An Insight into Geometries and Catalytic Applications of CeO$_2$ from a DFT Outlook

Hussein A. Miran $^{1,*}$, Zainab N. Jaf $^1$, Mohammednoor Altarawneh $^{2,*}$ and Zhong-Tao Jiang $^3$

Abstract: Rare earth metal oxides (REMOs) have gained considerable attention in recent years owing to their distinctive properties and potential applications in electronic devices and catalysts. Particularly, cerium dioxide (CeO$_2$), also known as ceria, has emerged as an interesting material in a wide variety of industrial, technological, and medical applications. Ceria can be synthesized with various morphologies, including rods, cubes, wires, tubes, and spheres. This comprehensive review offers valuable perceptions into the crystal structure, fundamental properties, and reaction mechanisms that govern the well-established surface-assisted reactions over ceria. The activity, selectivity, and stability of ceria, either as a stand-alone catalyst or as supports for other metals, are frequently ascribed to its strong interactions with the adsorbates and its facile redox cycle. Doping of ceria with transition metals is a common strategy to modify the characteristics and to fine-tune its reactive properties. DFT-derived chemical mechanisms are surveyed and presented in light of pertinent experimental findings. Finally, the effect of surface termination on catalysis by ceria is also highlighted.

Keywords: cerium oxide (CeO$_2$); fluorite structure; catalytic applications; density functional theory (DFT); oxygen vacancies; surface stability

1. Introduction

Rare earth (RE) elements have gained considerable interest due to the distinguished electronic configuration triggered by their 4$f$ electrons. They differ from other elements in that their valence electrons can occupy more than one shell, offering them several possible oxidation states. This is clearly displayed in acquiring different electronic characteristics, spanning insulating, conducting, and superconducting behaviors [1,2]. It has been reported that oxides of rare earth elements, including Sc and Y along with lanthanoids, find a variety of applications most notably in automobile, electronic industries, catalysis, catalyst support, lighting, and biomedicine [3,4]. Along the same line of inquiry, the valence of cerium displays a significant influence on the structure of cerium dioxides in that tetravalent Ce comprises cerium dioxide (CeO$_2$) that exhibits a cubic fluorite lattice (Fm$ar{3}$m space group) and the oxygen anions occupy the eight tetrahedral 8c sites, whereas trivalent cerium displays the sesquioxide Ce$_2$O$_3$. The latter displays a hexagonal lattice (P$\bar{6}$m1 space group). The contribution of valence electrons to the chemical bond in CeO$_2$ suggests that the Ce 4$f$ electrons participate directly in chemical bond formation in CeO$_2$ [5]. In addition, owing to paired and unpaired electrons in CeO$_2$ orbitals, CeO$_2$ shows exceptional magnetic behavior involving paramagnetism, ferromagnetism, and diamagnetism [6]. Moreover, nanostructured cerium oxide films reveal exceptional corrosion resistance performance and durability of the superhydrophobic surface [7]. It is also revealed that the oxides of...
rare earth metals, mainly Ce, La, and Y, could enhance the high-temperature oxidation resistance of various metal alloys up to 1000 °C [8].

2. Crystals Structure and Electronic Properties of Stoichiometric and Nonstoichiometric CeO₂

A great number of studies have been devoted to studying the crystal structure and geometries of RE oxides. Depending on the operational temperature and pressure, Ln₂O₃ species can adopt three distinct phases at temperatures below 2000 °C. The light rare earth element Ln₂O₃ oxides (A-type, space group of P3m1, no.164) (164 refers to Patterson space group) feature a hexagonal structure as depicted in Table 1. The heavy RE element Ln₂O₃ oxides (C-type, space group of Ia3, No. 206) are known to adopt cubic structures, whilst the remaining rare earth elements oxides generally crystallize in either C-type structure or B-type structure (monoclinic crystallography) [9]. All RE elements oxidize readily but to varying extents of oxidation. In the presence of air, for instance, cerium (Ce) oxidizes to ceria (CeO₂), which possesses a fluorite structure as presented in Figure 1. On the other hand, praseodymium (Pr) occurs naturally as Pr₃O₁₁, whilst terbium (Tb) is found as Tb₂O₇. Both oxides transform into PrO₂ and TbO₂ under oxygen pressure. These three dioxides are crystallized as cubic fluorite face-centered structures. However, the rest of the lanthanide oxides are found in nature in the form of sesquioxides (Ln₂O₃) [10]. It is worth mentioning that most of the rare earth oxides are thermally stable and expected to be highly active against H₂O and CO₂. The most common oxidation state they have is that of a trivalent state, but they can also switch to either a divalent or a tetravalent oxidation state [11].

![Figure 1. Unit cells of Ln₂O₃: (a) A-type (hexagonal), (b) B-type (monoclinic), and (c) C-type (cubic).](image)

The geometric, electronic, and mechanical properties of rare earth sesquioxides and the phase transition pressure from cubic (C-type) to hexagonal (A-type) have been extensively investigated by means of first-principle calculations predominantly based on the density functional theory (DFT) approach. Richard et al. [12] calculated and validated their theoretical findings on structural and mechanical properties along with the pressure at which phase transition from cubic to hexagonal occurs against corresponding experimental values. Besides, a computational study has shed light on structural, electronic, and thermal properties of bulk and surface terbium dioxide (TbO₂) as a material that offers wide spectra of catalytic and optical applications. The calculated lattice parameter of 5.36 Å matches well with the analogous experimental value of 5.22 Å. The density of states (DOS) of the bulk structure displays a semiconducting character [13].

Promising agreement was obtained between the theoretical and empirical studies for the investigated properties. The reported findings indicated that the inclusion of Hubbard parameter U in the methodology resulted in a noticeable correction to the structural
properties. The theoretically calculated bulk moduli B, its pressure derivative B', and the phase transition pressures are compared with some experimental results and depicted in Table 1. The influence of including Hubbard parameter DFT+U on assessing the structural, electronic, and thermomechanical properties of cubic (C-type) lanthanide sesquioxides (Ln$_2$O$_3$) has been reported [14]. Figure 2b portrays the total and partial density of states with conduction and valence bands clearly shown. Besides, the plot displays that the experimental value of the band gap is obtained at $U_{\text{eff}}$ of 6.5 eV. Regarding the negative values in Table 1, they indicate that the C-type phase is the preferred (most stable) phase.

![Figure 2](image.png)

**Figure 2.** (a) Cubic fluorite structure of the lanthanide dioxide. (b) The theoretically predicted total and partial density of states for Ce$_2$O$_3$ sesquioxides [14].

| Compound | Functional | C-Phase | A-Phase |
|----------|------------|---------|---------|
|          |            | $B$ (GPa) | $B'$ (GPa) | $P_{C\rightarrow A}$ (GPa) |
| La$_2$O$_3$ | LDA | 155.2 | 4.34 | 133.9 | 4.15 | 0.0 |
|            | GGA + U    | 142.8 | 4.39 | 124.4 | 4.18 |   |
|            | Exp. [15]  | 113  | 6.0  | 135.5 | 4.00 |   |
| Ce$_2$O$_3$ | LDA        | 166.8 | 4.45 | 148.5 | 5.62 | 0.0 |
|            | GGA + U    | 142.0 | 4.29 | 155.4 | 4.00 |   |
| Pr$_2$O$_3$ | LDA        | 170.6 | 4.38 | 148.2 | 4.46 | 0.0 |
|            | GGA + U    | 152.3 | 4.00 | 157.9 | 4.00 |   |
| Nd$_2$O$_3$ | LDA        | 173.5 | 4.43 | 150.5 | 4.38 | 0.0 |
|            | GGA + U    | 155.1 | 3.62 | 122.0 | 4.54 |   |
| Pm$_2$O$_3$ | LDA        | 176.2 | 4.50 | 153.8 | 4.50 | 0.0 |
|            | GGA + U    | 156.1 | 4.01 | 129.0 | 4.00 |   |
| Sm$_2$O$_3$ | LDA        | 177.4 | 4.42 | 153.4 | 4.22 | 0.0 |
|            | GGA + U    | 147.0 | 4.49 | 138.3 | 4.29 |   |
|            | Exp. [15]  | 130  | 6.9  | 116   | 4.00 |   |
| Eu$_2$O$_3$ | LDA        | 177.7 | 4.39 | 156.1 | 4.33 | 0.0 |
|            | GGA + U    | 134.3 | 4.00 | 143.1 | 4.17 |   |
|            | Exp. [15]  | 134.0 | 4.1  | 115   | 5.9  |   |
| Gd$_2$O$_3$ | LDA        | 178.1 | 4.32 | 158.3 | 4.42 | 0.0 |
|            | GGA + U    | 160.7 | 4.39 | 144.7 | 4.24 |   |
|            | Exp. [15]  | 145.0 | 4.2  | 125.0 | 4.7  |   |
| Tb$_2$O$_3$ | LDA        | 179.5 | 4.22 | 158.6 | 4.31 | 0.0 |
|            | GGA + U    | 159.9 | 4.53 | 139.0 | 4.67 |   |
|            | Exp. [15]  | 159.9 | 4.37 | 139.0 | 4.67 |   |
| Dy$_2$O$_3$ | LDA        | 180.9 | 4.24 | 159.9 | 4.37 | 1.5 |
|            | GGA + U    | 160.4 | 4.64 | 148.9 | 5.14 |   |

Table 1. Bulk modulus B, its pressure derivative B', and the phase transition pressure for the complete series of Ln$_2$O$_3$. Reproduced from [12].
The oxidation of cerium metal is known to result in the formation of many different phases of cerium oxide ranging from CeO$_2$ (IV) to Ce$_2$O$_3$ (III). The oxidation processes of these two extreme oxidations are exothermic by $-1796$ and $-1089$ kJ mol$^{-1}$, respectively, at a temperature of 298 K [17]. Between these two phases, partially oxidized phases (CeO$_{2-y}$) prevail depending on the temperature and oxygen pressure. Ceria exhibits a fluorite structure crystallized as a centered cubic face (fcc) with the space group of Fm-3m ($a = 0.541134$ nm, JCPDS 34–394), comprising a cubic close-packed combination of metal atoms with tetrahedral holes filled by oxygen atoms. Reduced CeO$_{2-y}$ forms by releasing oxygen atoms from the cluster, leaving oxygen vacancies behind. The Kröger–Vink notation governs the process of creation of vacancies as follows [17]:

$$2\text{Ce} + \text{O}_2 \rightarrow \text{V}_\text{O} + 2\text{Ce}^{+} + \frac{1}{2}\text{O}_2$$  \hspace{1cm} (1)

where Ce and O denote cerium and oxygen atoms, respectively, and V$_O$ signifies oxygen vacancy. On the basis of the notation above, the exact nature of the resultant phase relies on the amount of oxygen released from CeO$_2$. X-ray diffraction (XRD) was employed to determine the structural parameters of reduced CeO$_{2-y}$ oxides, but this technique exhibits some limitations due to the low scattering power of oxygen. As Table 2 portrays, at temperatures over 685 °C and low oxygen pressure, CeO$_2$ exhibits several forms of nonstoichiometric oxidation states (CeO$_{2-y}$).

### Table 1. Continued.

| Compound | Functional | A-Phase | C-Phase | $P_{C\rightarrow A}$ (GPa) |
|----------|------------|---------|---------|---------------------------|
| Ho$_2$O$_3$ | LDA | 180.9 | 4.63 | 161.6 | 4.50 | 3.4 |
| | GGA + U | 179.1 | 3.71 | 152.0 | 4.48 |
| | Exp. [16] | 204 | 3.8 | 161.6 | 4.48 |
| Er$_2$O$_3$ | LDA | 180.4 | 4.64 | 161.2 | 4.46 | 5.7 |
| | GGA + U | 173.6 | 4.51 | 157.2 | 3.98 |
| Tm$_2$O$_3$ | LDA | 178.5 | 4.56 | 161.6 | 4.52 | 7.0 |
| | GGA + U | 168.4 | 4.65 | 157.7 | 4.36 |
| Yb$_2$O$_3$ | LDA | 177.8 | 4.61 | 161.6 | 4.52 | 7.5 |
| | GGA + U | 178.7 | 4.33 | 160.9 | 4.27 |
| Lu$_2$O$_3$ | LDA | 198.8 | 4.33 | 179.4 | 4.30 | 7.7 |
| | GGA + U | 179.9 | 4.29 | 163.0 | 4.29 |

### Table 2. Structural changes of stoichiometric and nonstoichiometric CeO$_2$ with temperature.

| Material | Oxidation Extent, $y$ | Temperature (°C) | Thermal Treatment | Structural Phase |
|----------|----------------------|------------------|------------------|-----------------|
| CeO$_{2-y}$ | 0 | <685 | – | Fluorite structure (fcc) |
| CeO$_{2-y}$ | 0 < $y$ < 0.286 | >685 | – | $\alpha$ phase (disordered fluorite structure) |
| CeO$_{2-y}$ | 0.166 | >685 | Thermally treated | $\beta$ phase (ordered fluorite, monoclinic structure) |
| CeO$_{2-y}$ | 0.181 | >685 | Thermally treated | $\delta$ phase (triclinic structure) |
| CeO$_{2-y}$ | 0.285 | >685 | Thermally treated | Rhombohedral structure |
| CeO$_{2-y}$ | >0.286 | >685 | – | $\sigma$ phase (C-type Ce$_2$O$_3$, fcc) |

With $y$ ranging from 0 to 0.286, a disordered structure of a fluorite-related system termed the $\alpha$ phase develops [18]. All phases in this oxidation range adopt a fluorite-type structure but with an ordered arrangement. Formed phases include [19–22] Ce$_6$O$_{11}$ (the
β phase, monoclinic) [22], Ce$_{11}$O$_{20}$ (the δ phase, triclinic) [23], and Ce$_7$O$_{12}$ (rhombohedral) [23]. When y increases to exceed 0.286, a new phase termed the σ phase emerges. The σ phase exists as a body-centered cubic (bcc) structure. The C-type sesquioxide Ce$_2$O$_3$ formed in the bixbyite structure (space group Ia-3) is the compositional final member of the σ phase which is related to the fcc structure of CeO$_2$. The lattice parameters of the C-type Ce$_2$O$_3$ are nearly twice those of CeO$_2$. This is attributed to the two cation groups being nearly identical, with oxygen anions residing in all tetrahedral sites in the fcc structure, whereas only three-quarters exist in the bcc structure in an ideally ordered array. Due to the high reactivity of the cubic sesquioxide structure (C-type Ce$_2$O$_3$) [24] with atmospheric oxygen, the final crystal structure, called the θ phase, is formed. This phase is well known as the A-type Ce$_2$O$_3$ which is crystallized in a hexagonal structure form, belonging to the P32/m space group (a = 0.389 nm, c = 0.607 nm; JCPDS 23-1048) [25].

3. Recent Computational Modeling Based Literature

It is worth mentioning that from an atomistic point of view, numerous density functional theory (DFT)-based studies with various functionals such as the HSE06 (Heyd–Scuseria–Ernzerhof hybrid functional) and the DFT+U approach (U corresponds to Hubbard parameter describing the on-site Coulomb interactions) have been reported. In reference to corresponding experimental studies, DFT investigations accurately predict chemical bonding, vacancy-defect formation, band structures, surface character, thermomechanical properties, and doping effect. The defective nature of CeO$_2$ (111) has been demonstrated under the framework of DFT with several functionals. It is generally suggested that two excess electrons are localized on the next-nearest neighbors, not on the nearest neighbors [26]. A combination study employing scanning tunneling microscopy (STM) and DFT calculations has been carried out to identify the synergy between an oxygen vacancy and the associated Ce$^{3+}$ ion pair in a defective CeO$_2$ (111) plane. The two Ce$^{3+}$ ions can occupy different cationic shells around the vacancy. Both reported results reveal that at least one excess electron localizes in a Ce ion that is not next to the O vacancy [27].

