Mechanochemically Prepared $\text{Co}_3\text{O}_4$-$\text{CeO}_2$ Catalysts for Complete Benzene Oxidation

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Abstract: Considerable efforts to reduce the harmful emissions of volatile organic compounds (VOCs) have been directed towards the development of highly active and economically viable catalytic materials for complete hydrocarbon oxidation. The present study is focused on the complete benzene oxidation as a probe reaction for VOCs abatement over $\text{Co}_3\text{O}_4$-$\text{CeO}_2$ mixed oxides (20, 30, and 40 wt.% of ceria) synthesized by the more sustainable, in terms of less waste, less energy and less hazard, mechanochemical mixing of cerium hydroxide and cobalt hydroxycarbonate precursors. The catalysts were characterized by BET, powder XRD, $\text{H}_2$-TPR, UV resonance Raman spectroscopy, and XPS techniques. The mixed oxides exhibited superior catalytic activity in comparison with $\text{Co}_3\text{O}_4$, thus, confirming the promotional role of ceria. The close interaction between $\text{Co}_3\text{O}_4$ and $\text{CeO}_2$ phases, induced by mechanochemical treatment, led to strained $\text{Co}_3\text{O}_4$ and $\text{CeO}_2$ surface structures. The most significant surface defectiveness was attained for 70 wt.% $\text{Co}_3\text{O}_4$-30 wt.% $\text{CeO}_2$. A trend of the highest surface amount of $\text{Co}^{3+}$, $\text{Ce}^{3+}$ and adsorbed oxygen species was evidenced for the sample with this optimal composition. The catalyst exhibited the best performance and 100% benzene conversion was reached at 200 °C (relatively low temperature for noble metal-free oxide catalysts). The catalytic activity at 200 °C was stable without any products of incomplete benzene oxidation. The results showed promising catalytic properties for effective VOCs elimination over low-cost $\text{Co}_3\text{O}_4$-$\text{CeO}_2$ mixed oxides synthesized by simple and eco-friendly mechanochemical mixing.

Keywords: $\text{Co}_3\text{O}_4$-$\text{CeO}_2$ mixed oxides; mechanochemical preparation; complete benzene oxidation

1. Introduction

The volatile organic compounds (VOCs) are air pollutants from both outdoor and indoor sources. They have a strong detrimental effect on human health and the global environment, causing photochemical smog and ozone depletion. Different methods for VOCs abatement (low-temperature condensation, adsorption, absorption, biochemical degradation) were reported in addition to the conventional way of pollutant thermal incineration. The latter process has disadvantages of high temperatures (exceeding 800–1000 °C) imposing high operating costs as well as undesirable byproducts due to incomplete combustion. On the contrary, catalytic deep oxidation is economically favorable demanding much lower temperatures than thermal incineration but it is also an environmentally friendly technology preventing contamination with harmful side products of incomplete oxidation. This determines the continuing efforts for the development of efficient combustion catalysts with high oxidation activity and long-time stability but also high selectivity to harmless CO$_2$. Generally, two major types of catalysts—supported noble metals and
transition metal oxides—are reported as the most promising materials for VOCs complete oxidation [1]. Noble metal-based catalysts exhibit high specific activities at relatively low temperatures. However, the drawback of noble metals is not only the limited sources and expensive costs but also the requirement of nano-sized particles, which are sensitive to agglomeration and poisoning. Many efforts have been focused on economically feasible transition metal oxides and their preparation, characterization, and activity in VOCs complete oxidation. Busca et al. [2] summarized the obtained results for mixed transition metal oxides with spinel-, corundum-, and perovskite-type structures. The review of Li et al. [3] covered the development in catalytic combustion of VOCs over non-noble metal catalysts including mixed metal oxide and perovskite formulations. Kim [4] investigated the catalytic oxidation of hazardous aromatic hydrocarbons (benzene, toluene, and xylene) over different alumina-supported metal oxides. Recent extensive review revealed the major types of VOCs emitted from various sources and the dependence of catalytic oxidation on the pollutant nature and reaction conditions, including also proposed oxidation mechanisms for some representative VOCs [5]. Among transition metal oxides for environmental remediation, spinel Co3O4 has attracted considerable attention [6]. Co3O4 is characterized by high reducibility, abundance of oxygen vacancies providing active surface oxygen species and unique textural properties. In addition, it has advantages of low-cost, chemical and thermodynamical stability. Co3O4-based catalysts with nanocrystalline [7,8], ordered mesoporous [9–12] and controlled porous structures of nano-wires and nanorods [13] or hollow Co3O4 polyhedral nanocages [14] were studied in VOCs total oxidation. In order to reduce the amount of cobalt oxide, which is unfortunately rather toxic, Co3O4 on appropriate carriers have been also investigated [15–17] with the view that supported Co3O4 nanoparticles with higher surface area and sintering resistance could be preferred to single Co3O4 nanomaterials. However, Solsona et al. have found that the activity in propane oxidation over high surface area bulk Co3O4 was better as compared to Co3O4-Al2O3 oxides with a high amount of well-dispersed but less reducible Co-Al species [18]. The advantages of thin Co3O4 layers deposited on appropriate supporting material (stainless steel meshes) for VOCs abatement have been also reported [19,20]. The role of the support (CeO2, TiO2, and Al2O3) for complete oxidation of propene over supported Co catalysts was investigated by Wyrwalski et al. [21]. Ceria, which is a non-toxic oxide, was often used as component and promoter for oxidation reactions, due to the unique redox properties determined by fast Ce4+ ⇌ Ce3+ transfer assuring oxygen storage and oxygen supplying. Among different Co3O4 mixed oxides, Co3O4-CeO2 have attracted much attention. The highest oxidation activity was established using ceria as a support due to the best synergistic coupling of CeO2 and Co3O4 redox properties. Co3O4 nanocrystals and Co3O4-MOx binary oxides for CO, CH4, and VOCs oxidation were subject of reviewing in 2013, by Liotta et al., and the results of Co3O4-CeO2 mixed oxides were discussed in particular ([22] and references therein). The most often used preparation techniques such as co-precipitation, impregnation, combustion, and surfactant-template method and the obtained textural and morphological properties were summarized. The presented data highlighted the relationship between structure, active sites including oxygen vacancies, surface and bulk oxygen mobility, and oxidation activity. Results for methane, propene, and toluene oxidation obtained with differently prepared x%Co3O4-CeO2 (x = 5, 15, 30, 50, 70 wt.% as Co3O4) were also shown in the above-mentioned review. An increased specific surface area and Co3O4 crystallites dispersion was obtained by adding ceria up to 30% in Co3O4-CeO2. These binary oxides’ composition was optimal in respect to the reducibility and Co0 re-oxidation ability. The enhanced redox properties as a result of strong interaction between Co3O4 and CeO2 agreed with the better catalytic performance in the chosen oxidation reactions. It was concluded that depending on the reactant nature, the participation of active oxygen species related to surface oxygen vacancies and/or the high mobility of lattice oxygen are the key factors for the activity of the studied Co3O4 and Co3O4-CeO2 oxides [22]. In the following years, the scientific interest in these catalytic systems continued. More recent publications for the combustion of commonly studied
VOCs (without focusing on formaldehyde and halogenated hydrocarbons) referred to CoO3.4-CeO2 [23–28] and supported CoO3.4-CeO2 catalysts [29–31]. Differently prepared Co-Ce mixed oxides were tested in ethyl acetate [23, 24] and toluene [25] abatement as model reactions. The effect of Co loading on the catalytic performance was also discussed (optimal atomic ratio Co/Ce = 1 for ethyl acetate oxidation over materials prepared by evaporation and Co/Ce = 0.75 for toluene oxidation over catalysts prepared by impregnation). The superior activity of binary systems in comparison to single oxides was related to the mutual effect, which leads to improved textural, structural, and redox properties. Similar results for better activity in total oxidation of propane over CoCeOx catalysts prepared by double template combining sol-gel method with different Co to Ce ratios (optimal ratio Co/Ce = 1:1) in comparison with bare CoO3.4 and CeO2 were established [26]. The best performance of CoO3.4 catalyst sample was explained by the existence of strong interaction in the formed solid solution leading to a large surface area, small grain size, high concentration of oxygen vacancies, and improved reducibility. Li et al. [27] established that propene oxidation can be improved by Ce-doping of CoO3.4 nanorod catalysts (preparation by mesoporous silica SBA-15 as a template). The dopant (CeO2/CoO3.4 ratio of 0.25) occupied the Co2+ sites in CoO3.4 and facilitated the extraction of both adsorbed and lattice oxygen. Very recently Ismail et al. [28] have reported strong interaction between cobalt and cerium in the CoO3.4-Ce1-xO2-x catalysts leading to modification of surface area, crystallinity and redox properties. CoO3.4Ce0.5O2-x exhibited the best activity for toluene oxidation due to the presence of more surface Co3+ and Ce4+ ions that contribute to the abundance of surface active oxygen species. These literature data confirmed the better catalytic behavior in VOCs combustion of CoO3.4-CeO2 mixed oxides in comparison to mono-oxides, highlighting the key role of loosely bounded surface oxygen species and lattice oxygen supply. Balzer et al. [29] investigated cobalt catalysts (10 and 20 wt.% of cobalt loading) supported by impregnation on γ-Al2O3-CeO2 for catalytic oxidation of n-hexane, benzene, toluene, and o-xylene. The support was obtained by mechanical mixing of γ-Al2O3 and CeO2 in ratio 1:1. In the case of all studied hydrocarbons, the lower combustion activity was registered for the catalysts without ceria. It was concluded that the positive role of CeO2 was to supply oxygen to cobalt, keeping its higher valence state. Wang et al. [30] prepared Co-Ce mixed oxide catalysts with nanosheet structure by electrodeposition on nickel foam with different Co/Ce ratios (15:1, 10:1 and 5:1). The authors found that only a suitable Ce doping amount could ensure high reducibility and catalytic activity for toluene oxidation. The best performance in the case of Co/Ce = 10:1 was related to the higher amount of lattice oxygen, active at low temperatures, high concentration of Co3+ species, oxygen vacancies, and Ce4+/Ce3+ redox couples. Differently, in a very recent paper [31], Blin and co-authors studying Co-Ce catalysts supported on mesoporous SBA-15 (prepared by ‘two solvent’ technique) in combustion of methane, propane, and n-hexane, and n-hexane have established lower catalytic activity as compared to that of the mono-component cobalt oxide catalyst, whose highest activity was explained by enhanced reducibility because of weaker interaction with the SBA-15 support. On the contrary, the strong interaction of finely dispersed cobalt and cerium oxide in the SBA-15 channels resulted in difficult to reduce oxide phases and, respectively, in lower oxidation activity.

