimen surface normal). The analysed specimen area was a 4×7 mm² rectangle, placed near the center of each specimen surface on an Al plate sample holder.

3. Results and discussion

3.1 Textural/structural characterization (BET & XRD analysis)

Table 1 shows the main textural characteristics (BET surface area and total pore volume) of CeO₂, Co₃O₄ single oxides as well as of Co/CeO₂ mixed oxides with different Co loading. Bare CeO₂ exhibits the highest surface area (71.6 m²/g) and total pore volume (0.27 cm³/g) among all bare or mixed oxides. In contrast, Co₃O₄ has the smallest BET area (3.0 m²/g) and pore volume (0.01 m²/g). Increasing Co addition to CeO₂ results in a gradual degradation of textural characteristics, which however is not monotonic. The BET area decreases to 35, 45 and 15 m²/g, by increasing Co content to 20, 30 and 60 wt.%, respectively. The decrease of BET area, which is in general obtained upon increasing the Co loading, could be explained by taking into account the significant different crystallite sizes of Co₃O₄ and CeO₂ phases, as shown by XRD experiments (Table 1). The size of Co₃O₄ is about 3-fold higher than that of CeO₂, implying cobalt species segregation by formation of large Co₃O₄ particles over the catalyst surface. Therefore, a decrease of surface area is expected upon Co addition to CeO₂, due to a certain blockage of support pores. A similar trend was observed upon increasing the Cu content in Cu/CeO₂ catalysts [22]. However, depending on the mixed oxide composition, the crystallite size of different phases formed, as well as on the interactions between them, some deviations in BET area-from the general trend that is followed upon increasing Co loading-could be obtained. This probably explains the higher BET area of 30Co/Ce sample (45 m²/g), compared to 20Co/Ce (34 m²/g).

Table 1. Summary of textural (BET), structural (XRD), surface (XPS) and redox (TPR) characteristics of single and mixed Co_3O_4 - CeO_2 oxides. TPR temperatures: peak maxima (bold), shoulders (plain text).

Samples	BET		XRD		TPR	XPS
	S_{BET} (m^2/g)	Total Pore volume (cm^3/g)	Phase detected	Crystallite size (nm)	TPR peaks ($^{\circ}\text{C}$)	Ce (III) %
CeO_2	71.5	0.27	CeO_2	11.9	500, 750	25
20CoCe	34	0.13	CeO_2	10.2	295, 360	29
			Co_3O_4	37.6		
30CoCe	45	0.21	CeO_2	10.4	318, 373	27
			Co_3O_4	37.7		
60CoCe	15	0.07	CeO_2	11.7	373, 433	26
			Co_3O_4	39.5		
Co_3O_4	3.0	0.01	Co_3O_4	22.1	370, 433	-
			CoO	42.0		

Figure 2 and Table 1 present the information obtained by XRD spectra of CeO_2 , Co_3O_4 and Co/ CeO_2 catalysts, in relation to the phase identification and crystallite size. In CeO_2 sample, only CeO_2 cerianite is identified with a crystallite size of about 12 nm. In Co_3O_4 , both Co_3O_4 and CoO are detected, with crystallite sizes of about 22 and 42 nm, respectively. Co addition to CeO_2 , does not modify notably the structural characteristics of bare CeO_2 ; both the crystallite size and the lattice constant of CeO_2 remain almost constant. The latter implies no Co incorporation into ceria lattice in Co/ CeO_2 catalysts. Moreover, the CoO phase, detected in bare Co_3O_4 , is not observed in Co/ CeO_2 composites, probably implying the facilitation of CoO oxidation to Co_3O_4 in the presence of CeO_2 .

Figure 1. X-ray patterns of Co/CeO₂ catalysts with 20 (b), 30 (c) and 60 (d) wt.% Co loading as well as of bare CeO₂ (a) and Co₃O₄ (e).

3.2 Reducibility Studies (TPR)

To reveal the impact of Co content on the redox properties of Co/CeO₂ materials, temperature programmed reduction (TPR) were carried out. The H₂-TPR profiles of bare and mixed Co₃O₄-CeO₂ oxides are shown in Figure 2, whereas the main TPR peaks are summarized in Table 1.