Moving toward the thermodynamic aspect, Fronzi et al. [28] employed an ab initio atomistic thermodynamics approach to assess relative thermodynamic stability and Wulff constructions of the three low-index surfaces of CeO$_2$, namely (100), (110), and (111). Among the studied surfaces, the stoichiometric (111) surface under “oxygen-rich” conditions is predicted to be the most stable surface. Under reducing conditions, the stoichiometric (111) face with subsurface oxygen vacancies becomes the most thermodynamically stable facet. However, near the O-lean region, the (111) Ce-terminated surface becomes the most stable surface. A combination of DFT results and Monte Carlo simulations was achieved to investigate the dopant dispersion and its impact on the oxygen ion conductivity of ceria alloyed with rare earth oxides [29]. The consensus in the literature suggests that an accurate description of the electronic system of CeO$_2$ requires the inclusion of the U term in the DFT calculations. Pure DFT methods incorrectly describe ceria as a conducting material. DFT-based investigation revealed that in the near-surface region of CeO$_2$ (111), at low temperatures and vacancy concentrations, subsurface oxygen vacancies showed more stability than surface ones [30].

4. The Role of Dopants Introducing on CeO$_2$ Properties

It has been reported that the addition of various dopants into the crystallite structure of ceria would enrich thermal and chemical stability and lead to strong ultraviolet (UV) absorption of the crystal. Thus, when introducing an element with an oxidation number lower than that of cerium, oxygen is removed, forming oxygen vacant sites in the ceria structure. This suggests that the defect chemistry of ceria lattice and structural changes can be produced by doping. Defect structures and changes in the lattice as a function of dopant concentration in doped CeO$_2$ have been probed using extended X-ray absorption fine structure (XAFS) and X-ray absorption near-edge structure (XANES) spectroscopies [31]. XAFS data for doped ceria for various dopants at several concentrations (Ce$_{1-x}$ Ln$_x$O$_{2-x/2}$
(Ln refers to Sc, Y, Nd, Sm, Gd, Yb, x = 0–0.30)) show that interatomic distance decreases with increasing Ln concentration, suggesting that the oxygen ions are relaxed toward oxygen vacancies around Ce, Y, and Gd. The decrease in the Ln–O interatomic distances can be explained by the formation of the defect correlated with two Ln\(^{3+}\) ions and one oxygen vacancy and/or four Ln\(^{3+}\) ions and two oxygen vacancies. Figure 3 depicts the reduction in interatomic distances with increasing dopant fraction which is associated with increasing disorder. This signifies that the oxygen ions are accumulated near oxygen vacant sites nearby Ce, Y, and Gd. The reduction trend of the Sc–O interatomic distances is almost constant with increasing concentration due to the existence of two phases of fluorite (CeO\(_{1−x}\)Sc\(_x\)O\(_{2−x/2}\)) and Sc\(_2\)O\(_3\) structures. In the same manner, when introducing dopants larger than \(\sim 102\) pm, such as Gd\(^{3+}\) and Sm\(^{3+}\), the average lattice parameter in the fluorite phase as obtained using X-ray diffraction technique increases with increasing doping concentration [32].

![Graph depicting the Trends of the Ce–O interatomic distances in ceria doped with Sc, Y, Yb, Gd, Sm, and Nd as a function of dopant concentration x][31].

Previous works on CeO\(_2\) and CeO\(_2\)-based materials concluded that dopant introduction induces lattice distortion that in turn leads to positional disorder and atomic displacement of constituent atoms. Furthermore, introducing elements with less than 4\(^+\) valence electrons, such as Ca\(^{2+}\), Nd\(^{3+}\), and Pb\(^{2+}\), would promote structural defects (i.e., oxygen vacancies) in the ceria lattice, which in turn impact the redox activity of these materials [33]. Another study reported that introducing trivalent lanthanide ions in ceria results in distorting the lattice constant and thereafter forming oxygen vacancies by replacing the 4\(^+\) site, which is crucial in catalytic reactions [34]. The luminescence property of CeO\(_2\) has significantly improved by incorporating lanthanide ions in the lattice structure. This has been noticed via variant types of obtained luminescence peaks, linked with oxygen vacancies and dopant types causing symmetry distortion [35]. Practically, this distortion in the structures can be determined by Raman spectroscopy via testing the factors influencing the line shape, width, and position of the Raman peaks of doped and pure ceria. Furthermore,
literature has nominated Y$_{3+}$-doped CeO$_2$ as an efficient system in converting wavelengths of photons near the UV to IR range [36]. Moreover, RE elements, such as La, Ce, and Y or their oxides, would enrich the high-temperature oxidation resistance of alumina and chromia alloys via an enhancement of their reactive-element effect (REE) [37,38]. Thanneeru et al. [39] coated AISI 304 stainless steel (SS) with nanocrystalline ceria and La$_{3+}$-doped nanocrystalline ceria particles with the aim of studying their high-temperature oxidation resistance at 1243 K in dry air for 24 h. Results were then compared to those of similar coatings in the absence of microceria coatings. The nanocrystalline ceria coatings were observed to enhance the oxidation resistance character by 90% compared to those cases of uncoated and microceria-coated steels. Likewise, Fernandes and Ramanathan [40] reported the effect of surface coatings of Ce, La, Pr, and Y oxide gels on the oxidation behavior of a Fe-20Cr alloy at 1000 °C. Alloying small quantities of rare earth elements to chromia or alumina enhances their high-temperature oxidation resistance. Usually, rare earth elements are added or doped with oxides to form a protective layer for chromia and alumina alloys. In addition, it is important to mention that the morphology of RE oxide coatings varies with the nature of the RE. For instance, the oxidation rate of RE oxide coated Fe-20Cr was considerably less than that of the uncoated alloy. The influence of Mn and Fe doping into the CeO$_2$ (111) surface on the simultaneous removal of mercury (Hg) and H$_2$S was examined under the framework of DFT. In this study, the adsorptions of Hg-containing species on perfect CeO$_2$ (111), Mn/CeO$_2$ (111), and Fe/CeO$_2$ (111) surfaces were investigated. The results showed that Mn and Fe dopants expedited Hg adsorption [41]. Besides, in this work, the redox activity of a low praseodymium (Pr)-doped CeO$_2$ (111) surface was examined via DFT. Findings reveal that Pr doping stimulates oxygen donation by dropping the required energy to produce surface anionic vacancies [42].

5. Solid Solutions and the Influence of Reduction Energies of Ceria

It is well known that the fluorite structure of CeO$_2$ has the capability of forming solid solution systems with a wide array of oxides. The lattice dimensions of the solid solution typically obey Vegard’s rule, i.e., a linear relation between lattice constant and solute concentration. It must be emphasized that the term “dopant” should be utilized for cases involving the introduction of a foreign cation in the ceria lattice, as opposed to situations in which two oxides are mixed [17]. Kim [43] reported an empirical equation clarifying the relationship between the lattice parameters of the solid solution, along with the ionic radius and the cation charge of the dopant introduced into the CeO$_2$ and fluorite-like oxide structures. The relation is expressed as follows:

$$a = 0.5413 + \sum_k \left(0.0220\Delta r_k + 0.00015\Delta z_k\right)m_k$$

where $a$ (in nm) signifies the unit cell constant of the solid solution containing CeO$_2$, $\Delta r_k = r_k - r_{Ce} (IV)$ in nm corresponds to the variance between the $k$th dopant and Ce (IV) ionic radii, $\Delta z = z_k - z_{Ce} (IV)$ in nm denotes the charge variance of the $k$th dopant and Ce (IV), and $m_k$ signifies the molar focus of the $k$th dopant. Kim [44] indicated that the solubility of either oxide material into the fluorite crystallographic structure of CeO$_2$ relies on the elastic energy per ion present into the unit cell due to the variance in ionic radius. Therefore, a greater magnitude of $\Delta r_k$ drives a higher elastic energy and a lower solubility limit. The most soluble cations possess a radius that corresponds to the matching radius, $r_m$, the one that results in Vegard’s slope being equal to 0. According to Kim’s equation, $r_m$ must have a value of 0.097 nm for tetravalent dopant cations, 0.1038 nm for trivalent dopants, and 0.1106 nm for divalent dopants. Similar amounts were reported in previous works [44,45]. Below, Figure 4 displays the measured and computed lattice parameters of fluorite-structure CeO$_2$ solid solutions formed with different rare earth oxides. CeO$_2$-ZrO$_2$ mixed oxides have received significant attention in literature because of their wide deployment in the so-called three-way catalysts (TWCs). As such, the structural
properties of CeO$_2$-based solid solutions have been thoroughly investigated. The difference between the ionic radius of Zr$^{4+}$ (0.084 nm for a 8-fold coordination) and [46] that of Ce$^{4+}$ (0.097 nm) is only 15%. In addition, metal oxide solid solutions, e.g., CeO$_2$-ZrO$_2$, have received significant attention in literature because of their wide deployment in the so-called three-way catalysts (TWCs).

![Graph showing lattice parameters of fluorite-structure CeO$_2$ solid solution](image)

**Figure 4.** Experimental and calculated lattice parameters of fluorite-structure CeO$_2$ solid solution containing variant rare earth sesquioxides [43].

Yashima and his colleagues [47] conducted studies on the CeO$_2$-ZrO$_2$ solid solution annealed in a Na$_2$B$_2$O$_7$-NaF atmosphere. They studied the properties of the system below 1000 °C using XRD analysis, displaying the entire equilibrium phase diagram of the CeO$_2$-ZrO$_2$ solid solution. Analysis of their phase diagram reveals three crystalline structures depending on the temperature [47], namely cubic phase with high CeO$_2$ percentage and tetragonal or monoclinic phases with high ZrO$_2$ percentage. The balanced compositions of the tetragonal, monoclinic, and cubic phases occur at $x = 0.112$, 0.009, and 0.84 in Ce$_x$Zr$_{1-x}$O, respectively, at a temperature of 1055 °C [47], as depicted in Figure 5.

![Phase diagram of CeO$_2$-ZrO$_2$ system](image)

**Figure 5.** Phase diagram study of CeO$_2$-ZrO$_2$ system with different CeO$_2$ concentrations as a function of temperature. $t$, $t'$, and $t''$ demonstrate the three forms of the tetragonal phases, $m$ refers to the cubic phase, and $m$ denotes the monoclinic phase [48].
Detailed interpretation of the phase diagram is that a monoclinic crystalline phase belonging to the $P2_1/c$ space group is obtained for $\text{ZrO}_2$ and $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ system at $x$ values lower than 0.12. With the increase in $\text{CeO}_2$ concentration in the system, the $a_m$ (m refers monoclinic) value approaches that of $b_m$ and the angle $\beta_m$ lessens, indicating a distortion of the monoclinic phase, and all approach those of the tetragonal structure [49,50]. It must be noted that the phase boundary of $x = 0.12$ is substantially affected by some parameters such as the preparation of the sample and the grain size. These two parameters in turn affect the nucleation, growth, and kinetics of the transformation [50]. The three tetragonal phases denoted as $t$, $t'$, and $t''$ [51,52] are crystallized when the oxygen content becomes higher than 0.12, and at a monoclinic phase, the O content would be so low as 0.12. The $t$ phase is stable at elevated temperature and for lower $\text{CeO}_2$ concentrations. As the $\text{CeO}_2$ content increases, the other two metastable phases of $t'$ and $t''$ are formed. For the $t$ and $t'$ forms, the $c/a$ ratio is slightly higher than 1, whereas the ratio of the $t''$ phase belonging to the $P4_2/nmc$ space group equals 1.

According to the vacancy formation energy in a $\text{CeO}_2$ cluster calculated via DFT, for systems with dopant amounts of 3 mol%, tetravalent dopants such as $\text{Ti}$, $\text{Zr}$, and $\text{Hf}$ (IVb in the periodic table) can be inserted into the bulk of $\text{CeO}_2$. On the contrary, other elements such as $\text{C}$, $\text{Si}$, $\text{Ge}$, $\text{Sn}$, and $\text{Pb}$ (IVb in the periodic table) are segregated on the surface [53]. It is found that the vacancy creation energy of 4.035 eV per vacancy calculated by LDA functional and 3.097 eV per vacancy obtained by PBE functional are reduced with increasing dopant size, reaching the best size that matches the Ce$^{4+}$ ions.

$\text{CeO}_2$-$\text{HfO}_2$ samples have been the subject of extensive structural investigations. Findings obtained from these studies revealed similar structures to those observed for the $\text{CeO}_2$-$\text{ZrO}_2$ system. On the basis of XRD studies [54] for samples annealed at 1400 °C for 48 h and cooled down slowly, stable $\text{Ce}_x\text{Hf}_{1-x}\text{O}_2$ solid solutions with $x > 0.85$ ($\text{CeO}_2$-rich materials) are crystalized with cubic fluorite structure. Meanwhile, when $x < 0.15$ ($\text{HfO}_2$-rich materials), solid solutions are formed with monoclinic structure. The samples characterized by a combination of XRD and Raman analysis adopted the metastable tetragonal phases ($t'$ as well as $t''$) [55].

6. Influence of the Reduction Energies of $\text{CeO}_2$

It is important to investigate the redox properties of a catalyst by calculating its reduction/oxidation energy. This in turn helps to predict the capability of that material in performing catalytic oxidation reactions. This investigation is carried out by calculating the vacancy formation energy $E_{\text{vac}}$ needed to remove oxygen from the system for oxidation and hence create a vacancy. An improvement by lowering the reduction energies of oxides is achieved via replacing the cations of the catalyst with others [56–58]. DFT investigations undertaken by Hu and Metiu [57] studied the influence of the addition of various cations to $\text{CeO}_2$ catalyst on its reduction energy. In this study, the authors surveyed the effect of adding some dopants such as $\text{Pt}$, $\text{Ru}$, $\text{Zr}$, $\text{Ta}$, $\text{Mo}$, and $\text{W}$ dopants in $\text{CeO}_2$ (111) on the neighboring oxygen or distant ones. For the neighboring oxygen atoms, the calculated energies of oxygen vacancy creation caused by the added cations (added dopants) were found to be almost identical. By contrast, an effect of these dopants on the reduction energy of the distant oxygen has not been recorded. Figure 6 displays the removal of oxygen atoms from different positions in the $\text{CeO}_2$ (111) slab as a result of introducing dopants.

In another instance, first-principle calculations reported by Yang et al. [59] surveyed the impact of introducing $\text{Zr}$ into a $\text{CeO}_2$ system on the redox properties of $\text{CeO}_2$. They reported that the reduction energy needed to remove a neighboring oxygen atom was reduced by 0.6 eV in reference to undoped $\text{CeO}_2$. In a separate work, Yang and his collaborators [60] evaluated the vacancy formation energy of $\text{Pd}$-alloyed $\text{CeO}_2$. They concluded that introducing $\text{Pd}$ atoms into the ceria system lowered the vacancy formation energy from 3.0 to 0.6 eV. To acquire an accurate understanding of the role of trivalent and tetravalent cations such as $\text{Zr}^{4+}$, $\text{La}^{3+}$, and $\text{Eu}^{3+}$ incorporated into the ceria lattice, Vinodkumar et al. [61] used DFT calculations to reveal that alloyed ceria materials exhibit
a better efficiency than unalloyed ceria for soot oxidation and this is attributed to an enhancement in the oxygen defects, specific surface area, and redox properties. Under the exposure of air under tight contact conditions, trivalent-alloyed CeO₂ was proven to be more efficient than tetravalent-alloyed ceria for soot combustion. Finally, Eu³⁺-doped CeO₂ has been demonstrated to be catalytically more active than La³⁺-doped CeO₂, and this was ascribed to higher surface area and an increase in oxygen vacancies. Kim et al. [62] assessed the thermodynamic characteristics of Ce₁₋ₓ Zrₓ O₂₋ₙ solid solutions.