Benzene, arising mainly from petrochemical, steel, and paint industries is one of the most harmful air pollutants among the non-halogenated aromatic hydrocarbons with toxic, carcinogenic, and mutagenic effects [32]. CoO3.4-based catalysts have been studied as appropriate materials for the total oxidation of benzene and the attention was focused mainly on the supported systems. Ataloglou et al. studied complete benzene oxidation over differently synthesized cobalt oxide catalysts supported on alumina [33, 34]. The effect on the structure and catalytic performance of co-precipitation conditions for the preparation of Co-Al layered double hydroxides as precursors of Co-Al mixed oxides (Co/Al = 3:1) was investigated [35, 36]. There are several studies of benzene oxidation on cobalt catalyst supported on mesoporous silica with and without ceria doping [37–40]. Opposite effects
of the ceria promotion were reported and were related to differences in the structural and morphology properties of the carrier.

The briefly presented literature sources show the extensive research of Co$_3$O$_4$ and Co$_3$O$_4$-CeO$_2$ catalysts for complete VOCs oxidation. The explanation of observed catalytic activity in the case of supported materials is even more complicated as compared to bulk oxides because it is depending not only on the structure and properties of the active Co-Ce phases but in addition the optimal strength of their interaction with the support is of crucial importance.

The goal of the present work is to develop well-performing and cost-effective catalytic systems for VOCs abatement. The complete oxidation of stable benzene molecule was chosen as a model reaction. The investigation is focused on the catalyst behavior of mixed oxide catalysts with Co$_3$O$_4$ as a major phase and the role of different amounts of CeO$_2$ as a modifier. Unlike the methods widely reported in the literature for the preparation of mixed oxides ([22] and references therein), the Co$_3$O$_4$-CeO$_2$ (20, 30, and 40 wt.% of ceria) composites were synthesized by less waste, less energy, and a less hazard preparation method involving a simple mechanochemical mixing under controlled conditions. The relationship between activity in complete benzene oxidation (CBO) and catalyst surface and near-surface features determined by the applied preparation method and mixed oxides composition was commented.

2. Results and Discussion

2.1. Catalytic Activity Measurements

Sample pretreatment procedure in air at moderate temperature of 200 °C was chosen having in mind the finding of Yu et al. [41] that at these conditions the p-type semiconductors like Co$_3$O$_4$ form abundance of loosely bonded molecular oxygen species adsorbed at surface oxygen vacancies. Catalytic results in CBO as a function of the reaction temperature are illustrated in Figure 1. Products of partial oxidation were not detected. The lowest catalytic activity was observed over single Co$_3$O$_4$ as compared to Co$_3$O$_4$-CeO$_2$ mixed oxides prepared via mechanochemical mixing of cerium hydroxide and cobalt hydroxycarbonate precursors (Figure 1a).

[Figure 1. Comparison of benzene conversion over: (a) Co$_3$O$_4$ and Co-Ce mixed oxides; (b) differently prepared catalysts with optimal 70Co-30Ce composition.]