The reduction profile of bare CeO₂ consists of two characteristic peaks at ca. 550 and 775°C. The peak at ca. 500°C can be attributed to surface oxygen reduction, whereas the peak at ca. 775°C to the reduction of bulk oxygen [1]. On the other hand, bare Co₃O₄ showed one main peak centered at 433°C, accompanied by a shoulder at ca. 370°C. The low temperature peak is usually attributed to the reduction of Co₃O₄ to CoO, whereas the high temperature peak to the reduction of CoO to metallic Co [13,15].

Figure 2. Temperature reduction (TPR) profiles of single and mixed Co_3O_4 - CeO_2 oxides.

By comparing the reduction profiles of Co/CeO_2 binary oxides with that of bare CeO_2 and Co_3O_4 oxides, some significant remarks can be drawn: (i) the reduction of all Co/CeO_2 mixed oxides occurs at much lower temperature, in relation to that required for bare oxides, ii) the reduction behavior of Co/CeO_2 mixed oxides is strongly influenced by Co content.

Based on TPR peaks maxima the following reducibility order is obtained: $20\text{Co}/\text{Ce} > 30\text{Co}/\text{Ce} > 60\text{Co}/\text{Ce} > \text{Co}_3\text{O}_4 > \text{CeO}_2$. Interestingly, the $20\text{Co}/\text{Ce}$ sample with the lower Co content (Co/Ce atomic ratio=0.73, Table 2) exhibited the optimum redox properties, in terms of reduction temperature. In a similar manner, it has been reported that at a nominal Co/Ce atomic ratio close to 1, the most favorable redox behavior of Co-ceria binary oxides can be obtained [2,8,10]. The presence of finely dispersed Co species in close proximity with ceria can be mainly accounted for the enhanced

reducibility of Co/ceria catalysts, with a Co content of about 20-30 wt.%, which then is reflected in the catalytic activity [2,8,10].

The actual amount of H₂ consumption, estimated from the quantification of H₂ uptake in TPR experiments (Figure 2), is presented in Table 2. For comparison purposes the theoretical amount of H₂ required for complete reduction of Co₃O₄ to Co⁰ is also included.

Table 2: H₂ consumption of single and mixed Co₃O₄-CeO₂ oxides.

Samples	Nominal Co content (wt.%)	Nominal Co ₃ O ₄ content (wt.%) ^a	Theoretical H ₂ consumption (mmol g ⁻¹) ^b	Actual H ₂ consumption (mmol g ⁻¹) ^c	H ₂ excess per g of catalyst (mmol g ⁻¹)	H ₂ excess per g of ceria (mmol g ⁻¹)
20CoCe	20	25.4	4.2	4.5	0.3	0.4
30CoCe	30	36.8	6.1	6.5	0.4	0.6
60CoCe	60	67.1	11.1	11.3	0.2	0.5
Co₃O₄	100	100	16.6	16.2	-	-

^abased on the assumption that Co is oxidized to Co₃O₄ during the calcination procedure, as indicated by XRD.

^bamount of H₂ required for the complete reduction of Co₃O₄ to metallic Co (theoretical molar ratio of H₂/Co=1.33)

^cestimated by quantification of H₂ uptake in TPR experiments

By comparing the actual with the theoretical amount of H₂ consumption in bare Co₃O₄ oxide (Table 2), it is evident that the real H₂ uptake is very close to the theoretical one (although slightly lower), implying a nearly complete reduction of Co₃O₄ to Co⁰. It should be noted, however, that a part of cobalt in bare oxide exists also in the form of CoO (Table 1), which requires lower amount of H₂ to be fully reduced (molar ratio of H₂/Co=1). The latter can be further accounted for the small difference between the real and the theoretical H₂ consumption for the Co₃O₄ sample.