Figure 6. Side and top views of CeO₂ (111) slab, doped with a dopant. (a) Removal of neighboring oxygen in the doped slab. (b) Removal of furthest oxygen in the doped slab [57].

7. Ceria Surface Reactions with Inorganic Molecules

7.1. Interaction of H₂, O₂, and H₂O with Ceria

Hydrogen molecules (H₂) have been reported in many studies as a reducing agent for CeO₂ powders at high temperature and at atmospheric pressure [63,64]. Results obtained by experimental work revealed that H₂ cannot adsorb or react with CeO₂ surfaces under ultrahigh vacuum (UHV) conditions [65–68]. Furthermore, DFT-based investigations provided potential energy surfaces for the dissociative uptake of hydrogen molecules over CeO₂ (111) and CeO₂ (110) surfaces via exothermic reactions [69,70]. It has been proven that at low exposure of nonreduced CeO₂ (111) to D atoms at 115 K, surface OD is formed. As a consequence of this reaction, Ce⁴⁺ states are reduced to Ce³⁺ states. A comprehensive review on the basis of XPS analysis revealed that at greater coverage (>50 L), water is detected in a high-resolution XPS examination of O 1 s photoelectron, suggesting that D(g) (g meaning gas) adsorbed on the surface reacts with OD to produce chemisorbed D₂O. The surface OD group reacts with D on the surface to form D₂O(g) between 200 and 600 K. It is demonstrated that the chemisorbed D₂O(g) molecules are desorbed at temperature close 200 K, whereas D₂ desorbs between 400 and 500 K [65]. Exposing reduced CeO₂₋ₙ (111) to D(g) formed OD on the surface, but the trend of producing D₂O at higher exposure lessens with further reduction of the surface. It has been observed that the stability of the OD formed on reduced CeO₂₋ₙ (111) is greater than that of pristine CeO₂ (111). For the different CeO₂₋ₙ (111) configurations, water and D₂ were found to desorb at 570 K. From a theoretical standpoint, DFT studies on the adsorption of H₂(g) on CeO₂ surfaces have reported that dissociative uptake of H₂(g) O sites in CeO₂ (111) and CeO₂ (110) surfaces result in the partial reduction of neighboring Ce cations [71]. Another theoretical approach of ultra-accelerated quantum chemical molecular dynamic simulations demonstrated a mechanism for the release of water molecules following adsorption of H₂ molecules [72].
The high oxygen storage of ceria renders it a favorable material for wide deployment in the TWC technology in vehicles.

As stated earlier, CeO$_2$ acts as an oxidizing agent in fuel-rich/oxygen-deficient periods and as a reducing agent in the oxygen-rich periods. Consequently, it is crucial to understand the physisorption and chemisorption reactions of O$_2$ occurring on CeO$_2$ surfaces. It has been reported that the oxidation of Ce metal occurs at a temperature of 300 K, leading to a form of CeO$_2$ covered by a layer of CeO$_2$ [73]. When the polycrystalline structure was heated to 600 K, XPS examinations of the Ce 3d and Ce 4d photoelectrons peak showed complete reduction to Ce$_2$O$_3$. In contrast, reducing a CeO$_2$ (100) surface by Ar$^+$ ion sputtering at 300 K displayed partial reoxidation as it is annealed to 600 K in vacuum [66]. These two findings indicate that O is redistributed between the surface and the bulk below 600 K. Along the same line of inquiry, DFT calculations were used to determine reaction routes for the interaction of O$_2$ with stoichiometric and reduced ceria surfaces. Dissociative adsorption of oxygen molecules over the CeO$_2$ (111) surface is predicted to be endothermic with values residing on the range of 0.91–0.98 eV [74]. In another DFT+U study, reactions of O$_2$ with the partially reduced CeO$_2$−y (111) surface promote superoxo species bonded weakly to its surface O-vacancy (−0.30 to −0.38 eV) and peroxo species that are more strongly bonded (−2.80 to −3.25 eV) [75]. In another related study on the partially deficient CeO$_2$−y (110) and CeO$_2$−y (100) surfaces, bonding of the peroxo species was found to involve an adsorption energy of −2.0 eV [76]. Experimental work on the adsorption of H$_2$O on CeO$_2$ (111) and CeO$_2$ (100) demonstrated that H$_2$O can be physisorbed, chemisorbed, or both depending on the applied temperature [77–79]. This is consistent with analogous computational results for CeO$_2$ (111). For instance, Fronzi et al. [80] and Marrocchelli and Yildiz [81] concluded in separate studies that H$_2$O preferentially adopts several physisorbed states on CeO$_2$ (111), whereas Watkins et al. [70] illustrated that water fragmentation into H and OH is a feasible process. Molinari et al. [82] studied the adsorption of water on the most stable surfaces, CeO$_2$ (111), (100), and (110), employing DFT-GGA-U calculations. They reported that H$_2$O molecules readily dissociate on the studied surface and that the most stable surface towards the chemisorbed H$_2$O is the CeO$_2$ (111) surface. They further concluded that the molecular adsorption of water becomes more preferable when the water coverage increases. Fernandez-Torre et al. used different DFT calculations to estimate energy barriers for the steps governing water adsorption where they reported very similar energy barriers for the different steps [83]. As stated earlier, ceria fluctuates between two extreme oxidation states of 4$^+$ and 3$^+$, and the reduction occurs via the releasing of oxygen atoms from CeO$_2$. As such, the creation of oxygen vacancies as a result of CeO$_2$−y (111) surface undergoing a reduction reaction leads to the production of Ce cations with two coordination vacancies and three-fold hollow adsorption sites [84]. Below, Figure 7 illustrates the active sites on the CeO$_2$ (111) surface.

A number of computational-based studies have reported similar conclusions that vacancies created on CeO$_2$−y (111) surface enhance and stabilize the decomposition of H$_2$O. A survey of the literature suggests that the reaction between -OH on CeO$_{1.7}$ (111) leads to the release of H$_2$. It must be noted that H$_2$ desorption following adsorption of water on CeO$_{1.7}$ (111) is contradictory to the desorption from reduced CeO$_{1.7}$ (100) in which the primary desorption route remains recombination to form water with only a trivial amount of H$_2$ formation. The energy of vacancy creation on CeO$_2$ (111) is found to be greater than that on CeO$_2$ (100). Hence, it is expected that the driving force to fill the vacancy is greatest on CeO$_2$−y (111) surfaces.

The decomposition pathways of H$_2$O and H$_2$ on both the pristine and defective ceria (111) surfaces have been assessed by means of DFT+U method [70]. The H$_2$O physisorption reaction is an exothermic process on both configurations (see Figure 8); however, the physisorption of water is more exothermic on the vacancy site. The dissociation of water on the two studied surfaces results in the formation of two hydroxyl groups, one in the initial water physisorbed site and the other on a surface oxygen ion. Furthermore, Watkins and coworkers [70] reported a potent exothermic chemisorption reaction for H$_2$ on the perfect
ceria (111) surface, which is ascribed to the low-lying 4f states, and thereafter great electron affinity of ceria. Another study concluded that the decomposition of water is preferred on the perfect surface of ceria (111) due to the formation of a strong hydrogen bond between the OH⁻ and H⁺ moieties created upon decomposition. It also has been demonstrated that H₂O can strongly bind the CeO₂ (111) surface over O vacant sites [81].

![Figure 7. Active sites on CeO₂ (111) surface: (a) side and top views of perfect CeO₂ (111) surface; (b) side and top views of reduced CeO₂ (111) surface.](image)

**Figure 7.** Active sites on CeO₂ (111) surface: (a) side and top views of perfect CeO₂ (111) surface; (b) side and top views of reduced CeO₂ (111) surface.

**Figure 8.** H₂O and H₂ reactions on the defective and perfect ceria (111) surfaces [70].

### 7.2. Sulfur Dioxide (SO₂)

It is understood that trace concentration of sulfur-based molecules in fossil fuels results in the production of sulfur oxides (SOₓ) in the exhaust. Adsorption of such molecules on ceria has a negative effect on its oxygen storage capacity properties in automotive catalytic convertors. However, the high affinity for SOₓ can, in principle, be exploited by trapping sulfur in the effluent gases. SO₂ adsorption on cerium oxide thin films has been investigated by two studies, and two different conclusions were reached. Through surface measurements on a SO₂-CeO₂ (111)/Ru (0001) system, Overbury et al. [85] concluded...
that SO\textsubscript{2} is adsorbed as sulfite ion SO\textsubscript{3}\textsuperscript{2−} on the stoichiometric surface at temperatures from 100 to 600 K. According to S2p high-resolution XPS spectra, the SO\textsubscript{2} adsorbs via a Lewis acid–base interaction at the basic O\textsuperscript{2−} surface sites. SO\textsubscript{2} molecularly desorbs with main desorption peaks close to 200 and 400 K. There was no evidence to suggest that the oxidation process yield SO\textsubscript{4}\textsuperscript{2−} or the reduction process yields SO\textsubscript{3}\textsuperscript{2−} or S\textsuperscript{2−}, which is in agreement with a previous study [86]. They utilized vibrational spectroscopy to study CeO\textsubscript{2} powders, observing that only SO\textsubscript{3}\textsuperscript{2−} forms after SO\textsubscript{2} is exposed to room temperature [87].

Sulfate formation occurs following exposure at 673 K and is encouraged by simultaneous exposure to O\textsubscript{2}. Contradictory to these studies, Rodriguez et al. [88] observed that SO\textsubscript{2} was adsorbed almost exclusively as SO\textsubscript{3}\textsuperscript{2−} on stoichiometric, polycrystalline CeO\textsubscript{2}/Pt (111). To elucidate the contradiction, a number of additional experiments were performed in which different parameters were assessed. The adsorption of SO\textsubscript{2} on polycrystalline CeO\textsubscript{2} films deposited on Al\textsubscript{2}O\textsubscript{3} utilizing an SO\textsubscript{2} pressure of 2.5 mbar was studied by Smirnov et al. [89]. In their study, they demonstrated SO\textsubscript{3}\textsuperscript{2−} formation at temperature below 473 K and SO\textsubscript{4}\textsuperscript{2−} formation above 573 K. As O\textsubscript{2} gas with an identical pressure was introduced alongside SO\textsubscript{2} exposure, SO\textsubscript{3}\textsuperscript{2−} formation was suppressed at the low temperatures, but SO\textsubscript{4}\textsuperscript{2−} was still apparent at the higher temperatures. Interestingly, the sulfate concentrations were enhanced by the introduction of O\textsubscript{2} at higher temperatures. Likewise, Ferrizz and his coworkers used polycrystalline ceria films deposited on Ta foil by spray pyrolysis to carry out TPD measurement. In their XPS examinations, they utilized a different substrate, Mo (100), to deposit CeO\textsubscript{2} in an O\textsubscript{2} atmosphere synthesized by Ce vapor deposition. After SO\textsubscript{2} introduction at 298 K, a major SO\textsubscript{2} desorption peak was evident at 473 K [90], which agreed well with analogous literature findings [85]. However, another SO\textsubscript{2} desorption peak was noted residing in the range of 800–1000 K, which was not observed in their results [85]. As SO\textsubscript{2} exposure temperature increases to 573 K, the intensity of peaks located at higher temperatures increases, unlike those in the lower temperature range that start to decay. The S2p photoelectron line obtained by XPS suggested that the SO\textsubscript{2} adsorbed mainly as sulfite at 298 K but some of this transformed to sulfate when the sample was annealed. Increasing the exposure temperature to 923 K resulted in more transformation of the sulfate into sulfide. Analogous findings were reported with the pure SO\textsubscript{2} exposure and as a mixture with O\textsubscript{2}.

The adsorption of SO\textsubscript{2} has been carried out over CeO\textsubscript{2} (111)/Cu (111) [91]. The XPS analysis suggested that sulfite is the main surface species at 300 K. When the sample was annealed, some of the sulfur was reduced to S\textsuperscript{0} and S\textsuperscript{2−}. There was no sulfate observed at any temperature. The physisorption and chemisorption reactions of sulfur dioxide (SO\textsubscript{2}) were investigated on single-crystal metals such as Cu, Au, and Pt and on pure CeO\textsubscript{2} (111), as well as on the metal-supported forms of CeO\textsubscript{2} (111) such as Cu-supported, Au-supported, and Pt-supported CeO\textsubscript{2}. In these previous investigations, SO\textsubscript{2} adsorption and dissociation on CeO\textsubscript{2} (111) doped with Cu, Au, and Pt results in different products. For instance, it was found that SO\textsubscript{2} interacts with the surface oxygen on CeO\textsubscript{2} (111) to produce the sulfite ion SO\textsubscript{3}\textsuperscript{2−} or sulfate ion SO\textsubscript{4}\textsuperscript{2−}. At higher temperatures, SO\textsubscript{3}\textsuperscript{2−} and SO\textsubscript{4}\textsuperscript{2−} were found to be desorbed without dissociating as S\textsuperscript{0} or S\textsuperscript{2−} on the catalyst surface. The reaction of SO\textsubscript{2} occurs spontaneously in the case of metal-based CeO\textsubscript{2} (111). At over 250 K, SO\textsubscript{2} has been observed as a molecule on Au/CeO\textsubscript{2} (111) without decomposing. On Cu/CeO\textsubscript{2} (111), the dissociation to S\textsuperscript{0} is improved by contrast to Cu single crystals. The activity peaks at Cu coverage ranging from 0.5 to 1.0 ML, and beyond this the activity decays back. However, the overall reaction of SO\textsubscript{2} on Pt/CeO\textsubscript{2} (111) catalyst is rather complicated. At a temperature of 150 K, on the CeO\textsubscript{2} (111) surface, SO\textsubscript{2} adsorbs as sulfite standing upright on the Pt nanoparticles depending on the XPS high-resolution S2p photoelectron line. This is in line with those cases of metal-free CeO\textsubscript{2} (111) and Pt (111), except for the absence of SO\textsubscript{2} lying flat on the Pt nanoparticles.
Given the importance of ceria’s catalytic performance for treating NOx in automobile exhaust, the adsorption of nitrogen oxide in its forms as N2O, NO, and NO2 on ceria surfaces has been investigated [92]. Ferrizz et al. [93] indicated the non-adsorption of NO at 300 K on the fully oxidized CeO2 (111) single crystal or on CeO2 deposited on α-Al2O3 (0001). Overbury et al. [94] further reported that NO does not interact with CeO2 (100) at 160 or 300 K; however, NO was observed to interact rather weakly at 90 K on stoichiometric CeO2 (111)/Ru (0001) [94]. Literature reported that NO is physisorbed below 200 K with small amounts of N2O and N2 desorbing in the same temperature window. The wide temperature range of NO desorption between 300 and 400 K was attributed initially to adsorption of NO on the sample holder and on the back of the Ru (0001) substrate [94]. This weak adsorption on the stoichiometric surface is in line with a study by Yang et al. [95] that concluded that there was an adsorption of NO over the Ce4+ cation site on CeO2 (111) with a physisorbed energy amounting to only −0.1 eV. The XPS high-resolution N1s spectra showed that at 90 K, NO and N2O physisorbed over CeO2 (111). These more stable adsorbates were not reported in the study by Yang et al. [95]. In two different studies conducted by Ferrizz et al. [93] and Overbury et al. [94], NO was shown to adsorb more strongly on nonstoichiometric CeO2−y, and these indications are in agreement with work conducted by Daturi et al. [96]. These studies linked the so-called “deNOx” catalytic capacity of ceria with the number of vacancies created on the ceria surface.