All Co-Ce samples exhibited high catalytic activity and 100% benzene conversion was reached at relatively very low temperatures for noble metal-free catalysts: 250 °C over 60Co-40Ce and 80Co-20Ce, only 200 °C over 70Co-30Ce. Complete benzene oxidation over...
noble metal (Au, Pd)-containing catalysts on different type supports (studied in our lab using the same equipment and experimental conditions) are compared in Supplementary material (Figures S1 and S2), allowing assessment of the high catalytic activity of reported in this work noble metal-free catalysts. The displayed, in Figure 1a, CBO activity in the lower temperature range of 80Co-20Ce is higher than that of 60Co-40Ce, the optimal 70Co-30Ce composition is confirmed in the entire temperature interval. The values of surface area for laboratory prepared and commercial Co$_3$O$_4$ (44 and 49 m$^2$ g$^{-1}$, respectively) and average particles size of Co$_3$O$_4$ phase estimated by XRD (18.0 and 18.7 nm, respectively) were very similar. However, the comparison between 70Co-30Ce and catalyst with the same composition synthesized using commercial Co$_3$O$_4$, 70Co-30Ce(c) (Figure 1b) revealed the less favorable performance in the latter case. A crucial role in the observed high CBO activity of mixed Co-Ce oxides plays the way of mechanochemical preparation. The addition of ceria (30 wt.%) to Co$_3$O$_4$ (prepared after calcination of cobalt hydroxycarbonate) by physical mixing, namely 70Co-30Ce(ph), enhanced slightly CBO activity as compared to Co$_3$O$_4$ and this improvement was insignificant as compared to the markedly higher oxidation activity achieved by mechanochemical mixing (Figure 1b). The mechanochemical method of catalyst preparation is not very often applied but its beneficial effect on the catalytic properties has been shown. Carabineiro et al. [42] have reported that gold catalysts supported on different MeO$_x$ (including Ce and Co metal oxides) on alumina are more active in CO oxidation when the supports were obtained by simple mixing as compared to the traditional way of alumina impregnation. Ilieva et al. [43] established that the preparation method (co-precipitation or mechanical mixing) of Co$_3$O$_4$-CeO$_2$ supports (10 wt.% Co$_3$O$_4$) of gold-based catalysts significantly affected the activity in CBO. In addition to the role of gold, the mechanical treatment allowed obtaining surface modified ceria and a separate Co$_3$O$_4$ phase with improved redox properties responsible for much higher oxidation activity. Liu et al. [7] reported preparation of very active cobalt spinel catalyst for propane oxidation using prolonged citrate-precursor grinding, producing highly strained Co$_3$O$_4$. The authors explained the observed high catalytic activity and stability by the induced lattice distortion and abundance of surface defects as a result of this preparation method based on mechanochemical activation. Similarly, the present superior activity in combustion of stable benzene molecule at relatively low temperatures could be ascribed to the role of defects of Co$_3$O$_4$ and CeO$_2$ phases created by mixed oxides interfacial interaction under mechanochemical treatment. Comparison of the performance for CBO of noble metal-based catalysts on supports prepared by coprecipitation, impregnation, or mechanical mixing (Figures S1 and S2) provided additional insights on our motivation to apply mechanochemical mixing in this work. The catalyst characterization allows highlighting the impact of chosen preparation method and Co$_3$O$_4$-CeO$_2$ mixed oxides composition on the CBO activity.

2.2. Sample Characterization

Specific surface areas (SSA) of the studied samples are listed in Table 1. A tendency of SSA increasing with higher CeO$_2$ amount in the mixed oxides as compared to bare Co$_3$O$_4$ is visible. The possible explanation could be related to the rearrangement of single oxide crystals during the mixed oxides preparation [25].

Crystal phase composition of mono-component Co$_3$O$_4$ and CeO$_2$, and their mixed oxides were analyzed by XRD as illustrated in Figure 2a. The patterns of Co-Ce oxides showed the coexistence of the same oxide phases (Co$_3$O$_4$ cubic spinel-type structure and CeO$_2$ cubic fluorite structure) as those registered for the respective bare oxides. The presence of CoO was not detected. Calculated particle size (D$_{CeO2}$ and D$_{Co3O4}$) and lattice parameter values of CeO$_2$ and Co$_3$O$_4$ crystalline phases ($a_{CeO2}$ and $a_{Co3O4}$) are listed in Table 1. The average size of ceria particles in mono CeO$_2$ and all mixed oxides is similar. However, comparing pure cobalt oxide and mixed oxides, a tendency of Co$_3$O$_4$ particle size lowering with increasing ceria content is visible. This finding is in agreement with the reported effect of decrease in the crystallite size caused by more refractory rare earth
oxide as ceria compared to Co$_3$O$_4$ (melting point of 2400 and 895 °C, respectively) [25]. The values of SSA and D$_{Co3O4}$ confirmed the statement of Wang et al. [44] about the role of ceria in better dispersing cobalt oxide crystallites and increasing the surface area of Co-Ce catalysts.

Table 1. Surface area (SSA), average size of ceria (D$_{CeO2}$) and Co$_3$O$_4$ particles (D$_{Co3O4}$), and lattice parameter of ceria ($a_{CeO2}$) and Co$_3$O$_4$ ($a_{Co3O4}$) estimated by XRD.

| Sample       | SSA (m$^2$ g$^{-1}$) | D$_{CeO2}$ (nm) | a$_{CeO2}$ (Å) | D$_{Co3O4}$ (nm) | a$_{Co3O4}$ (Å) |
|--------------|----------------------|-----------------|----------------|-----------------|----------------|
| Co$_3$O$_4$  | 44                   | -               | -              | 18.0 (2)        | 8.0868 (7)     |
| CeO$_2$      | 61                   | 5.0 (4)         | 5.4118 (2)     | -               | -              |
| 80Co-20Ce    | 54                   | 5.1 (2)         | 5.4093 (2)     | 18.0 (2)        | 8.0717 (4)     |
| 70Co-30 Ce   | 64                   | 5.2 (3)         | 5.4043 (5)     | 17.0 (4)        | 8.0630 (6)     |
| 60Co-40Ce    | 67                   | 4.8 (2)         | 5.3980 (4)     | 16.0 (4)        | 8.0557 (4)     |

The figures in parentheses give the error of the last listed decimal digit.

The lattice parameter of stoichiometric CeO$_2$ is 5.41 Å [45]. A decrease of ceria lattice parameter is shown in Table 1, e.g., a tendency of lattice contraction with increasing Co$_3$O$_4$ amount occurs. Reduction of the ceria lattice parameter takes place through Co-O-Ce bonds formation [46,47]. Cobalt ions can enter the ceria lattice because the radius of the Ce$^{4+}$ ion (1.01 Å in eight-fold coordination) is larger than that of the Co$^{2+}$ ion (0.79 Å).

Zou et al. observed lattice expansion of Co$_3$O$_4$ studying Co-Ce oxides for catalytic oxidation of diesel soot [48] and explained it by probable incorporation of cerium ions with larger radius into the lattice of Co$_3$O$_4$. The authors found a confirmation in the magnified XRD patterns of Co$_3$O$_4$ (311 plane), which illustrated negative shifts as compared to single Co$_3$O$_4$ with a shift maximum over the catalyst with the highest ceria content.