Nevertheless, the H_2 amount required for the reduction of Co/CeO₂ mixed oxides is always higher compared to the theoretical values (Table 2). This “extra H_2 ” can be related both to the ceria reduction and to the H_2 spill over to the ceria support. Interestingly, the H_2 amount related to ceria seems to be proportional to Co content, especially in the range of 20-30 wt.% Co loadings. This implies that cobalt catalyzes the reduction of ceria by the H_2 .

The above findings clearly indicate the improved reducibility of Co/CeO₂ catalysts, compared to single oxides. The latter can be ascribed to strong interactions between cobalt and ceria, which in turn leads to the improved reduction of CeO₂ surface oxygen [2,7,8,10,13]. Similar conclusions have been drawn for Cu/CeO₂ catalysts; metal-support interactions can lead to the improvement of catalyst redox properties, which then is reflected in catalytic activity [1].

3.3 Surface characterization (SEM and XPS)

Samples were also analysed by SEM. Figure 2a shows that CeO₂ had a “compact” type of appearance, consisting of fragments of several sizes. Figure 2b shows the Co₃O₄ material that has a “softer, cotton-like” appearance. The 20Co/CeO₂ (Figure 2c) showed a homogeneous appearance, with larger and smaller particles well mixed together, as also shown by EDS (not shown). Figure 2d shows the 30Co/CeO₂ sample, with some darker and lighter zones being observed. EDS showed that the lighter areas are Ce-rich (Figure 2e) and the darker zones are Co-rich (Figure 2f). Similar results were obtained for the 60Co/Ce material (not shown). It seems that for lower Co loadings, a uniform distribution of Ce and Co species can be obtained, whereas for higher loadings (>30 wt.%) a moderate agglomeration was observed. These results are in consistency with the XPS studies, presented in the sequence.

Figure 3. SEM images of CeO_2 (a), Co_3O_4 (b), 20% Co/CeO_2 (c), 30% Co/CeO_2 (d) and EDS spectra of zones marked as Z1 (e) and Z2 (f).

XPS measurements are carried out to obtain information about the elemental chemical states and surface composition [23]. Figure 4 depicts the XPS spectra in the 2p region of Co for bare Co_3O_4 and Co/CeO₂ binary oxides with different Co content. It is evident that the Co2p spectra of all calcined samples are characterized by a main peak at ca. 780 eV accompanied by a low intensity satellite and a spin-orbit doublet Co2p_{1/2}-Co2p_{3/2} of about 15 eV. These characteristics point to the formation of Co³⁺ species in Co₃O₄-like phase [1,24]. Furthermore, the similarity of Co2p spectra between bare and mixed oxides is evident, suggesting no significant modifications on Co oxidation state upon increasing Co content in Co/ceria mixed oxides.

To further justify the above findings the Co2p spectra of the reduced 30Co/Ce-R (see experimental section) is comparatively shown. Reduction pretreatment results in a strong satellite at ca. 786 eV, which points to the reduction of Co³⁺ to Co²⁺ in octahedral sites [8,10,25,26]. In a view of this fact, Co³⁺ species are in a low spin state, in contrast to Co²⁺, thus no energy transfer to an unpaired electron is occurred, which in turn results in the absence of satellites [8,10,25,26]. In addition, both Co2p_{1/2} and Co2p_{3/2} peaks were shifted to about 1.0 eV toward higher BE values in relation to calcined samples (Figure 4), which further points to the appearance of more reduced Co species [14, 27]. Bonelle *et al.* [27] ascribed this upward shift to the smaller effective charge of Co³⁺, compared to Co²⁺, which in turn resulted in higher BE values of Co²⁺ by about 1.0 eV. The latter is accompanied by a shift in BE of O1s core level electrons; the BE of O1s in Co₃O₄ is at higher BE than in CoO [27], as indeed observed in the present study (see below).

Figure 4. XPS Co2p spectra of bare Co₃O₄ and Co₃O₄-CeO₂ mixed oxides subjected to oxidation or reduction pretreatment.