Ferrizz et al. [93] reported that after the NO adsorption at 300 K on nonstoichiometric CeO2/α-Al2O3 (0001), only N2 molecules were formed and desorbed. The N2 desorption profile is dependent on the method by which the reduced surface is synthesized. A film that was prepared in a lower O2 pressure led to a sharp N2 desorption in the range of 300 to 400 K. The desorption of N2 extended from 400 to 800 K by removing the O from fully oxidized films that were formed because of N2 desorption. Overbury et al. [94] revealed a diversity of desorbed species and showed that the desorbed product distribution was generally affected by the desorption [94]. NO, N2, and N2O molecules are formed mainly below 200 K as a consequence of adsorption at 90 K being followed by the desorption of NO and N2 in the range of 200 to 400 K. As the adsorption temperature increases to 150 K, the low-temperature desorption diminishes, and only additional N2 desorption is captured at 350 K. As the adsorption temperature rises to 400 K, new desorption characteristics appear with a considerable amount of N2 in addition to the desorption of NO represented by peaks located at 500 and 740 K. A study evaluated the adsorption of the NO2 molecule onto ceria defective planes of (111), (110), and (100) via DFT+U approach. The adsorption of NO2 with the reactive sites which can perform as sites for free radical scavenging comprises an expansion in the N–O bond length as compared to that of the gas phase N–O bond length in NO2 [97].

8. Ceria Surface Reactions with CO/CO2 and Organic Molecules

8.1. Carbon Monoxide (CO)

Ceria powder and nanocrystals are known to effectively reduce CO at high temperature, forming CO2 and CeO2−y. It is very well known that the function of ceria when used in three-way catalysis is to oxidize CO gas into CO2. Similar to the case of H2, the adsorption of CO has not been reported on CeO2 (111) or CeO2 (100) under UHV conditions [98–100]. Many studies have reported that the adsorption of CO on ceria surfaces is very weak with a binding energy of 0.2 eV [101–103]. On the other hand, several studies conclude that the formation of carbonate species on the CeO2 (110) is an exothermic process with energy >2 eV. In another study by Nolan and Watson, the formation of carbonate was found to be more exothermic on CeO2 (100), −3.2 eV, than that on CeO2 (110), −1.95 eV [101]. Stubenrauch and Vohs [98] argued that CO could not be detected in its physisorbed state over the CeO2 (100) surface at 300 K. They demonstrated that 0.1 ML of CO potentially adsorbed on the CeO2 (100) at 100 K completely desorbed at 200 K. A projector-augmented wave (PAW) functional within generalized gradient approximation.
(GGA) was utilized to inspect the adsorption of CO over (111) and (110) facets. The adsorption energy on (111) and (110) surfaces was estimated to be 0.15 eV and to extended from 0.18 to 1.95 eV, respectively, which is attributed to the creation of a carbonate species [104]. A computational investigation explored CO oxidation over Pd catalyst supported over (100) and (111) directions of CeO$_2$ nanocubes. The investigators illustrated that CO oxidation proceeds via a Mars–van Krevelen mechanism, which is likely to take place over the (100) facet rather than the (111) facet due to the lower Ce–O binding energy of the former [105]. A study has concluded that oxidation of CO would improve when introducing transition metals into ceria, and the catalysts follow the order of Cu > Co > Ni > Mn > Fe > Zn > pure ceria [106].

8.2. Carbon Dioxide (CO$_2$)

Senanayake and Mullins [107] explored the weak interaction between CO$_2$ and CeO$_2$ (111) and found that at 90 K, the carbon dioxide was adsorbed on the surface, whilst complete desorption was recorded at 150 K. This study further reported that a minor quantity of carbonate species was produced and continued up to 300 K. In another instance, Senanayake et al. [108] demonstrated the formation of a small amount of carbonate on nonstoichiometric ceria (CeO$_{2-y}$) grown on Au (111) substrate. These carbonate molecules persisted until 300 K. In an attempt to reoxidize the nonstoichiometric CeO$_{2-y}$ (111) deposited on Cu (111) substrate, Lykhach et al. [109] and Staudt et al. [110] observed a negligible quantity of carbonate and carboxylate in the analyzed C 1s and O 1s curves [109]. However, a considerable concentration of Ce$^{3+}$ was oxidized into Ce$^{4+}$. A previous work conducted on the adsorption of CO$_2$ on CeO$_x$ (100) has explored a stronger interaction of CO$_2$ with the oxidized and reduced surfaces [111]. In relation to the fully oxidized CeO$_2$ (100), the CO$_2$ was seen to be desorbed in a group of peaks at 230, 410, 510, and 655 K. The rising part of CeO$_2$ (100) is indicative of CO$_2$ desorption from the sample holder. The DFT+U approach was utilized to calculate and investigate the most stable sites of CO$_2$ adsorption on CeO$_2$ (100) and CeO$_{1.7}$ (100). The carbonate species in tridentate form have been found to be the most stable arrangement as a result of the CO$_2$ adsorption on the surface, and the adsorption energy for this species amounts to $-1.93$ eV [65]. It has been demonstrated that the carbonate species on the reduced CeO$_{1.7}$ (100) is strongly stabilized at 765 K, whereas CO$_2$ desorption was observed at low temperature [111]. To the best of our knowledge, there are no reports on the desorption of CO molecules on the oxidized or reduced surfaces. This is evidenced by the obtained invariant intensity of the Ce–4f peak indicating that CeO$_{1.7}$ (100) surface has not been reoxidized by CO$_2$.

The adsorption of CO$_2$ on the CeO$_2$ (111) face has been evaluated by Hahn et al. [112] using pure DFT and DFT+U approaches. In their simulation, they found that the most stable configuration was a monodentate carbonate species with a weak adsorption energy of nearly $-0.3$ eV in both approaches. Another DFT+U study conducted by Cheng et al. [113] investigated the CO$_2$ adsorption on both stoichiometric and nonstoichiometric CeO$_x$ (110) to reveal a physisorbed reaction between CO$_2$ molecule and the surfaces with an adsorption energy of $-0.26$ eV. Carbonate species were not formed in their mechanism. In the last decade, CeO$_2$ was used as a support for noble metal catalyst studies by Hahn [112] and Cheng [113], who reported structures of CO/CO$_2$–CeO$_2$ with different binding energies.

8.3. Hydrocarbons

When the cerium oxide surfaces are supported by Rh or Pt, ethylene adsorption and dissociation have been observed. The thermal interaction of ethylene on Rh pure crystal faces leads to the formation of gaseous H$_2$ leaving C on the surface [114–116]. It is found that the hydrogen molecule leaves from the Rh surface between 300 and 500 K. If Rh is deposited on an unreactive material such as $\alpha$-Al$_2$O$_3$ (0001), ethylene dissociates in an analogous way and H$_2$ leaves close 440 K [117]. Ethylene dissociation over Rh/CeO$_2$ (111) surface [118] or Rh/CeO$_2$/$\alpha$-Al$_2$O$_3$ (0001) forms CO and H$_2$ molecules [117]. CO molecules are formed as a consequence of the reaction between the carbon layer deposited
on the Rh particles and O on the ceria’s substrate. Over successive cycles of ethylene adsorption, the temperature of CO desorption shifts to increasingly higher temperatures in subsequent TPD measurements, suggesting that it becomes more difficult to eliminate O from an increasingly reduced surface [117]. Aside from CO and H$_2$ production from the decomposition of ethylene on Rh/CeO$_2$/yttria-stabilized zirconia (YSZ) (100), CO$_2$ species were also present [119]. This indicates that the YSZ (100) substrate changes the reactivity of the O in ceria. In particular, H$_2$O is not recorded in any of these Rh/CeO$_2$ materials, suggesting that the H atoms produce H$_2$, leaving the surface instead of interacting with O in the ceria to produce water molecules. An analogous trend is observed for ethylene adsorbed on Pt/CeO$_2$ (111) catalyst [120]. The high-resolution XPS C1s spectra demonstrated the destruction of the ethylene to C on the Pt at elevated temperatures, with evidence for C atoms being desorbed. It has been shown that when CeO$_2$ reduces to Ce$_2$O$_3$ via interaction of carbon with the surface O, eliminated carbon steadily increases. In the same vein, Pt nanoparticles on CeO$_2$ (111) surfaces activate the dehydrogenation process of the ethylene at a lower temperature compared to Pt (111). Methane on Pt/CeO$_2$ (111) [121,122] was shown to improve the dehydrogenation activity as well. It has been observed that methane partly dehydrogenates to CH$_3$ at temperatures close to 100 K. Moreover, it has been shown that the methane species dehydrogenates to CH when reacted on Pt nanoparticles on CeO$_2$ (111). Supported methane activation was also detected for low-surface-area Rh, Pt, and Pd on CeO$_2$ during methane steam reforming [123].

8.4. Methanol

In order for organic molecules to interact with ceria surfaces under UHV conditions, the presence of a functional group including a heteroatom such as O, N, or S is essential. However, the literature presents several accounts on the interaction of a wide range of nonfunctionalized organic molecules with ceria. For instance, it has been demonstrated that ethylene leaves CeO$_2$ (111) surface as a molecule under 150 K [118]. Furthermore, ethylene was investigated on Rh/CeO$_2$/YSZ (100) [119], but the authors did not report ethylene’s re-action with the vacancy-free ceria surface. Instead, they focused on the interaction between the adsorbed ethylene and the Rh particles. Vile et al. studied the selective hydrogenation of alkynes to olefins at elevated conversion over polycrystalline ceria powders [124]. Carrasco et al. [125] conducted computational studies on the selective hydrogenation of acetylene to ethylene over CeO$_2$ (111) using DFT. In this study, β-C$_2$H$_2$ radical species were reported to have adsorbed on the surface of oxygen atoms, subsequently being converted to C$_2$H$_3$. The formation of this species requires a lower activation energy barrier to convert to gas-phase C$_2$H$_4$ with reference to the formation of a β-C$_2$H$_4$ radical that would result in more highly hydrogenated products. Furthermore, it has been revealed that the use of lanthanide oxides as CO$_2$ methanation catalysts showed an excellent catalytic activity of CO$_2$ conversion of acidity from CO$_2$ gas to CH$_4$ gas [126]. The physisorption and chemisorption of methanol at different positions over the CeO$_2$ (111) surface have been explored by DFT. The most favorable case corresponds to the dissociative adsorption of methanol via the cleavage of the C–H bond producing the coadsorbed hydroxymethyl group and hydrogen adatom. DFT results agreed with the experimental outcomes in that methanol can adsorb on a defect-free CeO$_2$ (111) plane [127].

8.5. Phenol

Phenol plays a crucial role as a raw material in many important industrial fields such as the chemical, petrochemical, and pharmaceutical industries. Despite the positive use of phenol in the aforementioned applications, researchers have also devoted significant effort to develop methods by which phenol can be efficiently degraded owing to its well-documented role as a precursor for notorious pollutants, most notably dioxins. This is because phenol is viewed as a harmful contaminant, most notably in wastewater even at a content as low as 0.001 mg/L [128]. Furthermore, a phenolic concentration of 50 mg/L is sufficient to have a bactericidal effect on microorganisms. Lin et al. [128] investigated
the catalytic efficiency of CeO$_2$ on phenol conversion and total organic carbon (TOC) conversion. They used XRD, O$_2$-TPD, and H$_2$-TPR techniques to investigate the catalytic wet air oxidation (CWAO) of a number of CeO$_2$ samples calcined under different thermal impacts, classified from the highest thermally calcined to the lowest thermally calcined, i.e., type A, type B, type C, and type D. They reported a number of conclusions. Firstly, CeO$_2$ calcined under different thermal conditions displays variable catalytic efficiency in the CWAO of phenol. The highest thermal impact sample (denoted as A CeO$_2$) exhibits a less stable structure, more structural oxygen exchange, and greater oxidizing capability for the intake of H$_2$ and conversion of phenol. For the A-type CeO$_2$, at phenol content in the range of 400 to 2500 mg/L, oxygen pressures between 0.5 and 1.0 MPa, and temperatures exceeding 160 °C, phenol conversion amounted to ratios greater than 90% after 4 h. The elimination process of total organic carbon is enhanced with the increase in the reaction temperature. Finally, CO$_2$ selectivity was found to be approximately $\geq$80% after a 4 h reaction. Yao and coworkers [129] classified three types of oxygen in CeO$_2$, namely capping, bulk, and shared oxygen. Below 500 °C, capping oxygen forms due to defects in the CeO$_2$ structure undergoing an elevated thermal impact [129]. Moreover, DFT+U calculations revealed that the interaction of phenol with the hydroxylated H–OH/Ce$_{0.875}$Mn$_{0.125}$O$_{1.9375}$ (111) plane is stronger than that with the clean plane [130].

9. Catalytic Applications

It is well known that ceria’s propensity for oxygen uptake and release, ascribed to reversible transition between Ce$^{3+}$ and Ce$^{4+}$, makes this material a crucial component for catalytic applications and reactions. Indeed, its catalytic activities are closely correlated to the surface structure in which different oxygen anions and cerium cations are existing on the low-index surfaces. In this section, various catalytic performances will briefly be presented.

9.1. Three-Way Catalysts (TWCs) in Automotive Cars

The most popular application of cerium dioxide is TWCs in which CeO$_2$ or CeO$_2$-based materials act as supporters to convert some harmful gases such as CO, HC, and NO$_x$ emitted from automotive vehicles into more benign forms. In this process, CO and HC are oxidized to be converted into CO$_2$ and H$_2$O, respectively, whereas NO$_x$ is reduced into N$_2$. In this catalytic technology, the oxidation reactions are supported by some noble elements, namely Pt and/or Pd, whereas Rh is required to efficiently catalyze the reduction of NO$_x$. Nonstoichiometric ceria (CeO$_{2-x}$) is a good store for oxygen during lean-to-rich transients and hence plays a crucial role in further reducing NO$_x$ molecules. In contrast, stoichiometric ceria (CeO$_2$) is an excellent provider of the oxygen atoms needed to oxidize CO and HC during rich-to-lean transients. The TWC was initially pioneered during the 1970s–1980s, fabricated from a combination of CeO$_2$ and noble metals on doped Al$_2$O$_3$ support. Improvements on this design were achieved in the mid-1980s by developing the CeO$_2$ concentrations and optimizing the CeO$_2$ distribution on the support alloyed Al$_2$O$_3$. Nonetheless, the formation of undesirable CeAlO$_3$ and the unwanted reaction between CeO$_2$ and the noble elements is significantly diminished. However, this version of TWS could not control car pollution because of poor thermal stability. The final generation of TWC convertors is the advanced TWCs that are based on CeO$_2$-ZrO$_2$ solid solution rather than pure CeO$_2$. This version has high efficiency in removing pollutant emissions. As stated earlier, introducing ZrO$_2$ into the CeO$_2$ lattice enhances the oxygen storage capacity (OSC) of the system, which is needed in the redox cycles, and hence improves the efficiency of the catalyst and reduces emissions at the starting of the engine.