Figure 2. XRD patterns of: (a) the studied catalysts; (b) magnified pattern of Co$_3$O$_4$ (311) in 2θ range 36–38°.

Differently, in the present case (Table 1), values of the lattice parameter of Co$_3$O$_4$ phase in the mixed oxides decreased as compared to pure Co$_3$O$_4$ (lattice constant 8.08 Å for stoichiometric Co$_3$O$_4$ [49]). This means a tendency of lattice contraction, not expansion as in the above case of supposed incorporation of cerium ions with larger radius. In Figure 2b, the magnified patterns in 2θ range 36–38° showed a shift toward the higher degrees and the displacement is more significant with the ceria amount increasing. A similar modification of Co$_3$O$_4$ cell parameter showing lattice contraction for the grinding-derived from citrate-precursor Co$_3$O$_4$ samples was reported by Liu et al. [7]. The authors also showed that in the same 2θ range, the reference Co$_3$O$_4$ catalysts prepared by coprecipitation or sol-gel method.
presented diffraction peaks at lower angles, therefore, greater d-spacing, as compared to the grinding-derived catalysts. The longer the grinding time, the bigger shift of (311) plane position and the higher contraction of the lattice parameters was observed. These results were explained by a high degree of lattice distortion in cobalt spinels caused by the grinding procedure of preparation [7]. A similar microstructural modification can be expected for the present mixed oxides synthesized via mechanochemical treatment, which led to highly strained Co3O4 nanocrystals. In addition to the positive role of ceria, the relationship between enhanced structural disorder at Co3O4 surface and CBO activity could explain the much better oxidation activity of mixed oxides relative to that of bare Co3O4 and physical Co3O4-CeO2 mixture. However, the reason for the maximal CBO activity over 70Co-30Ce as compared to 80/60Co-20/40Ce catalysts has to be searched in surface-oriented catalysts’ characterization.

H2-TPR was used to investigate the reducibility of Co3O4 and mixed Co-Ce oxides. Two reduction peaks are usually detected in TPR pattern of Co3O4 and assigned to step-wise reduction of Co3O4 to metallic cobalt. Yao [50] attributed the lower temperature TPR peak to Co3+→Co2+ and the high-temperature one to Co2+→Co0 transition. Later this assignment was followed by many other researchers. Location of the peaks was in the range up to 500 °C depending on different factors but mainly on the Co3O4 particle size. Higher dispersion produces lower temperature peak in the TPR pattern of the metal oxide ([23] and references therein). It is known that reduction of ceria proceeds in two steps: surface layers reduction without effect on the fluorite structure at about 500 °C and bulk reduction over 800 °C [51]. The surface layers ceria reduction is limited to 17% [52]–20% [53].

Different results for the reducibility of prepared by various methods mixed Co-Ce oxides as compared to Co3O4 were reported in the literature. Many authors observed that cobalt oxide reduction is positively influenced by the presence of CeO2 and optimal value of Co/Ce ratio exists for maximal enhancement [22,23,27,28,39,54]. In rare cases, an unfavorable effect on the reducibility by ceria addition was observed. Li and coworkers established that adding CeO2 to Co3O4 (molar ratio Ce/Co = 2.8) does not affect Co3+→Co2+ transition but broader and less intensive TPR peak for Co2+→Co0 reduction as compared to bare Co oxide appeared at a higher temperature. The explanation was that the presence of weakly reducible CeO2 made the reduction process of Co2+ ions more difficult [55]. Later, the reducibility of the same CeO2-Co3O4 catalyst was investigated by in situ XRD and it was established that the peaks related to Co3O4 disappeared at almost the same temperatures for both mono oxides and CeO2-Co3O4 mixture. However, higher temperature for CoO extinction was needed for CeO2-Co3O4 as compared to Co3O4 [56]. In some cases, decreasing Co3O4 reducibility of supported Co-Ce mixed oxides was observed [38] but the reason could be related to the role of ceria in higher dispersion and accordingly stronger interaction with the support as it was supposed in Ref. [31].

TPR profiles of mixed oxides containing 60, 70, and 80 wt.% Co3O4, registered in the present study, are illustrated in Figure 3a. In all cases, including bare Co3O4, the peaks related to Co3+→Co2+ and Co2+→Co0 are with Tmax at around 280 and 340 °C, correspondingly. These data are in agreement with the observation of Kang et al. [46] about the formation of more reducible cobalt oxide species with increasing Co loading in Co-Ce composite catalysts up to 20 wt.% but insignificant variation in the temperature of Co3O4→CoO→Co0 reduction above this limit. Reviewing the relationship between redox behavior, oxygen vacancies, and catalytic properties in VOCs oxidation, Liotta et al. ([22] and references therein) pointed out that the interaction of CeO2 with Co3O4 might inhibit the reduction of bulk Co3O4 by oxygen supply from ceria, thus, decreasing the driving force for oxygen diffusion from bulk to the surface. Similarity in the TPR peaks position in the present case should be also related to the way of mechanochemical mixing preparation where the bulk of Co3O4 was less affected but surface and near-surface regions were modified. The experimental hydrogen consumption (HC) for bare Co3O4 was lower than the stoichiometrically needed for Co3O4→Co0 reduction (15.9 as compared to 16.6 mmol g⁻¹). For all mixed oxides, slightly lower experimental as compared to the
theoretical HC for Co₃O₄ reduction was also calculated. These data do not allow evaluation of the degree of enhanced ceria surface layers reduction arising in the same temperature range [48] due to the close contact with Co phase and spill-over of hydrogen ([39] and reference therein, [54] and reference therein).

The experimental HC during TPR of commercial Co₃O₄ (inset Figure 3a) was 16.4 mmol g⁻¹—a similar value to the theoretical one confirming the supposition of non-stoichiometric Co₃O₄ prepared using cobalt hydroxycarbonate precursor.

Additional TPR measurements were performed at conditions enabling to focus on the temperatures below 250 °C, characteristic for the reduction of surface adsorbed oxygen species [27,39,54,57,58]. It is documented that, generally, the surface oxygen species are relevant to the VOCs oxidation activity ([22] and references therein). In Figure 3b is demonstrated the detected hydrogen uptake below 100 °C assigned to the physically adsorbed oxygen and that one between 100 and 200 °C related to the chemically adsorbed oxygen species that are of interest for the catalyst oxidation activity. The comparison of peak positions and calculated HC values for the latter case are given in Table 2. The highest HC of 70Co-30Ce sample agrees with the best CBO activity established using this optimal catalyst composition.