Figure 5 depicts the corresponding O1s spectra. Both Co₃O₄ and CeO₂ are characterized by an intense band at 529-530 eV, which can be ascribed to lattice oxygen. The high energy band at ~533.5 eV in Co₃O₄ could be attributed to adsorbed water [28-30]. Co/ceria mixed oxides are in addition characterized by a well resolved shoulder at 531.4 eV, which is related to adsorbed oxygen ions on surface oxygen vacancies [28-30]. The latter suggests the generation of more oxygen vacancies upon the addition of Co into CeO₂, which can be related to the strong Co-Ce interactions. This finding is in consistent with the improved reducibility of mixed oxides,

compared to single oxides (Figure 2, Table 2). Interestingly, the O1s spectrum of reduced 30Co/Ce-R sample indicates the formation of more oxygen adsorbed species (band at 531.4 eV) compared to surface lattice oxygen (529.4 eV). The latter could be ascribed to the facilitation of oxygen vacancies generation by the uniform distribution of cobalt and cerium species on the catalyst surface, which in turn results in a neighboring interaction between them. The latter is verified below by the difference in the surface composition between oxidized and reduced samples.

Figure 5. XPS O1s spectra of bare and mixed Co₃O₄-CeO₂ oxides subjected to oxidation or reduction pretreatment.

The corresponding Ce3d spectra are shown in Figure 6. For comparison purposes the spectrum of bare CeO₂ is also included. Ten peaks, related to Ce3d_{5/2} (v) and Ce3d_{3/2} (u) contributions are revealed by spectra deconvolution, employing mixed Gaussian-Lorentzian functions [31]. The peaks at 879.1 (v), 884.7 (v''), 889.3 (v'''), 900.4 (u), 907.6 (u'') and 916.7 eV (u'''), are assigned to Ce⁴⁺, whereas those at 881.9 (v'), 900.7 (u'), 874.2 (v0) and 897.6 eV (u0), to Ce³⁺ [32].

For 3d_{5/2} of Ce⁴⁺, a mixing of the Ce 3d⁹4f²Lⁿ⁻² and Ce 3d⁹4f¹Lⁿ⁻¹ states produces the peaks labeled v and v'', and the Ce 3d⁹4f¹Lⁿ final state forms the peak v'''. For 3d_{5/2} of Ce³⁺, the Ce 3d⁹4f²Lⁿ⁻¹ and Ce 3d⁹4f¹Lⁿ states correspond to peaks v and v', respectively. For Ce3d_{3/2} level with the u structure, the same assignment can be carried out. A relationship between the area of CeO₂ in the Ce 3d spectra and the % of u''' peak (which arises from a transition of the 4f'' final state from the 4f'' initial state) was established by Shyu *et al.* [33].

Taking into account the integrated XPS peak areas of Ce³⁺ and Ce⁴⁺ surface species, the concentration of Ce³⁺ can be determined from Ce³⁺/(Ce³⁺ + Ce⁴⁺) ratio [31]. The obtained values are depicted in Table 1. The concentration of Ce³⁺ species in Co/CeO₂ samples is 29, 27 and 26% for 20, 30 and 60 wt.% Co loading, respectively, compared to 25% in CeO₂-only sample. Interestingly, the 30Co/Ce-R sample, subjected to the reduction pretreatment, possesses by far the higher concentration of Ce³⁺ species (48%). The relatively higher concentration of Ce³⁺ species in mixed oxides compared to bare CeO₂ can be attributed to the synergistic interaction between cobalt and ceria, as already discussed during the analysis of TPR results. The reduction pretreatment, however, enhances the neighboring interaction between cobalt and ceria, due to the

uniform distribution of both species (see below), which then facilitates the redox cycles between $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$. This is in agreement with the reduction of Co^{3+} to Co^{2+} ions upon the reduction process (Figure 4). Furthermore, the facilitation of oxygen vacancies generation upon the reduction pretreatment (Figure 5) is in line with this explanation.

Figure 6. XPS Ce3d spectra of bare and mixed $\text{Co}_3\text{O}_4\text{-CeO}_2$ oxides subjected to oxidation or reduction pretreatment.