9.2. Conversion of CO$_2$ to Methanol and Ethanol

One of the major hazards to nations is the emission of large quantities of carbon dioxide (CO$_2$) into the atmosphere as it leads to increasing atmospheric CO$_2$ concentration which in turn causes serious climate change. Thus, reusing CO$_2$, instead of treating it as
waste, is highly needed. In fact, a promising approach is the catalytic hydrogenation of CO₂ to methanol. Typically, the industrial catalysts (CuO/ZnO/Al₂O₃) have widely been utilized according to the reaction CO₂ + 3H₂ → CH₃OH + H₂O, ΔH = −49.2 kJ/mol, in the temperature and pressure ranges of 250–300 °C and 50–100 bar, respectively [131,132]. However, this catalyst exhibits inadequate activity in converting a feed of CO₂ and H₂ to methanol due to the competing reverse water–gas shift (rWGS) reaction (CO₂ + H₂ → CO + H₂O, ΔH = 41.2 kJ/mol). DFT+U investigation of methanol decomposing over CeO₂ showed structure dependency in that the major product obtained depends on the facet exposed in the ceria nanostructures producing either formaldehyde or syngas as main products [133]. The high activity of CeO₂ and CeO₂-decorated catalysts towards CO₂ conversion has been well documented in the literature. It has been stated that a combination of surface-modified titanium dioxide (TiO₂) nanoparticles with reduced graphene oxide (rGO) and cerium oxide (CeO₂) exhibited high photo-reduction performances of CO₂ conversion into methanol and ethanol fuels by yielding methanol and ethanol at 641 and 271 μmol g⁻¹ h⁻¹, respectively [134]. Moreover, CO₂ hydrogenation activity demonstrated that the Cu/CeO₂ catalysts had higher methanol selectivity compared to Cu/SiO₂ catalyst. The superior methanol selectivity is attributed to the inhibition of the rWGS activity [135]. The hydrogenation of CO₂ to methanol over Au/CeO₂ catalysts has been reported [136]. Results demonstrate that CO hydrogenation to methanol over Au/CeO₂ is hindered by the presence of CO₂, indicating that the carbonate-like species can block the active sites at the Au-CeO₂ interface. Abdullah et al. [137] investigated the performance of a CeO₂-TiO₂ photocatalyst for the photocatalytic reduction of CO₂ into methanol under visible light irradiation, and their results suggested that the CeO₂-TiO₂ exhibited superior photocatalytic performance by producing methanol at 18.6 μmol/g under visible light irradiation when compared with the bare TiO₂ (6.0 μmol/g).

9.3. Oxidation of Volatile Organic Compounds (VOCs)

Chlorinated volatile organic compounds (CVOCs) are a group of widespread contaminants that are emitted as gases that may lead to short- and long-term health problems. Therefore, the elimination of these compounds that have been widely detected indoors and outdoors has gained considerable attention [138]. CeO₂ and CeO₂-based materials have been employed as economic alternatives to RuO₂-based catalysts to oxidize and decompose HCl, a harmful by-product produced by industrial processes such as polycarbonate production from dehydroxylated organics and organic chlorination reactions. The chlorine molecule Cl₂ is found to be the predominant industrial output for HCl removal [139]. CeO₂-based catalysts were noted to be active in O₂-rich feeds (O₂/HCl > 0.75), whereas the deactivation of the catalysts was explored in O₂-poor feeds (O₂/HCl < 0.25). High Cl coverage hinders the formation of oxygen vacancies. Hence in order for the original activity to be restored, the samples should be exposed to an excess of oxygen, indicating a reversible deactivation due to the chlorination [140]. Furthermore, CeO₂-ZrO₂ solid solution as an improved catalyst exhibits prolonged stability (700 h on stream) and lessens the chlorine uptake compared to undoped CeO₂ [141].

Various pathways for VOC treatments have been reported, including adsorption, direct combustion, regenerative combustion, and catalytic combustion [142]. CeO₂ and CeO₂-based compounds have served as oxidizing agents for the treatment of VOCs. The use of a catalyst reduces the activation energy and makes it possible to oxidize VOCs at a lower temperature. The catalytic oxidation of benzene (B), chlorobenzene (CB), and 1,2-dichlorobenzene (1,2-DCB) over W-modified Pt/CeO₂ catalysts has been studied [143]. A decrease in the strength of Cl adsorption on Ce and Pt sites can be promoted by the addition of W. The interaction of W with Pt species led to the formation of Pt-O-W structures, which promoted the reducibility and availability of surface oxygen. For controlling the emission of VOCs in industries such as painting, printing, and gluing, Pt/CeO₂-CeO₂ catalyst was effective in lowering the oxidation temperature of toluene, ethyl acetate, and isopropyl alcohol at less than 250 °C [144]. A Mars–van Krevelen-type mechanism governs the
reaction in which CeO$_2$ acts as the oxygen provider and at the same time is reoxidized by the gas-phase oxygen [145,146]. High-surface-area CeO$_2$ materials have been well known as promoters for noble metals (Pd, Pt, and Au). CeO$_2$ is now being deployed as a low-temperature catalyst in the decomposition of VOCs. This is because of the increase in metal dispersion and CeO$_2$ participation in the reaction [147]. Figure 9 illustrates the Mars–van Krevelen mechanism of the CeO$_2$ (110) surface towards oxidizing CO. This mechanism commences with the adsorption of CO and implicates the contribution of an oxygen atom resulting in the formation of desorbed CO$_2$ and an oxygen vacant site. Next, the oxygen vacancy is wrapped by O$_2$ that reoxidizes the surface.

**Mars-Van Krevelen Mechanism**

![Figure 9. Schematic illustration of the CO oxidation over CeO$_2$ (110) surface via Mars-van Krevelen mechanism [148].](image)

Methane (CH$_4$), as one of VOCs, is known to pose a number of issues such as its potential impact on global warming and its major contribution to ozone depletion [149]. The combustible nature of CH$_4$ adds further challenges in any process aimed at tackling its removal/conversion. The catalytic efficiency of a CeO$_2$-ZrO$_2$ solid solution synthesized by urea hydrolysis toward methane was demonstrated to depend on the Ce:Zr fraction. The most active composition was observed in Ce$_{0.75}$Zr$_{0.25}$O$_2$, and a gradual drop in the activity was recorded when Zr content decreased due to the phase change and modification of redox properties. Although these systems have been recognized to possess high thermal stability traits, they suffer from a general catalytic deactivation during light-off experiments (i.e., the catalyst light-off is the minimum temperature necessary to initiate the catalytic reaction). By a more precise definition, the light-off temperature is the temperature at which conversion reaches 50%. Liotta and coworkers suggested that the strong electron transfer between Ce$_3$O$_4$ and CeO$_2$ resulted in enhanced redox properties and improved methane oxidation.

This enhancement has also been observed with CuO/CeO$_2$ catalysts when optimizing the CuO dispersion, the metal loading, and the electronic interaction with ceria, resulting ultimately in the improved catalytic activity of the system. Despite the excellent efficiency of the CuO/CeO$_2$ solid solution, a noticeable decrease in the activity was observed due to the existence of H$_2$O. In a Ce$_{0.9-y}$Cu$_{0.1}$Ca$_{y}$O$_{2-y}$ system, a remarkable improvement was observed following the introduction of Ca as a result of the formation of oxygen vacancies. This system loses its activity over time due to the migration of Ca atoms to the surface, thereafter forming calcium and carbonate species. Finally, the incorporation of La in La$_x$Ce$_{1-x}$O$_{2-y/2}$ solid solutions led to the enhanced reducibility of ceria and, at the same time, an increase in the formation of oxygen vacancies and surface superoxide ions. In fact, these solid solutions were found to be crystalized in very small sizes as the ratio of Ce/(Ce + La) was kept in the range from 1.0 to 0.2.
The addition of noble metals such as Pt to different compositions of Ce$_x$Zr$_{1-x}$O$_2$ catalysts has been previously found to produce thermally stable structures. Among the investigated systems, Pt/Ce$_{0.67}$Zr$_{0.33}$O$_2$ was found to be the most thermally stable and the best active catalyst at 1000 °C. Pt/Ce$_{0.67}$Zr$_{0.33}$O$_2$ catalysts were also found to be much more active than Pt/Al$_2$O$_3$. Several important catalyst systems, along with a summary of their synthesis and other operational information (BET surface area, gas hourly space velocity (GHSV), and temperature), are tabulated in Table 3.

| Catalyst                  | Synthesis Technique           | BET Surface Area (m$^2$ g$^{-1}$) | VOC      | GHSV (mL g$^{-1}$ h$^{-1}$) | VOC Concentration | T$_{50}^b$ (°C) | Ref. |
|---------------------------|-------------------------------|-----------------------------------|----------|-----------------------------|------------------|----------------|------|
| Ce$_{0.75}$Zr$_{0.25}$O$_2$| sol–gel                       | 108.4                             | methane  | 60,000                      | 2%               | 545            | [150]|
| 5 wt% Cu/CeO$_2$          | hydrothermal                  | 22.6                              | methane  | 27,000                      | 1%               | 540            | [95]  |
| 1 wt% Cu/CeO$_2$          | thermal decomposition          | 68.7                              | methane  | 54,000                      | 1%               | 540            | [95]  |
| Ce$_{0.85}$Cu$_{0.15}$Ca$_{0.05}$O$_{2-δ}$| citric acid complexation combustion | 31.3                              | methane  | 30,000                      | 1%               | 478            | [151]|
| Ce(0.6)-La-O              | sol–gel                       | 52.4                              | methane  | 13,500                      | 0.2%             | 505            | [152]|
| Co$_3$O$_4$-CeO$_2$       | coprecipitation               | 31                                | methane  | 60,000                      | 0.3%             | 471            | [153]|
| 2 wt% Pt/Ce$_{0.67}$Zr$_{0.33}$O$_2$| impregnation                  | 79                                | methane  | 12,800                      | 1%               | 550            | [154]|
| CeO$_2$                   | sol–gel                       | 3                                 | toluene  | 200,000                     | 1000 ppm         | 430            | [147]|
| 5 wt% CeO$_2$/Al$_2$O$_3$ | impregnation                  | 156                               | toluene  | 54,000                      | 1400 ppm         | 275            | [155]|
| Ce$_{0.6}$Zr$_{0.4}$O$_2$ | sol–gel                       | 56                                | toluene  | 20,000                      | 1000 ppm         | 221            | [156]|
| Ce$_{0.6}$Zr$_{0.4}$O$_2$ | sol–gel                       | 56                                | ethanol  | 20,000                      | 1000 ppm         | 207            | [156]|
| CuO-CeO$_2$/γ-Al$_2$O$_3$ | impregnation                  | 156                               | propane  | 2300                         | 5.9%             | 350            | [157]|
| Cu$_{0.5}$Ce$_{0.95}$O$_2$| combustion                    | 27                                | acetone  | 60,000                      | 1000 ppm         | 200            | [158]|
| MnO$_x$-CeO$_2$           | modified coprecipitation      | 124                               | benzene  | 30,000                      | 200 ppm          | 260            | [159]|
| 3 wt% Ag/MnO$_x$-CeO$_2$  | deposition precipitation      | 124.0                             | formaldehyde | 30,000                     | 580 ppm          | 70             | [160]|
| 0.5 wt% Pt/CeO$_2$        | impregnation                  | 3                                 | toluene  | 200,000                     | 1000 ppm         | 180            | [147]|
| 1.5 wt% Au/CeO$_2$        | deposition precipitation      | 79                                | propene  | 35,000                      | 1000 ppm         | 230            | [161]|
| 0.25 wt% Pt/23wt% CeO$_2$/Al$_2$O$_3$| sol–gel                      | 95                                | acetic acid | 30,000                     | 1000 ppm         | 175            | [162]|

Ce$_{1-x}$Zr$_x$O$_2$ (x = 0–0.3) exhibits a very good catalytic efficiency towards the oxidation of some non-methane gases, especially benzene and toluene. The Ce$_{1-x}$Zr$_x$O$_2$ solid solution has been proven to be more efficient than unalloyed CeO$_2$ in the combustion of these harmful molecules. For instance, the Ce$_{0.9}$Zr$_{0.1}$O$_2$ solid solution demonstrated higher catalytic performance toward oxidizing benzene and toluene than pure CeO$_2$ at a temperature of 100 °C lower than light-off temperature, the temperature at which 50% of conversion (T$_{50}^b$) is completed [163]. In a similar context, MnO$_x$-CeO$_2$ mixed oxides exhibit excellent catalytic performance for formaldehyde combustion. The synthesis method of such a mixed oxide is an important factor in tuning its catalytic performance. The improvement is due to the formation of a higher oxidation state of manganese and more oxygen on the surface resulting in an enhancement in the energy barrier for the oxygen transfer mechanism [159].
9.4. Decomposition of Chlorinated Volatile Organic Compounds (CVOCs)

As stated previously, CVOCs are toxic materials that are emitted from industrial waste gases and contribute significantly to air pollution nowadays. These compounds are emitted from thermal processes whenever a trace of chlorine coexists with hydrocarbon entities. Among these pollutants are the notorious polychlorinated dibenzo-p-dioxins and dibenzofurans [164,165]. As a result, significant attention has been devoted to controlling the emission of these pollutants via the development of novel and efficient catalysts. Catalytic oxidative decomposition is currently deployed as an alternative for the commonly deployed high-temperature operations. Initially, noble metal (e.g., Pt and Pd) catalysts or supported noble metal catalysts were extensively employed to decompose VOCs [166–168]. These catalysts are very active in the catalytic destruction of chlorinated VOCs; however, they can be readily poisoned by emitted HCl and Cl₂ gases [169]. Transition metal oxide catalysts have now emerged as a cost-effective alternative candidate to noble metals to carry out deep catalytic oxidation for CVOCs. Although they are somewhat less active than noble metals, they are preferred because of their low price and resistance to HCl/Cl₂ poisoning [170].

The catalytic capacity of CeO₂ in acting as a stand-alone environmental catalyst toward the decomposition of a series of chlorinated volatile organic compounds, namely chloroethene, chloroethane, and chlorobenzene, has been highlighted via DFT approach [171]. The pyrolytic and oxidative decomposition of selected chlorinated compounds has been modeled on the most stable ceria surface, CeO₂ (111). The findings revealed that the separation of the C-Cl bond over oxygen vacancies systematically necessitates lower energy barriers in reference to clean surfaces. CeO₂ has been examined for the catalytic combustion of trichloroethylene (TCE), and Dai et al. investigated the catalytic performance in eliminating some chlorinated VOCs. They concluded that CeO₂ demonstrates an effective catalytic capacity in decomposing Cl-VOCs at low operating temperatures. They also found that the catalytic removal of chloroalkanes over the CeO₂ catalyst is easier than that of chlorinated allylenes [172]. Dia et al. [169] studied trichloroethylene combustion in a broad range of reaction temperatures over CeO₂ systems. Dia et al. attribute the lower efficiency of the CeO₂ calcined at 650 and 800 °C, in reference to that at 550 °C, to a diminution in BET surface area and an increase in crystallite size. The lower catalytic efficiency for CeO₂ calcined at 450 °C is attributed to it having fewer basic sites and active oxygen species.

9.5. Full Hydrogenation of Ethyne

The overall hydrogenation process of acetylene (C₂H₂) to ethane (C₂H₆) has been determined experimentally. A plausible hydrogenation mechanism was suggested based on DFT calculations. The entire energy landscape and primary reaction steps along with all intermediate configurations are depicted in Figure 10. It has been suggested that geometry optimizations for the adsorption of each of the investigated species preferentially occur over the surface O atoms. Hydrogen molecule adsorption and its subsequent dissociative adsorption on the surface are supposed to be the starting steps rather than the adsorption of a gas-phase C₂H₂ molecule. As a result, the reaction is initiated with the molecular adsorption of H₂ followed by homolytic dissociative adsorption to leave two H⁺ species and liberate 2.35 eV. The two H atoms adsorb over two closest neighboring surface O atoms to produce two hydroxyl groups and two Ce³⁺. This primary step necessitates an activation energy of 1.00 eV. The step to separate the two closest adjacent H⁺ species resulting in two separated species, (H, H⁺) → H⁺ + H⁺, is energetically unfavorable by 0.07 eV. The reaction continues with the adsorption of an acetylene molecule close to one hydroxy group to form (β-C₂H₂, H⁺)⁺ (step D in Figure 9). Subsequently, the radical can easily react with the adjacent hydroxy groups to produce C₂H₃⁺ and liberate 1.48 eV. Notably, this process involves only a very small energy barrier of 0.09 eV. In the subsequent step, an adsorbed hydrogen atom migrates to the radical center in the C₂H₃⁺, forming an ethene molecule. The fate of the ethene molecule is dictated by two competing channels, desorption into the gas phase or subsequent two hydrogenation steps toward the formation of an ethane molecule, i.e., full hydrogenation route. It has also been reported that various U values
would influence the reaction and activation energies for the full hydrogenation reaction of C\textsubscript{2}H\textsubscript{2} to C\textsubscript{2}H\textsubscript{6} over (111) CeO\textsubscript{2} surface catalyst [173].