Table 2. Position and experimental HC for the TPR peaks assigned to the reduction of chemically adsorbed oxygen species.

| Sample       | Tₘₐₓ (°C) | HC (µmol g⁻¹) |
|--------------|-----------|---------------|
| Co₃O₄        | 157       | 184           |
| 80Co-20Ce    | 157       | 154           |
| 70Co-30Ce    | 165       | 195           |
| 60Co-40Ce    | 176       | 97            |

Aiming to evaluate the crystal structure at surface and near-surface regions, UV resonance Raman spectroscopy was used for characterization of Co₃O₄, CeO₂, and Co-Ce mixed oxides. This relatively new application of UV resonance Raman spectroscopy started in 2009 with the identification of defects in ceria-based nanocrystals by Taniguchi et al. [59]. The registered UV-Raman spectra over 300–1500 cm⁻¹ spectral range are compared in Figure 4a. Despite rich Co₃O₄ content within the 60–80% range, UV-Raman spectra of
the Co-Ce samples are dominated by CeO$_2$ contributions. Assignment of the registered UV-Raman peaks and estimated fitting parameters (peak position and full width at half maximum, FWHM) are listed in Table 3. Thus, slight narrowing and red-shifting of the F$_{2g}$ band due to symmetrical Ce$^{4+}$O$_8$ stretching are noticeable in Figure 4a and Table 3 for all Co-Ce mixed oxides as compared to bare ceria. It is known that the half-width can vary linearly with the inverse of crystallite size, while the red-shift can be explained by strains due to the high curvature of nanocrystallites ([60] and references therein). Since all samples have almost the same average particle size (around 5 nm) calculated by XRD, the F$_{2g}$ narrowing might be explained by formation of small quantity of amorphous ceria phase during mixed oxides preparation via mechanochemical treatment. The biggest FWHM value (60 cm$^{-1}$) of the F$_{2g}$ modes of ceria in Co-Ce oxides was found for the 70Co-30Ce catalyst. This can be interpreted as relatively higher deficient CeO$_2$ surface in the case of the mixed oxide with this composition, since the defects contribute to the F$_{2g}$ band broadening ([60] and references therein).

Figure 4. UV-Raman spectra of: (a) Co$_3$O$_4$, CeO$_2$, and Co-Ce catalysts; (b) deconvolution of 60Co-40Ce and 70Co-30Ce spectra within the 330–850 cm$^{-1}$ range.

UV-Raman spectroscopy is a very sensitive method in analyzing defective structure of ceria at a lower penetration depth. Given the two right-shoulders of the ceria F$_{2g}$ band at ~490 and ~527–541 cm$^{-1}$ in Figure 4b, all Co-Ce samples show subsurface oxygen vacancies (V$_{O^-}$), and adsorbed peroxide (O$_2$)$^{2-}$) on ceria [60,61]. The latter spectral feature is also named D$_1$ band. The lower located D$_1$ at 527 cm$^{-1}$ (Table 3) might be assigned to Ce$^{4+}$O$_7$V$_{O^-}$ while the higher shifted band at 541 cm$^{-1}$ belongs to Ce$^{3+}$O$_7$V$_{O^-}$ ([60] and references therein). The second defective band, D$_2$, at about 600 cm$^{-1}$ is related to dopant-induced octahedral distorted sites with and/or without oxygen vacancies [59,61,62]. However, literature assignment of the D$_2$ band is still controversial. Slightly more intense D$_2$ than D$_1$ band is noticeable in the 70Co-30Ce spectrum (Figure 4 and Table 3) unlike the other two Co-Ce spectra. Moreover, the 2LO band attributed to the second-order longitudinal optical (2LO) mode in CeO$_2$ is less intense than the ones for 60Co-40Ce and 80Co-20Ce samples (inset Figure 4a).

Useful information about ceria defectiveness at the surface region related to the Co amount in the prepared by mechanochemical mixing Co-Ce oxides could be drawn on the basis of band intensity ratios (Table 3). The bigger integral intensity ratio ($A_{D2}/A_{F2g}$), the most defective structure of ceria is recorded [63], namely for the 70Co-30Ce catalyst.
Table 3. Fitting parameters (peak position/FWHM) of UV-Raman spectra over 330–1700 cm\(^{-1}\) spectral range, band assignments and rightness of the fit (R\(^2\)).

|          | CeO\(_2\) | 60Co-40Ce | 70Co-30Ce | 80Co-20Ce | Co\(_3\)O\(_4\) | Band Assignments                          | Refs. |
|----------|-----------|-----------|-----------|-----------|--------------|-------------------------------------------|-------|
| 399/113  | 389/146   | 385/139   | 404/132   | 355/143   |              | Transversal stretching of topmost O-Ce    | [61,64]|
| 443/71   | 446/55    | 444/60    | 445/56    | 410/69    |              | Symmetric stretching of the of Ce\(^{4+}\)O\(_8\) units with F\(_{2g}\) symmetry in CeO\(_2\) | [59,64]|
| 493/43   | 490/38    | 491/47    | 494/43    | 465/77    | E\(_g\) modes of Co\(_3\)O\(_4\) (470 cm\(^{-1}\)) | [65,66]|
| 534/52   | 527/72    | 541/74    | 541/52    | 625/54    | F\(_{2g}\) modes in CoO\(_6\) | [59–61]|
| 595/73   | 600/80    | 602/71    | 598/85    | 669/38    | A\(_{1g}\) of CoO\(_6\) (675 cm\(^{-1}\)) | [67]|
| 809/62   | 792/36    | 789/43    | 777/17    | 786/27    | O-O stretching of adsorbed O\(_2^{2-}\) | [64]|
| 852/10   | 828/30    | 827/29    |           | 1064/52   | Two-phonon mode in CoO | [66]|
| 1184/233 | 1181/210  | 1173/222  | 1178/225  | 1185/39   | Second-order longitudinal optical (2LO) mode in CeO\(_2\) | [59,64]|
|          |           |           |           | 1228/32   |              |                                           |       |
| 0.0724   | 0.1052    | 0.2131    | 0.1113    | 0.4454    | A\(_{2D}/A\(_{2D}\) (CeO\(_2\)) | [63]|
| 0.8675   | 1.4118    | 0.4867    | 0.8087    | 0.9913    | I\(_{D1}/I\(_{D2}\) | [59]|
| 0.9915   | 0.9962    | 0.9867    | 0.9913    | 0.9931    | R\(^2\)                                           |       |

Moreover, its lowest I\(_{D1}/I\(_{D2}\) ratio can be interpreted as the most abundant dopant-induced distorted sites. These findings are in agreement with assumption that the catalyst with 70% Co\(_3\)O\(_4\) and 30% CeO\(_2\) provides the best ceria contribution for the observed CBO activity (Figure 1). Enhancing of the second-order longitudinal optical (2LO) modes at about 1180 cm\(^{-1}\) (inset Figure 4a) for mixed oxides as decreasing ceria content points out that the absorbed oxygen species (O\(_2^{2-}\)) converts into lattice oxygen [64].