The surface composition of Co_3O_4 and Co/CeO_2 samples obtained by XPS analysis, along with the nominal atomic concentrations, is presented in Table 3. Nominal composition is estimated based on: i) the theoretical amount of all components on initially prepared catalysts, ii) the assumption that cobalt presents on the catalysts as

Co₃O₄ (due to cobalt oxidation during the preparation procedure). The validity of this assumption is confirmed by XRD results (Table 1), which implies that cobalt is mainly present in the form of Co₃O₄.

Comparison of the XPS and nominal values reveals a decrease in metal surface species for calcined Co/CeO₂ samples. This finding can be mainly ascribed to the low surface energy of Co species compared to ceria, which in turn results in the preferential localization of ceria on the outer surface. Similar conclusions have been drawn for Cu-Co binary systems [34].

Table 3. Nominal and surface (XPS) atomic concentrations (at.%) of Co/CeO₂ catalysts.

Sample	XPS ^a				Nominal ^b			
	Co	Ce	O	Co/Ce	Co	Ce	O	Co/Ce
Co₃O₄	29.4	-	70.6	-	42.9	-	57.1	-
20Co/Ce	6.5	24.2	66.2	0.27	15.5	21.3	63.2	0.73
30Co/Ce	3.3	27.2	69.5	0.12	21.1	16.9	62	1.25
60Co/Ce	13.2	21.9	64.9	0.6	33.2	7.5	59	4.4
30Co/Ce-R	18.0	12.0	69.9	1.5	21.1	16.9	62	1.25

^a estimated from XPS spectra

^b calculated from the nominal catalyst composition, assuming that Co is oxidized to Co₃O₄ during the preparation procedure.

Interestingly, 30Co/Ce sample possesses the lower concentration in surface cobalt species, despite the high nominal content. In the view of this fact, the Co/Ce surface ratio in 30Co/Ce sample is 0.12, *i.e.* 10 times lower than the nominal one (Table 2).

This implies the impoverishment of catalyst surface in Co species during the calcination procedure. In complete contrast, the reduction procedure results in a significant increase in surface Co species. The Co/Ce surface ratio is about the same to the nominal one, implying a uniform distribution of cobalt and cerium species over the entire surface area. Therefore, the preparation procedure (reduction or oxidation) can be lead to a surface reconstruction, notably affecting the relative surface population of cobalt and cerium species. The latter in turn is expected to affect notably the cobalt-ceria interactions and consequently the surface and catalytic properties. Concerning the atomic concentration (at.%) of surface oxygen species all catalyst demonstrate a higher surface proportion compared to bulk oxygen. This finding implies the synergistic interaction between cobalt-cerium species toward the formation of surface oxygen vacancies.

Conclusions

The impact of Co content and pretreatment atmosphere on the surface and redox properties of cobalt/ceria mixed oxides was investigated by means of several complementary techniques. The results clearly showed the improved reducibility of Co/CeO₂ mixed oxides compared to single oxides, following the order: 20Co/Ce>30CoCe>60CoCe>Co₃O₄>CeO₂. A synergistic effect between Co and Ce toward the easier reduction of mixed oxides was considered, which is exacerbated at Co/Ce nominal ratios close to 1. The formation of more oxygen vacancies in mixed oxides was revealed, justifying their superior reducibility compared to bare oxides.

Significant differences on the local surface structure (elemental chemical states and surface composition) of binary oxides were obtained upon pretreatment process. Calcination procedure always lead on the impoverishment of catalyst surface on

cobalt species, in complete contrast to reduction pretreatment, which results in a uniform distribution of cobalt and cerium species. The latter favors the neighboring interactions between cobalt and ceria, which in turn facilitates the redox cycles between $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$. Under these perspectives the optimum Co/Ce ratio in several catalytic applications, must be always determined in relation to pretreatment atmospheres.

The above conclusions reveal the key role of composition and pretreatment conditions on the local surface chemistry of cobalt/ceria binary oxides. Therefore, beyond the knowledge gained at atomic level, the present findings are expected to lead to the optimization or even to the development of novel binary oxides by appropriately co-adjusting the bulk composition, the synthesis procedure and the pretreatment conditions.

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