![Reaction energy diagram for total hydrogenation of acetylene on CeO\textsubscript{2} (111) catalyst.](image)

**Figure 10.** Reaction energy diagram for total hydrogenation of acetylene on CeO\textsubscript{2} (111) catalyst. Energies are computed as a reference to the energy of H\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} in the gas phase and the clean CeO\textsubscript{2} (111) slab. Black line shows the routes of partial hydrogenation of acetylene to ethylene through R5, light brown displays the partial hydrogenation via dissociative acetylene adsorption, and red line represents the full hydrogenation to C\textsubscript{2}H\textsubscript{6}. The asterisk denotes a clean CeO\textsubscript{2} (111) surface. Reactants, intermediates, and products that are followed by an asterisk correspond to adsorbed moieties [125].

9.6. Soot Combustion

This context highlights the recent advances in preparing various shape-controlled CeO\textsubscript{2} particles and examining their catalytic performances in soot combustion. Nanofibers of CeO\textsubscript{2} were synthesized aiming at improving the soot–catalyst contact conditions and promoting soot combustion at lower temperatures than in the noncatalytic case. In particular, the nanofibers have been found to be very active with respect to other ceria catalyst morphologies due to their arrangement in a network that enhances the number of soot–fiber contact points [174]. Aneggi et al. [175] fabricated two types of shape-controlled nanoceria in the forms of cubes and rods by hydrothermal methods then examined their catalytic performance for soot combustion. Results showed that soot oxidation activity and conversion are higher for nanocubes and nanorods compared with conventional polycrystalline ceria and are affected by the nature of the exposed facets. Zhang et al. [176] synthesized three sorts of morphologies, namely nanorod, nanoparticle, and nanoflake, and examined the relation between the catalytic performance of ceria for soot combustion and the shapes. The findings indicated that CeO\textsubscript{2} with nanorod morphology revealed the best catalytic activity, and it reached a level comparable to that of a precious metal catalyst.

10. Applications

10.1. Photocatalytic Performance

Worldwide, efficient visible-light photocatalysis is an active area of research. Photocatalytic activity with the application of sunlight offers an inexpensive and green technology
for possible complete removal of refractory pollutants that damage the ecosystem, such as surfactants, pharmaceuticals, pesticides, textile dyes, and heavy metals, from industrial wastewater [177]. Literature reported the use of CeO$_2$ in photocatalytic applications, whether it is loaded, doped with metal species, or coupled with other materials. This use is supported by high bandgap energy, high refractive index [178], high optical transparency in the visible region [179], and excellent oxygen storage capacity resulting from the easy conversion of cerium ions between reduced and oxidized states (Ce$^{3+}$–Ce$^{4+}$) through fast creation and removal of oxygen vacancies in CeO$_2$. This section reports the recent photocatalysis-based studies of pure and doped CeO$_2$. The photocatalytic activity of CeO$_2$ is mainly related to particle size, surface structure, and morphology. An effective catalyst for the photodegradation of crystal violet dye under UV light has been fabricated based on noble metal oxide catalysts. Majumder et al. [180] tailored various crystallographic structures (hexagonal, rectangular, and square) and planes including (100), (111), and (101) of CeO$_2$ nanostructures and tested their photodegradation activities on methylene blue (MB) dye. The bandgap is reduced up to 1.93 eV and the complete degradation of methylene blue is achieved within 175 min, which is the shortest to be reported as compared with the complete degradation time of MB that is reduced from 23 to 14 h using samarium- and gadolinium-doped CeO$_2$ nanoparticles instead of bare ceria. A study was carried out to evaluate the role of various contents of Sn$^{4+}$ incorporated into CeO$_2$–Fe$_2$O$_3$ nanocomposites in the degradation of MB and methyl orange (MO) dyes under visible light. They found that the catalytic activity was improved due to the shifting of the Fermi level of CeO$_2$ by narrowing the bandgap energy (~2.3 eV) and enabling charge separation. Sm-doped CeO$_2$ nanorods were annealed in a N$_2$ atmosphere to obtain defective Sm-doped CeO$_2$ photocatalysts that demonstrated excellent performance in the photodegradation of MB under visible light irradiation [181]. Additionally, a DFT outlook showed that inserting Ti into the ceria lattice has an important influence on lowering the bandgap of the undoped system, which shows promise in the fields of photocatalysts [182]. Furthermore, the effect of Cr doping on CeO$_2$ nanostructure was investigated to assess the catalytic performances of Cr-doped CeO$_2$ nanocomposites with MB. They observed an improvement in the catalytic activity in MB degradation efficiency for photocatalysis [183]. In another study, CeO$_2$ nanoparticles were decorated on a graphene sponge and utilized for adsorption and photodegradation of methylene blue [184].

10.2. The Biomedical Applications

Nanoceria has substantial applications in the biomedical field, including orthopedic biomedicine and specifically bone tissue engineering, which have widely utilized ceria nanoparticles [185,186]. A wide array of biomedical applications have been covered in the literature [187]. In a recently published study, near-spherical cerium oxide nanoparticles (CeNPs) stabilized by various hydrophilic polymers were synthesized through a wet-chemical precipitation method to inspect the impacts of CeNP surface properties on their colloidal stability and catalytic activity in human cellular media. Two types of forces generated by surface functionalization have been deployed to stabilize the CeNPs: electrostatic forces, steric forces, or a combination of both. To enhance CeNP colloidal stability, polyacrylic acid (PAA) has been used as a good coating agent. Results indicate that the most stable sample in cell culture media was PAA-coated CeNPs with a combination of both electrostatic and steric forces on the surface. The sample also showed nontoxicity toward the osteoblastic cells and displayed promising biomedical applications [188]. Miri et al. [189] reported on the biosynthesis of CeO$_2$ nanoparticles with an estimated particle size ranging from 10 to 15 nm. The synthesized nanoparticles revealed a nontoxic effect against a colon cancer cell line. Moreover, nanoceria has demonstrated free radical scavenging activity and the ability to offer protection against ionizing radiation [190]. Besides, the inadequate radiopacity of dental adhesives applied under composite restorations makes the radiographic diagnosis of recurrent caries challenging. Therefore, the misdiagnosis leads to the unneeded replacement of restorations. To solve this issue, incorporating ele-
ments with a high atomic weight can enhance the radiopacity of dental adhesives. This motivated researchers to employ CeO$_2$ particles to enhance the radiopacity of the dental adhesives [191].

11. The Effect of Facets on the Catalytic Applications of CeO$_2$

The morphology- and surface-dependent catalytic activity of CeO$_2$ nanomaterials has drawn much attention in the literature, and findings suggest that the shape of CeO$_2$ crystals is mainly related to defect sites of the well-defined crystal planes. Thus, the correlation between catalytic properties and specific morphology (in which different crystal planes are exposed) can be achieved via exposure of different surfaces in addition to the most stable (111)-type plane of the nanocrystal [192]. The adjusted morphologies of CeO$_2$ as particles, spheres, cubes, rods, wires, and tubes with specific directions (111), (110), and (100) can remarkably improve catalytic performances. It has been stated that designing heterogeneous junctions is an attractive approach for refining the catalytic properties of CeO$_2$-based nanomaterials. Moreover, modifying defective structures by inserting minor Mn contents as dopants can improve the catalytic activity. Thus, hydrothermally fabricated CeO$_2$ nanowires/MnO$_2$ nanosheets showed improved catalytic performance because of the strong synergistic interaction between CeO$_2$ and MnO$_2$ at the interface [193]. Two shapes of controlled nanoceria, namely spherical and cubical, were synthesized through the hydrothermal method and by tuning reaction temperatures. The cubical NPs demonstrated superior degradation of $\sim$70% under UV light irradiation compared to the spherical ones (degradation of $<$50%). The antibacterial activities of both NPs were also examined, and cubical NPs were found to exhibit superior antimicrobial potential. This implies that cubical NPs demonstrate a propensity for treating industrial wastewater and inhibiting the growth of different microorganisms which in turn be useful in developing medical devices and tailoring various antimicrobial systems [194].

Dong et al. [195] used hydrothermal and solvothermal methods to synthesize a series of Cu/CeO$_2$ catalysts with diverse morphology and size, comprising CeO$_2$ nanoparticles (20 nm), CeO$_2$ nanospheres (200 nm), CeO$_2$ nanorods (20–40 nm), and flower-like CeO$_2$ microspheres (4 $\mu$m). The prepared catalysts were tested for the catalytic oxidation of CO under dry and humid conditions to explore the shape effect on CO oxidation performance. Cu/CeO$_2$ nanorods demonstrated the smaller particles size of CeO$_2$ and CuO and displayed the higher concentration of oxygen vacancies. Moreover, the best catalytic performance of about 90% conversion of CO at the temperature of 58 $^\circ$C was detected. Li et al. [196] used the hydrothermal method to fabricate ruthenium (Ru) catalysts on various shapes of supported CeO$_2$, including nanorods, nanocubes, and nano-octahedra. Ru supported on CeO$_2$ nanorods revealed boosted low-temperature hydrogen consumption and superior room-temperature CO oxidation activity of $<$100 $^\circ$C and $\sim$9% CO conversion, respectively. Lastly, the surface morphologies of CoO$_x$-decorated CeO$_2$ heterostructured catalysts, including nanorods (NRs), nanocubes (NCs), and nanoparticles (NPs), were found to strongly correlate with the physicochemical properties and catalytic performance toward diesel carbon soot oxidation. The CoCeO$_2$-NRs boosted soot combustion activity and stability at lower temperatures compared to CoCeO$_2$-NCs and CoCeO$_2$-NPs. This result is mainly attributed to the high oxygen release rate and improved redox capability of the supported Co species. This originates from the high reactivity of oxygen atoms on (110) surfaces compared to (100) and (111) surfaces over CeO$_2$ [197]. Finally and from another prospect, it has been stated that the catalytic properties of CdS can be enhanced by rare earth doping [198].

12. Conclusions

In this review, we summarized the fundamental aspects pertinent to catalytic properties, applications, morphologies, and structures of ceria. Due to the remarkable properties such as high surface area, superior electronic properties, and outstanding optical properties, ceria has widely been utilized in electronics and organic synthesis reactions. On the
other hand, distinctive redox properties and defect-rich geometry enable ceria to exhibit excellent catalytic performance in various reactions. CeO$_2$ (ceria) can catalyze a wide range of reactions by assisting oxidation and reduction and hydrogenation and dehydrogenation. Besides, ceria can be active as a crystal or as a polycrystalline layer supported by a metal or metal oxide, commonly Al$_2$O$_3$. The present review also highlights the recent applications of ceria in electronic components and nanomedicine. Defective ceria shows enhanced catalytic activity, and solid solutions (e.g., ceria with zirconia) display enhanced catalytic activity. Furthermore, zirconia-doped ceria (i.e., Ce$_x$Zr$_{1-x}$O$_2$) makes an effective catalyst when $x$ is optimized. Achieving desired morphologies with tailored crystal facets and oxygen vacancy in ceria through a controlled synthesis process has been reported, as this is necessary for highly active/selective heterogeneous catalysts. In addition, ceria nanostructures are more effective than polycrystalline ceria. Finally, this account involved computational modeling investigations highlighting the effects of ceria crystal facets and morphology on the desired properties and applications. We envisage that future research can focus on several aspects, most notably the following:

- The effect of new dopants such as Nb and Ta should be assessed in deriving the capacity of ceria in low-temperature oxidation.
- Molten metals have been recently deployed as heat transfer media and catalytic reagents. It would be insightful to assess the influence of Ce atoms in the emerging energy application of liquid metals.
- In an analogy to the role of ceria in dehalogenation reactions, it would be insightful to explore the potential role of ceria in fixing the fluorine content in $\text{C}_n\text{F}_m$ chemicals.

**Author Contributions:** Writing—original draft preparation H.A.M.; writing—review and editing, Z.N.J.; supervision, Z.-T.J.; funding acquisition, supervision, M.A. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by a start-up grant from the United Arab Emirates University (project number 31N421).

**Acknowledgments:** Hussein A. Miran and Zainab N. Jaf express their gratitude to the University of Baghdad.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Balaram, V. Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geosci. Front.* 2019, 10, 1285–1303. [CrossRef]
2. Omodara, L.; Pitkäaho, S.; Turpeinen, E.-M.; Saavalainen, P.; Oravissärvi, K.; Keiski, R.L. Recycling and substitution of light rare earth elements, cerium, lanthanum, neodymium, and praseodymium from end-of-life applications—A review. *J. Clean. Prod.* 2019, 236, 117573. [CrossRef]
3. Tiwari, S.; Rathore, G.; Patra, N.; Yadav, A.; Bhattacharya, D.; Jha, S.; Tseng, C.; Liu, S.; Biring, S.; Sen, S. Oxygen and cerium defects mediated changes in structural, optical and photoluminescence properties of Ni substituted CeO$_2$. *J. Alloy. Compd.* 2018, 782, 689–698. [CrossRef]
4. Miran, H.A.; Jiang, Z.-T.; Altarawneh, M.; Veder, J.-P.; Zhou, Z.-F.; Rahman, M.M.; Jaf, Z.N.; Dlugogorski, B.Z. Influence of DC magnetron sputtering reaction gas on structural and optical characteristics of Ce-oxide thin films. *Ceram. Int.* 2018, 44, 16450–16458. [CrossRef]
5. Maslakov, K.L.; Teterin, Y.A.; Ryzhkov, M.V.; Popel, A.J.; Teterin, A.Y.; Ivanov, K.E.; Kalmykov, S.N.; Petrov, V.G.; Petrov, P.K.; Farnan, I. The electronic structure and the nature of the chemical bond in CeO$_2$. *Phys. Chem. Chem. Phys.* 2018, 20, 16167–16175. [CrossRef]
6. Ishizaki, T.; Masuda, Y.; Sakamoto, M. Corrosion Resistance and Durability of Superhydrophobic Surface Formed on Magnesium Alloy Coated with Nanostructured Cerium Oxide Film and Fluoroalkylsilane Molecules in Corrosive NaCl Aqueous Solution. *Langmuir* 2011, 27, 4780–4788. [CrossRef]
7. Liu, C.; Jiang, Z.; Zhao, J.; Cheng, X.; Liu, Z.; Zhang, D.; Li, X. Influence of rare earth metals on mechanisms of localised corrosion induced by inclusions in Zr-Ti deoxidised low alloy steel. *Corros. Sci.* 2020, 166, 108463. [CrossRef]
8. Petit, L.; Svane, A.; Szotek, Z.; Temmerman, W.M. Electronic Structure of Rare Earth Oxides. *Top. Appl. Phys.* 2006, 106, 331–343. [CrossRef]
10. Bartos, A.; Lieb, K.P.; Uhrmacher, M.; Wiarda, D. Refinement of atomic positions in bixbyte oxides using perturbed angular correlation spectroscopy. Acta Crystallogr. Sect. B Struct. Sci. 1993, 49, 165–169. [CrossRef]

11. Sato, S.; Takahashi, R.; Kobune, M.; Gotoh, H. Basic properties of rare earth oxides. Appl. Catal. A Gen. 2009, 356, 57–63. [CrossRef]

12. Richard, D.; Errico, L.; Renteria, M. Structural properties and the pressure-induced C → A phase transition of lanthanide sesquioxides from DFT and DFT + U calculations. J. Alloy. Compd. 2016, 664, 580–589. [CrossRef]

13. Miran, H.A.; Altarawneh, M.; Jaf, Z.N.; Dlugogorski, B.Z.; Jiang, Z.-T. Structural, electronic and thermodynamic properties of bulk and surfaces of terbium oxide (TbO$_2$). Mater. Res. Express 2018, 5, 085901. [CrossRef]

14. Thanneeru, R.; Patil, S.; Deshpande, S.; Seal, S. Effect of trivalent rare earth dopants in nanocrystalline ceria coatings for high-temperature oxidation resistance. Acta Mater. 2007, 55, 3457–3466. [CrossRef]

15. Conesa, J. Computer modeling of surfaces and defects on cerium dioxide. Surf. Sci. 1995, 339, 337–352. [CrossRef]

16. Grieshammer, S.; Grope, B.O.H.; Koettgen, J.; Martin, M. A combined DFT + U and Monte Carlo study on rare earth doped ceria. Thin Solid Films 2016, 653, 37–48. [CrossRef]

17. Yashima, M.; Ishimura, D.; Yamaguchi, Y.; Ohoyama, K.; Kawachi, K. High-temperature neutron powder diffraction study of cerium dioxide CeO$_2$ up to 1770 K. Chem. Phys. Lett. 2003, 372, 784–787. [CrossRef]

18. Knappe, P.; Eyring, L. Preparation and electron microscopy of intermediate phases in the interval Ce$_{1-x}$La$_x$O$_2$. J. Solid State Chem. 1985, 58, 312–324. [CrossRef]

19. Mcclure, J.P. High Pressure Phase Transitions in the Lanthanide Sesquioxides. Bachelor’s Thesis, University of Nevada, Las Vegas, NV, USA, 2009.