Co\(_3\)O\(_4\) in the mixed oxides is depicted only in the 70Ce-30Ce spectrum (Figure 4a,b) by the small band at about 669 cm\(^{-1}\) due to A\(_{1g}\) modes of CoO\(_6\) [65]. In the UV-Raman spectrum of single Co\(_3\)O\(_4\), the presence of CoO was evidenced by the registered two-phonon mode band at 1064 cm\(^{-1}\) (inset Figure 4a) [66]. The latter band might be obscured by the strong and wide 2LO band of ceria in the Co-Ce spectra and/or vanished by full power Raman measurements enabling conversion to Co\(_3\)O\(_4\). Moreover, difference between theoretical and experimental HC needed for Co\(_3\)O\(_4\)→Co\(^0\) reduction during TPR measurements of all studied catalysts suggests a non-stoichiometric Co\(_3\)O\(_4\) phase in the as-prepared samples. Additional UV-Raman spectra collected after TPR and TPO experiments (Figure S3) pointed out that full-power excited TPR treated samples causes oxidation of metallic cobalt to well crystallized Co\(_3\)O\(_4\).

Analogous to data reported by Konsolakis et al. [24] for impregnated cobalt-cerium mixed oxides (15 to 30 wt.% Co\(_3\)O\(_4\)) where CoO was X-ray depicted in bare Co\(_3\)O\(_4\) but not in mixed oxides, CoO oxidation to Co\(_3\)O\(_4\) in case of Co-Ce catalysts under discussion might be facilitated under ceria influence and laser exposure. The easier reoxidation of cobalt species such as Co\(^0\) and Co\(^{2+}\) caused by interaction between CeO\(_2\) and Co\(_3\)O\(_4\) was commented in the literature ([22] and references therein). The presence of both Co\(_3\)O\(_4\)
and some small CoO amount (not detectable by XRD) can explain the lower values of experimental as compared to theoretical HC in the present TPR study.

Co-Ce mixed oxides surfaces, with respect to element percentage composition and oxidation state, were investigated by X-ray photoelectron spectroscopy. Co 2p spectra of Co₃O₄ are illustrated in Figure 5a. The spectra are characterized by the 2p³/2 and 2p½ spin-orbit components, about 15 eV apart and with an intensity ratio of 2:1 [68]. Each component was fitted by two curves corresponding to two different cobalt oxidation states. As given in Table 4, and as shown in Figure 5 for all samples, the Co 2p½ was fitted with a more intense peak at 780.1 ± 0.2 eV, typical of Co³⁺ and a weaker peak at 782.1 ± 0.2 eV assigned to Co²⁺ ions. According to literature, each of the two Co 2p components typical of Co²⁺ was accompanied by a shake-up feature at the high energy side about 10 eV apart from the main peak [68]. The intensity ratio for the peaks related to the Co³⁺ and Co²⁺ chemical species for the reference cobalt oxide (Table 4) is lower than the nominal 2:1 of the spinel Co₃O₄ [69], therefore, suggesting surface segregation of the Co²⁺ species. This agrees with the TPR result of lower experimentally obtained HC as compared to the theoretical one. However, the Co³⁺/Co²⁺ values are substantially higher in the mixed oxides as compared to Co₃O₄. The effect of ceria to maintain a high valence state of cobalt, e.g., the promotion of more Co³⁺ active species, which can improve the catalytic oxidation performance, was reported in the literature ([29,30,46] and references therein, [54] and references therein). It is worth to notice that the 70Co-30Ce catalyst exhibited the highest Co³⁺/Co²⁺ surface ratio among the tested samples.

Supplementary to the dominant contribution of Ce⁴⁺, the presence of surface Ce³⁺ cations was also established on the basis of recorded Ce 3d spectra with 3d½/2 and 3d½ spin-orbit components (Figure 5b). The atomic ratios Ce³⁺/Ce_tot (Ce_tot = Ce⁴⁺ + Ce³⁺), as obtained from the fitting of the Ce 3d spectra with the various final state components (Vs and Us) as shown in Figure 5, are listed in Table 4. The typical ratio for bulk ceria is in the range 0.06–0.10 and the higher values obtained in the present case (0.19–0.22) can be interpreted as indicative of surface oxygen vacancies formation [70]. These vacancies represent sites for adsorbing oxygen, which decreases the surface Gibbs energy, leads to the surface charge compensation, and generates surface active oxygen species [71]. The Ce⁴⁺ → Ce³⁺ reduction, promoted by the presence of Co₃O₄, was considered favorable for the oxidation of hydrocarbons ([29] and reference therein). As given in Table 4, a higher charge imbalance in CeO₂ phase in terms of Ce³⁺, e.g., more defective structure with surface oxygen vacancies, is seen for the sample containing 30 wt.% ceria.

The comparison between calculated and nominal atomic ratio of Ce/Co indicated ceria enrichment at the surface of catalysts with higher CeO₂ content, namely 70Co-30Ce and 60Co-40Ce samples. Surface ceria enrichment had also been reported by other authors [54, 57]. Ismail et al. [28] supposed that the interaction between Co and Ce phases can drive redox transfer reaction Co²⁺ + Ce⁴⁺ ↔ Co³⁺ + Ce³⁺, creating defective surface with oxygen vacancy for charge compensation. XPS results for both Co and Ce valence state revealed a trend of more Co³⁺ and Ce³⁺ species on the surface of 70Co-30Ce, i.e., the catalyst with the best CBO activity.
Figure 5c depicts the corresponding O 1s spectra. Three components can be identified in the spectra after deconvolution (see Figure 5c and Table 4). The most intense band at ~530 eV is ascribed to the lattice oxygen (O\textsubscript{l}). The intermediate energy O 1s component (around 532 eV) can be related to surface chemisorbed species containing oxygen (O\textsubscript{s}). In the literature these latest species are considered as forms of adsorbed oxygen (O\textsuperscript{2−}, O\textsuperscript{−}, O\textsubscript{2}\textsuperscript{2−}) \cite{28,30,44,72}, surface hydroxyl groups, and/or defect oxide oxygen \cite{26,39,54}. The small component at higher BE could be due to some oxygen–carbon bond likely arising from some impurity. Very recently, studying Co\textsubscript{3}O\textsubscript{4} supported on nanorod CeO\textsubscript{2}, Bao et al. additionally to the lattice and adsorbed oxygen species, assigned the broad shoulder at higher BE of 533.5 eV to the presence of carbonated oxygen \cite{72}. The best catalytic benzene oxidation activity over mesostructured Co\textsubscript{3}O\textsubscript{4}-CeO\textsubscript{2} composites was associated with the larger quantities of surface hydroxyl groups and surface oxygenated species by Ma et al. \cite{39}. The O\textsubscript{s}/O\textsubscript{l} ratios, given in Table 4, revealed more abundant adsorbed oxygen and oxygen containing species at the surface of Co\textsubscript{3}O\textsubscript{4}-CeO\textsubscript{2} mixed oxides as compared to mono-component Co\textsubscript{3}O\textsubscript{4}. UV Raman spectroscopy results for all Co-Ce samples showed the presence of subsurface oxygen vacancies and adsorbed peroxide O\textsubscript{2}\textsuperscript{2−} species.
Table 4. XPS Binding energies and atomic ratios.