20. Sørensen, O. Thermodynamic studies of the phase relationships of nonstoichiometric cerium oxides at higher temperatures. J. Solid State Chem. 1976, 18, 217–233. [CrossRef]

21. Conesa, J. Computer modeling of surfaces and defects on cerium dioxide. Surf. Sci. 1995, 339, 337–352. [CrossRef]

22. Zinkevich, M.; Djurovic, D.; Aldinger, F. Thermodynamic modelling of the cerium–oxygen system. J. Solid State Chem. 1985, 116, 600–611. [CrossRef]

23. Akümmerleab, E.E.; Heger, G. The Structures of C–Ce$_{2}$O$_{3+x}$, Ce$_{2}$O$_{12}$, and Ce$_{11}$O$_{20}$. J. Solid State Chem. 1999, 147, 485–500. [CrossRef]

24. Palmqvist, A.; Wirde, M.; Gelius, U.; Muhammed, M. Surfaces of doped nanophase cerium oxide catalysts. Nanostruct. Mater. 2004, 17, 995–1006. [CrossRef]

25. Han, Z.-K.; Zhang, L.; Liu, M.; Ganduglia-Pirovano, M.V.; Gao, Y. The Structure of Oxygen Vacancies in the Near-Surface of Reduced CeO$_2$ (111) Under Strain. J. Solid State Chem. 2019, 270, 436. [CrossRef] [PubMed]

26. Schnitt, R.; Nenning, A.; Kravins, O.; Korobko, R.; Frenkel, A.I.; Lubomirsky, I.; Haile, S.M.; Rupp, J.L.M. A review of defect structure and chemistry in ceria and its solid solutions. Chem. Soc. Rev. 2019, 49, 554–592. [CrossRef] [PubMed]

27. Thanneeru, R.; Patil, S.; Deshpande, S.; Seal, S. Effect of trivalent rare earth dopants in nanocrystalline ceria coatings for high-temperature oxidation resistance. Acta Mater. 2007, 55, 3457–3466. [CrossRef]

28. Patil, S.; Seal, S.; Guo, Y.; Schulte, A.; Norwood, J. Role of trivalent La and Nd dopants in lattice distortion and oxygen vacancy generation in ceria oxide nanoparticles. Appl. Phys. Lett. 2006, 88, 243110. [CrossRef]

29. Liu, X.; Chen, S.; Wang, X. Synthesis and photoluminescence of CeO$_2$:Eu$^{3+}$ phosphor powders. J. Lumin. 2007, 127, 650–654. [CrossRef]

30. Jwa, J.; Tanabe, S. Broadband near ultra violet sensitization of 1 μm luminescence in Yb$^{3+}$-doped CeO$_2$ crystal. J. Appl. Phys. 2011, 110, 73104. [CrossRef]

31. Li, J.; Yuasa, T.; Endo, K.; Muguruma, T.; Ohno, H.; Mizoguchi, I. Corrosion behavior of ion implanted nickel-titanium orthodontic wire in fluoride mouth rinse solutions. Dent. Mater. J. 2010, 29, 53–58. [CrossRef] [PubMed]

32. Thanneeru, R.; Patil, S.; Deshpande, S.; Seal, S. Effect of trivalent rare earth dopants in nanocrystalline ceria coatings for high-temperature oxidation resistance. Acta Mater. 2007, 55, 3457–3466. [CrossRef]
72. Alam, K.; Ahmed, F.; Miura, R.; Suzuki, A.; Tsuboi, H.; Hatakeyama, N.; Endou, A.; Takaba, H.; Kubo, M.; Miyamoto, A. Study of reduction processes over cerium oxide surfaces with atomic hydrogen using ultra accelerated quantum chemical molecular dynamics. *Appl. Surf. Sci.* 2010, 257, 1383–1389. [CrossRef]

73. Praligne, G.; Koel, B.; Hance, R.; Lee, H.-I.; White, J. X-Ray photoelectron study of the reaction of oxygen with cerium. *J. Electron Spectrosc. Relat. Phenom.* 1980, 21, 17–30. [CrossRef]

74. Choi, Y.; Abernathy, H.; Chen, H.-T.; Lin, M.C.; Liu, M. Characterization of O₂–CeO₂ Interactions Using In Situ Raman Spectroscopy and First-Principle Calculations. *ChemPhysChem* 2006, 7, 1957–1963. [CrossRef]

75. Nolan, M. Healing of oxygen vacancies on reduced surfaces of gold-doped ceria. *Phys. Chem. Chem. Phys.* 2009, 11, 15986–15991. [CrossRef]

76. Nolan, M. Healing of oxygen vacancies on reduced surfaces of gold-doped ceria. *J. Phys. Chem. C* 2012, 116, 19419–19428. [CrossRef]

77. Dvorak, F.; Stetsovych, O.; Steger, M.; Cherradi, E.; Matejka, T.; Škoda, M.; Škoda, T.; Myśliwiecz, J.; Matolín, V.; et al. Adjusting Morphology and Surface Reduction of CeO₂(111) Thin Films on Cu(111). *J. Phys. Chem. C* 2011, 115, 7496–7503. [CrossRef]

78. Dvorak, F.; Stetsovych, O.; Steger, M.; Cherradi, E.; Matolínová, I.; Tsud, N.; Škoda, M.; Skála, T.; Myśliwiecz, J.; Matolín, V.; et al. Adjusting Morphology and Surface Reduction of CeO₂(111) Thin Films on Cu(111). *J. Phys. Chem. C* 2011, 115, 7496–7503. [CrossRef]

79. Henderson, M.; Perkins, C.; Engelhard, M.; Thevuthasan, S.; Peden, C. Redox properties of water on the oxidized and reduced surfaces of CeO₂(111). *Surf. Sci.* 2003, 526, 1–18. [CrossRef]

80. Fronzi, M.; Piccinin, S.; Delley, B.; Traversa, E.; Stampfl, C. Water adsorption on the stoichiometric and reduced CeO₂(111) surface: A first-principles investigation. *Phys. Chem. Chem. Phys.* 2009, 11, 9188–9199. [CrossRef]

81. Marrocchelli, D.; Yildiz, B. First-Principles Assessment of H₂S and H₂O Reaction Mechanisms and the Subsequent Hydrogen Absorption on the CeO₂(111) Surface. *J. Phys. Chem. C* 2012, 116, 2411–2424. [CrossRef]

82. Molinari, M.; Parker, S.C.; Sayle, D.C.; Islam, M.S. Water Adsorption and Its Effect on the Stability of Low Index Stoichiometric and Reduced Surfaces of Ceria. *J. Phys. Chem. C* 2012, 116, 7073–7082. [CrossRef]

83. Fernandez-Torre, D.; Kośmider, K.; Carrasco, J.; Ganduglia-Pirovano, M.V.; Pérez, R. Insight into the Adsorption of Water on the Clean CeO₂(111) Surface with van der Waals and Hybrid Density Functionals. *J. Phys. Chem. C* 2012, 116, 13584–13593. [CrossRef]

84. Esch, F.; Fabris, S.; Zhou, L.; Montini, T.; Africh, C.; Fornasier, P.; Comelli, G.; Rosei, R. Electron Localization Determines Defect Formation on Ceria Substrates. *Science* 2005, 309, 752–755. [CrossRef]

85. Overbury, S.H.; Mullins, D.R.; Huntley, D.R.; Kundakovic, L. Chemisorption and Reaction of Sulfur Dioxide with Oxidized and Reduced Ceria Surfaces. *J. Phys. Chem. C* 2009, 113, 11038–11045. [CrossRef]

86. Waqif, M.; Babin, P.; Saur, O.; Lavallee, J.; Blanchard, G.; Touret, O. Study of ceria sulfation. *Appl. Catal. B Environ.* 1997, 11, 193–205. [CrossRef]

87. Bazin, P.; Saur, O.; Lavallee, J.; Blanchard, G.; Visciglio, V.; Touret, O. Influence of platinum on ceria sulfation. *Appl. Catal. B Environ.* 1997, 13, 265–274. [CrossRef]

88. Rodriguez, J.A.; Jirsaek, T.; Freitag, A.; Hanson, J.C.; Larese, J.; Chatuvedi, S. Interaction of SO₂ with CeO₂ and Cu/CeO₂ catalysts: Photoemission, XANES and TPD studies. *Catal. Lett.* 1999, 62, 113–119. [CrossRef]

89. Smirnov, M.Y.; Kalininkin, A.V.; Pashis, A.V.; Sorokin, A.M.; Noskov, A.S.; Kharas, A.K.C.; Bukhtiyarov, V. Interaction of Al₂O₃ and CeO₂ Surfaces with SO₂ and SO₂ + O₂ Studied by X-ray Photoelectron Spectroscopy. *J. Phys. Chem. B* 2005, 109, 11712–11719. [CrossRef] [PubMed]

90. Ferrizz, R.M.; Gorte, R.; Vohs, J. TPD and XPS Investigation of the Interaction of SO₂ with Model Ceria Catalysts. *Catal. Lett.* 2002, 82, 123–129. [CrossRef]

91. Happel, M.; Lykhach, Y.; Tsud, N.; Skala, T.; Prince, K.C.; Matolín, V.; Libuda, J.; Libuda, J. Mechanism of Sulfur Poisoning and Storage: Adsorption and Reaction of Stoichiometric and Reduced Ceria Films on Cu(111). *J. Phys. Chem. C* 2011, 115, 19872–19882. [CrossRef]

92. Castoldi, L. An Overview on the Catalytic Materials Proposed for the Simultaneous Removal of NOₓ and Soot. *Materials* 2020, 13, 3551. [CrossRef]

93. Ferrizz, R.; Egami, T.; Wong, G.; Vohs, J. Reaction of NO on CeO₂ and Rh/CeO₂ thin films supported on α-Al₂O₃(0001) and YSZ(100). *Surf. Sci.* 2001, 476, 9–21. [CrossRef]

94. Overbury, S.; Mullins, D.; Huntley, D.; Kundakovic, L. Chemisorption and Reaction of NO and N₂O on Oxidized and Reduced Ceria Surfaces Studied by Soft X-Ray Photoemission Spectroscopy and Desorption Spectroscopy. *J. Catal.* 1999, 186, 296–309. [CrossRef]

95. Yang, W.; Li, D.; Xu, D.; Wang, X. Effect of CeO₂ preparation method and Cu loading on CuO/CeO₂ catalysts for methane combustion. *J. Nat. Gas Chem.* 2009, 18, 458–466. [CrossRef]

96. Daturi, M.; Bion, N.; Saussey, J.; Lavallee, J.-C.; Hedouin, C.; Seguelong, T.; Blanchard, G. Evidence of a lacunar mechanism for deNOₓ activity in ceria-based catalysts. *Phys. Chem. Chem. Phys.* 2000, 3, 252–255. [CrossRef] [PubMed]

97. Nolan, M.; Parker, A.S.C.; Watson, G.W. Reduction of NOₓ on Ceria Surfaces. *J. Phys. Chem. B* 2006, 110, 2256–2262. [CrossRef] [PubMed]

98. Stubenrauch, J.; Vohs, J. Interaction of CO with Rh Supported on Stoichiometric and Reduced CeO₂(111) and CeO₂(100) Surfaces. *J. Catal.* 1996, 159, 50–57. [CrossRef]

99. Mullins, D.; Zhang, K. Metal–support interactions between Pt and thin film cerium oxide. *Surf. Sci.* 2002, 513, 163–173. [CrossRef]
100. Senanayake, S.; Zhou, J.; Baddorf, A.; Mullins, D. The reaction of carbon monoxide with palladium supported on cerium oxide thin films. *Surf. Sci.* 2007, 601, 3215–3223. [CrossRef]

101. Nolan, M.; Watson, G.W. The Surface Dependence of CO Adsorption on Ceria. *J. Phys. Chem. B* 2006, 110, 16600–16606. [CrossRef]

102. Müller, C.; Freysoldt, C.; Baudin, M.; Hermansson, K. An ab initio study of CO adsorption on ceria(110). *Chem. Phys.* 2005, 318, 180–190. [CrossRef]

103. Herschend, B.; Baudin, M.; Herrmann, K. CO adsorption on CeO$_2$(110) using hybrid-DFT embedded-cluster calculations. *Chem. Phys.* 2006, 328, 345–353. [CrossRef]

104. Yang, Z.; Woo, T.K.; Hermansson, K. Strong and weak adsorption of CO on CeO$_2$ surfaces from first principles calculations. *Chem. Phys. Lett.* 2004, 396, 384–392. [CrossRef]

105. Spezzati, G.; Benavidez, A.D.; DeLaRiva, A.T.; Su, Y.; Hofmann, J.P.; Assahina, S.; Olivier, E.J.; Neethling, J.H.; Müller, J.T.; Datye, A.K.; et al. CO oxidation by Pd supported on CeO$_2$(100) and CeO$_2$(111) facets. *Appl. Catal. B Environ.* 2018, 243, 36–46. [CrossRef]

106. Polychronopoulou, K.; AlKhoori, A.A.; Efstathiou, A.M.; Jaoude, M.A.; Damaskinos, C.M.; Baker, M.A.; Almutawa, A.; Anjum, D.H.; Vasilidades, M.A.; Belabbes, A.; et al. Design Aspects of Doped CeO$_2$ for Low-Temperature Catalytic CO Oxidation: Transient Kinetics and DFT Approach. *ACS Appl. Mater. Interfaces* 2021, 13, 22391–22415. [CrossRef] [PubMed]

107. Senanayake, S.; Mullins, D.R. Redox Pathways for HCOOH Decomposition over CeO$_2$(110) Surfaces. *J. Phys. Chem. C* 2008, 112, 9744–9752. [CrossRef]