| Sample   | BE Co 2p3/2 (eV) | BE Ce 3d5/2 (eV) | BE O 1s (eV) | Ce/Co | Ce^{3+}/Ce_{tot} | Co^{3+}/Co^{2+} | O_{s}/O_{l} |
|----------|------------------|------------------|--------------|-------|-----------------|-----------------|------------|
| CoO$_4$  | 780.1(63) (Co^{3+}) 782.0(37) (Co^{2+}) | 530.1 (78) 532.0 (20) 533.5 (02) | 1.70 0.26 |
| 80Co-20Ce | 780.0(69) (Co^{3+}) 781.9(31) (Co^{2+}) | 530.0 (67) 531.8 (21) 533.2 (12) | 0.07 0.20 2.25 0.31 |
| 70Co-30Ce | 780.3(73) (Co^{3+}) 782.3(27) (Co^{2+}) | 530.1 (75) 532.4 (23) 533.6 (02) | 0.16 0.22 2.70 0.31 |
| 60Co-40Ce | 780.2(72) (Co^{3+}) 782.1(28) (Co^{2+}) | 530.1 (70) 532.1 (24) 533.9 (06) | 0.22 0.19 2.57 0.33 |

Values in parentheses are the relative areas of Co$^{3+}$ and Co$^{2+}$ peaks; b Values in parentheses are the nominal atomic ratio of Ce/Co; c Calculated from the ratio of the low energy O 1s component (at about 530 eV) over the intermediate energy O 1s component (around 532 eV).

According to literature, high bulk oxygen mobility (through the Mars–van Krevelen mechanism) and formation of highly active oxygen species activated by the oxygen vacancies are the main factors determining the performance of Co$_3$O$_4$-CeO$_2$ binary oxides [22,30]. In the present investigation, despite the significantly lower CBO activity of Co$_3$O$_4$ as compared to Co-Ce mixed oxides (Figure 1), the reduction features of all studied samples illustrated in Figure 3a are very similar. Ceria did not influence the step-wise reduction of Co$_3$O$_4$ because its bulk structure was not affected by the mechanical treatment of the precursors. The observed trend of better cobalt oxide dispersion and increased SSA of Co-Ce catalysts did not produce visible differences in the temperature range for both Co$^{3+}$→Co$^{2+}$ and Co$^{2+}$→Co$^{0}$ reduction. The applied mechanochemical way of preparation determined predominantly surface interaction at the boundaries between cobalt and cerium oxide phases and formation of defective structures with lattice distortion at the near-surface region. The XRD results revealed mechanochemically initiated structural modification leading to strained Co$_3$O$_4$ crystallites as well as a tendency of ceria lattice contraction with increasing Co$_3$O$_4$ amount, therefore, evidenced the mixed oxides interaction. The obtained catalytic results could be explained by the assumption of the prevailing role of the active surface oxygen species as compared to the participation of lattice oxygen. Accordingly, Li et al., recently studying CoCeO$_x$ mixed oxides [26], concluded that the labile chemisorbed oxygen plays a key role in the oxidation reactions because of its higher mobility than the lattice oxygen. Concerning the surface Co$^{3+}$ ions and active oxygen species as the major active sites, the authors accepted the Langmuir–Hinshelwood mechanism for the reaction of propane combustion. Similarly, the crucial role of CeO$_2$ and Co$_3$O$_4$ interaction for the high oxidation activity was related to the enhanced availability of active surface oxygen and high valence state of cobalt by Lu et al. [57]. In a recent study, the Co$^{3+}$→Co$^{2+}$ reduction was seen as a driving force for the mobility of both Co$_3$O$_4$ lattice and adsorbed surface oxygen by Li et al. [27]. However, the easy reverse process of Co$^{2+}$ re-oxidation is also needed and the role of ceria for the retention of Co ions in higher valence state, documented in the literature ([22] and references therein, [24,29,46]), was assumed by the present UV Raman spectra collected after TPR and TPO experiments with 70Co-30Ce sample (Figure S3). The data confirmed the possible promotion of metallic
cobalt or CoO to Co$_3$O$_4$ oxidation by the influence of ceria. The cooperation between Co$_3$O$_4$ and CeO$_2$ could be of crucial importance for the hydrocarbon oxidation reaction. It is important to underline the significantly higher CBO activity of all studied mixed oxides compositions (Figure 1a) as compared to the mono-component Co$_3$O$_4$, thus, revealing the promotional role of ceria. The synergy between cobalt oxide and ceria can be described by the following mechanism: the reactant causes partial Co$^{3+}$ reduction to Co$^{2+}$ or even Co$^{0}$, followed by re-oxidation strongly enhanced by the participation of neighboring CeO$_2$ lattice, which is accompanied by creation of oxygen vacancies around the binary oxides interface, e.g., re-formation of sites for activated oxygen species generation [22].

Combining XPS and Raman analyses, it can be considered that the surface chemical state of the Co-Ce mixed oxides was affected by ceria amount. The most significant surface defectiveness as a result of the close interaction between Co$_3$O$_4$ and CeO$_2$ phases induced by mechanochemical treatment was achieved in the case of 70Co-30Ce sample for which the trend of the highest surface amount of Co$^{3+}$, Ce$^{3+}$, and adsorbed oxygen species was observed. One hundred percent benzene conversion was reached over the catalyst with this optimal composition at 200 °C and a stable activity was maintained without products of incomplete oxidation. To explore the role of mechanochemical treatment under controlled conditions, a physical mixture of Co$_3$O$_4$ with 30 wt.% CeO$_2$ was also tested in CBO. The result (Figure 1a) clearly showed the crucial role of mechanochemically initiated interaction at the boundaries of two oxides.

Future research efforts will be directed to study potential of these catalysts in abatement of other VOCs, in particular indoor pollutants such as formaldehyde.

3. Materials and Methods
3.1. Catalyst Preparation

A mixture of cerium hydroxide and cobalt hydroxycarbonate precursors (prepared by precipitation of Ce(NO$_3$)$_3$.6H$_2$O and Co(NO$_3$)$_2$.6H$_2$O with K$_2$CO$_3$ at 60 °C and pH = 9.0) was subjected to mechanochemical treatment by grinding in an electric mortar (Mortar Grinder RM 200, Retsch GmbH, Haan, Germany) for 1 min (longer grind did not lead to better CBO performance). Then the mixed oxides were obtained by calcination in air at 400 °C for 2 h. The corresponding quantity of precursors was calculated for preparing 20, 30, and 40 wt.% CeO$_2$ in the mixed Co-Ce oxides. The obtained materials were denoted mentioning the wt.% amount of cobalt and cerium single oxides, namely 80Co-20Ce, 70Co-30Ce, and 60Co-20Ce. Catalyst with the best performing composition, i.e., 70Co-30Ce, was also prepared by grinding an appropriate amount of cerium hydroxide and commercial Co$_3$O$_4$ (Sigma Aldrich, Steinheim, Germany) and then calcining at 400 °C for 2 h. It was named 70Co-30Ce (c). A physical mixture of cerium hydroxide and cobalt hydroxycarbonate precursors was manually prepared, calcined at 400 °C for 2 h and denoted as 70Co-30Ce (ph) to reveal the effect of mechanochemical treatment under controlled conditions.

Pure Co$_3$O$_4$ and CeO$_2$ were obtained after calcination of cerium hydroxide and cobalt hydroxycarbonate in air for 2 h at 400 °C.

3.2. Catalytic Activity Measurements

The catalytic activity in CBO was expressed as benzene conversion degree. It was rated over the temperature range 150–350 °C at atmospheric pressure using a microcatalytic continuous flow fixed bed reactor connected to gas chromatograph Hewlett Packard 5890 series II (Agilent, Germany, working with Agilent G2070 Chemstation Software, Waldbronn, Germany) supplied with flame ionization detector and capillary column HP Plot Q. The measurements were performed using catalyst with bed volume 0.5 cm$^3$ and particle size 0.25–0.50 mm, inlet benzene concentration 42 g m$^{-3}$ in air and space velocity 4000 h$^{-1}$. Preliminary tests with some supposed intermediate products of partial oxidation such as: phenol, maleic anhydride, benzoquinone, hydroxy-1,4-benzoquinone were carried
These compounds were injected as witnesses for detecting their retention time under identical GC conditions. Degree of benzene conversion was calculated by the equation:

$$\text{C}_6\text{H}_6\text{conversion (\%)} = \frac{[\text{C}_6\text{H}_6]_{\text{in}} - [\text{C}_6\text{H}_6]_{\text{out}}}{[\text{C}_6\text{H}_6]_{\text{in}}} \times 100 \quad (1)$$

where $[\text{C}_6\text{H}_6]_{\text{in}}$ and $[\text{C}_6\text{H}_6]_{\text{out}}$ are the benzene concentration at the inlet and outlet, respectively.

Catalyst activation at 200 °C for 1 h was conducted in situ by purified air before the catalytic measurements. Long term stability test over the best performing 70Co-30Ce catalyst at 200 °C (temperature of 100% complete benzene conversion) under the above experimental conditions was carried out within 24 h.

### 3.3. Catalyst Characterization

Specific surface area of the samples was evaluated by analysis of the N₂ adsorption isotherm at the temperature of liquid nitrogen using the Brunauer, Emmett, and Teller (BET) equation. The measurements were performed in a standard pressure range of 0.05–0.3 p/p₀ by means of Quantachrome Instrument NOVA 1200e (Quantachrome Instruments, Boynton Beach, FL, USA). The samples were previously degassed under vacuum at 200 °C for 90 min.

Powder X-ray diffraction (XRD) measurements were carried out on a PANalytical Empyrean apparatus (PANalytical B.V., Almelo, The Netherlands) equipped with a multichannel detector (Pixel 3D, PANalytical B.V., Almelo, The Netherlands) using Cu Kα 45 kV–40 mA radiation in the 2θ range 20–115° with a scan step of 0.01° for 20 s. Particle size of the crystalline phases and lattice parameters were calculated by the powder diffraction analysis software based on the Rietveld method—ReX [73].

Temperature programmed reduction (H₂-TPR) measurements were carried out at previously described apparatus [74] using 10% H₂ in Ar with a flow rate of 24 mL min⁻¹ and temperature increasing with 15 °C min⁻¹. Following the criterion proposed by Monti and Baiker [75], the chosen Co₃O₄ quantity was 0.007 g and the same amount of mixed oxides was loaded. The hydrogen consumption was calculated by calibration of the thermal conductivity detector (using stoichiometric NiO, obtained via oxide calcination at 800 °C for 2 h). The expected HC related to adsorbed oxygen species at temperatures up to 250 °C was not distinguished at these conditions and supplemental TPR measurements in the low-temperature range were undertaken. Chembet TPR/TPD apparatus (Quantachrome, Odelzhausen, Germany) was used at the following conditions: 0.03 g loaded sample, 5% H₂ in Ar with a flow rate of 80 mL min⁻¹, and a heating rate of 10 °C min⁻¹.

UV resonance Raman spectra of the Co-Ce catalysts were measured by means of LABRAM HR800 spectrometer (Horiba France SAS, Palaiseau, France) equipped with a He-Cd laser ($\lambda_L = 325$ nm) from Kimmon Kobe. The laser light was dispersed by a 2400-groove grating while its power was adjusted within 1–5 mW range to avoid sample heating. A microscope objective of 40 × NUV/0.47 focused the laser light on a sample at a spot diameter of ~0.8 µm. Fitting of the baseline corrected spectra was performed by a PeakFit 4.12 software.

X-ray photoelectron spectroscopy (XPS) analyses were carried out using a VG Microtech ESCA 3000 Multilab (VG Scientific, East Grinstead, Sussex, UK) spectrometer equipped with a dual Mg/Al anode following the previously describe procedure [76]. The constant charging of the samples was removed by referencing all the energies to the C 1s binding energy set at 285.1 eV arising from adventitious carbon. Analyses of the peaks were performed with the CasaXPS software. Atomic concentrations were calculated from peak intensity using the sensitivity factors provided by the software. The binding energy (BE) values are quoted with a precision of ±0.15 eV and the atomic percentage with a precision of ±10%.
4. Conclusions

Co$_3$O$_4$–CeO$_2$ mixed oxides (20, 30, and 40 wt.% of ceria) were synthesized by mechanochemical mixing of cerium hydroxide and cobalt hydroxy carbonate precursors. Significantly higher activity of all mixed oxides as compared to mono-component Co$_3$O$_4$ in complete benzene oxidation as a model reaction for VOCs total oxidation was established. One hundred percent benzene conversion was achieved at relatively low temperatures (200–250 °C). In particular, 100% complete oxidation over the best performing 70 wt.% Co$_3$O$_4$–30 wt.% CeO$_2$ sample was reached at 200 °C. A trend of the highest surface amount of Co$^{3+}$, Ce$^{3+}$, and adsorbed oxygen species was evidenced for the catalyst with this optimal composition. Much lower catalytic activity of a sample with the same composition but prepared by manual precursors' mixing confirmed the crucial role of mechanochemically initiated interaction leading to strained Co$_3$O$_4$ and CeO$_2$ surface structures. The results are promising in case of practical applications for VOCs abatement because of (i) the cost efficiency when using highly active but cheaper noble metal-free oxide catalysts prepared by a simple, less polluting, less energy demanding, and less hazardous mechanochemical method, and (ii) the possibility to realize an energy-saving catalytic process at relatively low temperatures for complete hydrocarbons oxidation without harmful byproducts.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11111316/s1, Figure S1: Comparison of benzene conversion over 70Co-30Ce (this work) and Au-based catalysts on ceria modified by MeOx (Me = Fe, Mn, Co and Sn, prepared by coprecipitation (CP) and mechanochemical mixing (MM); Figure S2: Comparison of benzene conversion over 70Co-30Ce (this work) and noble metal (Au, Pd)-based catalysts on alumina-supported Y-doped ceria, prepared by impregnation (IM) and mechanochemical mixing (MM); Figure S3: UV–Raman spectra of Co$_3$O$_4$ after TPR (grey line) and of 70Co-30Ce catalyst after TPR and TPO experiments. (PL stands for full power laser of about 5 mW at sample).

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