108. Senanayake, S.D.; Stacchiola, D.; Evans, J.; Estrella, M.; Barrio, L.; Pérez, M.; Hrbek, J.; Rodriguez, J.A. Probing the reaction intermediates for the water–gas shift over inverse CeO$_x$/Au(111) catalysts. *J. Catal.* 2010, 271, 392–400. [CrossRef]

109. Lykhach, Y.; Staudt, T.; Streber, R.; Lorenz, M.P.; Bayer, A.; Steinrück, H.-P.; Libuda, J. CO$_2$ activation on single crystal based ceria and magnesia/ceria model catalysts. *Eur. Phys. J. B* 2010, 75, 89–100. [CrossRef]

110. Staudt, T.; Lykhach, Y.; Tsud, N.; Skála, T.; Prince, K.C.; Matolin, V.; Libuda, J. Ceria reoxidation by CO$_2$: A model study. *J. Catal.* 2010, 275, 181–185. [CrossRef]

111. Albrecht, P.M.; Jiang, D.-E.; Mullins, D.R. CO$_2$ Adsorption as a Flat-Lying, Tridentate Carbonate on CeO$_2$(100). *J. Phys. Chem. C* 2014, 118, 9042–9050. [CrossRef]

112. Hahn, K.R.; Iannuzzi, M.; Seitsonen, A.P.; Hutter, J. Coverage Effect of the CO$_2$ Adsorption Mechanisms on CeO$_2$(111) by First Principles Analysis. *J. Phys. Chem. C* 2013, 117, 1701–1711. [CrossRef]

113. Cheng, Z.; Sherman, B.J.; Lo, C. Carbon dioxide activation and dissociation on ceria (110): A density functional theory study. *J. Chem. Phys.* 2013, 138, 014702. [CrossRef]

114. Slavin, A.; Bent, B.; Kao, C.-T.; Somorjai, G. Thermal fragmentation of ethylene on the Rh(100) single crystal surface in the temperature range of 200–800 K. *Surf. Sci.* 1988, 206, 124–144. [CrossRef]

115. Dubois, L.H.; Castner, D.G.; Somorjai, G.A. The chemisorption of acetylene and ethylene on Rh(111): A low energy electron diffraction (LEED), high resolution electron energy loss (ELS), and thermal desorption mass spectrometry (TDS) study. *J. Chem. Phys.* 1980, 72, 5234–5240. [CrossRef]

116. Castner, D.; Sexton, B.; Somorjai, G. Leed and thermal desorption studies of small molecules (H$_2$, O$_2$, CO, CO$_2$, NO, C$_2$H$_4$, C$_2$H$_2$, AND C) chemisorbed on the rhodium (111) and (100) surfaces. *Surf. Sci.* 1978, 71, 519–540. [CrossRef]

117. Ferriz, R.; Egami, T.; Vohs, J. Temperature programmed desorption study of the reaction of C$_2$H$_4$ and CO on Rh supported on $\alpha$-Al$_2$O$_3$(0001), YSZ(100) and CeO$_2$ thin films. *Surf. Sci.* 2000, 465, 127–137. [CrossRef]

118. Mullins, D.R.; Zhang, K. Interaction between NO and C$_2$H$_4$ on Rh-Loaded CeOx(111). *J. Phys. Chem. B* 2001, 105, 1374–1380. [CrossRef]

119. Ferriz, R.; Egami, T.; Vohs, J. The reaction of ethylene on a model automotive emissions control catalyst. *Catal. Lett.* 1999, 61, 33–38. [CrossRef]

120. Wilson, E.L.; Grau-Crespo, R.; Pang, C.L.; Cabailh, G.; Chen, Q.; Purton, J.A.; Catlow, C.R.A.; Brown, W.A.; De Leeuw, N.; Thornton, G. Redox Behavior of the Model Catalyst Pd/CeO$_2$–Pt(111). *J. Phys. Chem. C* 2008, 112, 10918–10922. [CrossRef]

121. Skála, T.; Tsud, N.; Prince, K.C.; Matolin, V. Formation of alumina–ceria mixed oxide in model systems. *Appl. Surf. Sci.* 2011, 257, 3682–3687. [CrossRef]

122. Skála, T.; Štšař, F.; Cabala, M.; Škoda, M.; Prince, K.C.; Matolin, V. A photoemission study of the interaction of Ga with CeO$_2$(111) thin films. *Appl. Surf. Sci.* 2008, 254, 6860–6864. [CrossRef]

123. Zhou, Y.; Zhou, J. Ti/CeO$_x$(111) interfaces studied by XPS and STM. *Surf. Sci.* 2012, 606, 749–753. [CrossRef]

124. Vilé, G.; Bridier, B.; Wichert, J.; Pérez-Ramírez, J. Ceria in hydrogenation catalysis: High selectivity in the conversion of alkynes to olefins. *Angew. Int. Ed. Chem.* 2012, 51, 8620–8623. [CrossRef]

125. Carrasco, J.; Vilé, G.; Fernández-Torre, D.; Perez, R.; Pérez-Ramírez, J.; Ganduglia-Pirovano, M.V. Molecular-Level Understanding of CeO$_2$ as a Catalyst for Partial Alkyne Hydrogenation. *J. Phys. Chem. C* 2014, 118, 5352–5360. [CrossRef]

126. Rosid, S.J.M.; Toemen, S.; Iqbal, M.M.A.; Abu Bakar, W.A.W.; Mokhtar, W.N.A.W.; Aziz, M.A. Overview of lanthanide oxide catalysts on mechanism reaction for natural gas production. *Environ. Sci. Pollut. Res.* 2019, 26, 36124–36140. [CrossRef]

127. Meil, D.; Deskins, N.A.; Dupuis, M.; Ge, Q. Methanol Adsorption on the Clean CeO$_2$(111) Surface: A Density Functional Theory Study. *J. Phys. Chem. C* 2007, 111, 10514–10522. [CrossRef]

128. Lin, S.S.; Chen, C.L.; Chang, D.J.; Chen, C.C. Catalytic wet air oxidation of phenol by various CeO$_2$ catalysts. *Water Res.* 2002, 36, 3009–3014. [CrossRef]
156. Bozoa, C.; Guilhaume, N.; Herrmannb, J.M. Role of the Ceria–Zirconia Support in the Reactivity of Platinum and Palladium Catalysts for Methane Total Oxidation under Lean Conditions. J. Catal. 2001, 203, 393–406. [CrossRef]

157. Del Angel, G.; Padilla, J.; Cuauhtémoc, I.; Navarrete, J. Toluene combustion on γ-Al2O3–CeO2 catalysts prepared from boehmite and cerium nitrate. J. Mol. Catal. A Chem. 2008, 281, 173–178. [CrossRef]

158. Gádlová, J.; Topka, P.; Káluža, L.; Solcová, O. Gold versus platinum on ceria–zirconia mixed oxides in oxidation of ethanol and toluene. Catal. Today 2011, 175, 231–237. [CrossRef]

159. Heynderickx, P.M.; Thybaut, J.W.; Poelman, H.; Poelman, D.; Marin, G.B. The total oxidation of propane over supported Cu and Ce oxides: A comparison of single and binary metal oxides. J. Catal. 2010, 272, 109–120. [CrossRef]

160. Hu, C.; Zhu, Q.; Jiang, Z.; Chen, L.; Wu, R. Catalytic combustion of dilute acetone over Cu-doped ceria catalysts. Chem. Eng. J. 2009, 152, 583–590. [CrossRef]

161. Tang, X.; Chen, J.; Li, Y.; Li, Y.; Xu, Y.; Shen, W. Complete oxidation of formaldehyde over Ag/MnOx–CeO2 catalysts. Chem. Eng. J. 2006, 118, 119–125. [CrossRef]

162. Ousmane, M.; Liotta, L.; Di Carlo, G.; Pantaleo, G.; Venezia, A.M.; Deganello, G.; Retailleau, L.; Boreave, A.; Giroir-Fendler, A. Supported Au catalysts for low-temperature abatement of propane and toluene, as model VOCs: Support effect. Appl. Catal. B Environ. 2011, 101, 629–637. [CrossRef]

163. Sedjame, H.-J.; Fontaine, C.; Lafaye, G.; Barbier, J. On the promoting effect of the addition of ceria to platinum based alumina catalysts for VOCs oxidation. Appl. Catal. B Environ. 2013, 144, 233–242. [CrossRef]

164. Hutchings, G.J.; Heneghan, C.S.; Hudson, I.D.; Taylor, S.H. Uranium-oxide-based catalysts for the destruction of volatile chloro-organic compounds. Nature 1996, 384, 341–343. [CrossRef]

165. Lin, L.; Chai, Y.; Zhao, B.; Wei, W.; He, D.; He, B.; Tang, Q. Photocatalytic oxidation for degradation of VOCs. Open J. Inorg. Chem. 2013, 3, 14–25. [CrossRef]

166. Scire, S. Pt catalysts supported on H-type zeolites for the catalytic combustion of chlorobenzene. Appl. Catal. B Environ. 2003, 45, 117–125. [CrossRef]

167. Brink, R.V.D.; Krzan, M.; Feijen-Jeurissen, M.; Louw, R.; Mulder, P. The role of the support and dispersion in the catalytic combustion of chlorobenzene on noble metal based catalysts. Appl. Catal. B Environ. 2000, 24, 255–264. [CrossRef]

168. Brink, R.V.D.; Louw, R.; Mulder, P. Increased combustion rate of chlorobenzene on Pt/γ-Al2O3 in binary mixtures with hydrocarbons and with carbon monoxide. Appl. Catal. B Environ. 2000, 25, 229–237. [CrossRef]

169. Dai, Q.; Wang, X.; Lu, G. Low-temperature catalytic combustion of trichloroethylene over cerium oxide and catalyst deactivation. Appl. Catal. B Environ. 2008, 81, 192–202. [CrossRef]

170. Agarwal, S.; Spivey, J.; Butt, J. Deep oxidation of hydrocarbons. Appl. Catal. A Gen. 1992, 81, 239–255. [CrossRef]

171. Miran, H.A.; Altarawneh, M.; Jiang, Z.-T.; Oskierski, H.; Almatarneh, M.; Dlugogorski, B.Z. Decomposition of selected chlorinated volatile organic compounds by ceria (CeO2). Catal. Sci. Technol. 2017, 7, 3902–3919. [CrossRef]

172. Dai, Q.; Wang, X.; Lu, G. Low-temperature catalytic combustion of chlorobenzene on activated carbon. Catal. Sci. Technol. 2013, 4, 172–181. [CrossRef]

173. Miran, H.A.; Altarawneh, M.; Jaf, Z.N.; Rahman, M.M.; Almatarneh, M.H.; Jiang, Z.-T. Influence of the variation in the Hubbard parameter (U) on activation energies of CeO2 catalysts prepared from boehmite and cerium nitrate. J. Catal. 2008, 255, 233–242. [CrossRef]

174. Kumar, P.; Tanwar, M.; Bensaid, S.; Russo, N.; Fino, D. Soot combustion improvement in diesel particulate filters catalyzed with ceria nanofibers. J. Catal. 2011, 272, 191–195. [CrossRef]

175. Aneggi, E.; Wiater, D.; de Leitenburg, C.; Llorca, J.; Trovarelli, A. Shape-Dependent Activity of Ceria in Soot Combustion. Sci. Rep. 2016, 6, 29062. [CrossRef]

176. Kusmierek, E. A CeO2 Semiconductor as a Photocatalytic and Photoelectrocatalytic Material for the Remediation of Pollutants in Industrial Wastewater: A Review. Catalysts 2020, 10, 1435. [CrossRef]

177. Kanakaraju, S.; Mohan, S.; Sood, A. Optical and structural properties of reactive ion beam sputter deposited CeO2 films. Thin Solid Films 1997, 305, 191–195. [CrossRef]

178. Avellaneda, C.O.; Berton, M.A.; Bulhöes, L.O. Optical and electrochemical properties of CeO2 thin film prepared by an alkoxide route. Sol. Energy Mater. Sol. Cells 2008, 92, 240–244. [CrossRef]

179. Zong, M.; Song, D.; Zhang, X.; Huang, X.; Lu, X.; Rosso, K.M. Facet-Dependent Photodegradation of Methylene Blue by Hematite Nanoplates in Visible Light. Environ. Sci. Technol. 2020, 55, 677–688. [CrossRef] [PubMed]

180. Yang, J.; Xie, N.; Zhang, J.; Fan, W.; Huang, Y.; Tong, Y. Defect Engineering Enhances the Charge Separation of CeO2 Nanorods toward Photocatalytic Methyl Blue Oxidation. Nanomaterials 2020, 10, 2307. [CrossRef]

181. Miran, H.A.; Jaf, Z.N.; Khaleel, I.H.; Alkhafaji, A.A. Photocatalytic and Optical Performances of CeO2 by Substitution of Titanium. Phys. Chem. Res. 2021, 9, 553–564. [CrossRef]

182. Habib, I.Y.; Burhan, J.; Jaladi, F.; Lim, C.M.; Usman, A.; Kumara, N.; Tsang, S.C.E.; Mahadi, A.H. Effect of Cr doping in CeO2 nanostructures on photocatalysis and H2O2 assisted methylene blue dye degradation. Catal. Today 2020, 375, 506–513. [CrossRef]

183. Mohamadi, S.; Ghorbanali, M. Adsorption and UV-assisted photodegradation of methylene blue by CeO2-decorated graphene sponge. Sep. Sci. Technol. 2020, 1–11. [CrossRef]
185. Li, H.; Xia, P.; Pan, S.; Qi, Z.; Fu, C.; Yu, Z.; Kong, W.; Chang, Y.; Wang, K.; Wu, D.; et al. The Advances of Ceria Nanoparticles for Biomedical Applications in Orthopaedics. *Int. J. Nanomed.* 2020, 15, 7199–7214. [CrossRef]

186. Nadeem, M.; Khan, R.; Afridi, K.; Nadhman, A.; Ullah, S.; Faisal, S.; Mabood, Z.U.; Hano, C.; Abbasi, B.H. Green Synthesis of Cerium Oxide Nanoparticles (CeO$_2$ NPs) and Their Antimicrobial Applications: A Review. *Int. J. Nanomed.* 2020, 15, 5951–5961. [CrossRef]

187. Xu, C.; Qu, X. Cerium oxide nanoparticle: A remarkably versatile rare earth nanomaterial for biological applications. *NPG Asia Mater.* 2014, 6, e90. [CrossRef]

188. Ju, X.; Fučíková, A.; Šmíd, B.; Nováková, J.; Matolínová, I.; Matolín, V.; Janata, M.; Bělinová, T.; Kalbáčová, M.H. Colloidal stability and catalytic activity of cerium oxide nanoparticles in cell culture media. *RSC Adv.* 2020, 10, 39373–39384. [CrossRef]

189. Miri, A.; Darroudi, M.; Sarani, M. Biosynthesis of cerium oxide nanoparticles and its cytotoxicity survey against colon cancer cell line. *Appl. Organomet. Chem.* 2019, 34, e5308. [CrossRef]

190. Al-Mashhadani, A.H. Study of in vitro and in vivo free radical scavenging activity for radioprotection of cerium oxide nanoparticles. *Iraqi J. Phys. (IJP)* 2018, 15, 40–47. [CrossRef]

191. Garcia, I.M.; Leitune, V.C.B.; Takimi, A.S.; Bergmann, C.P.; Samuel, S.M.W.; Melo, M.A.; Collares, F.M. Cerium Dioxide Particles to Tune Radiopacity of Dental Adhesives: Microstructural and Physico-Chemical Evaluation. *J. Funct. Biomater.* 2020, 11, 7. [CrossRef]

192. Trovarelli, A.; Llorca, J. Ceria Catalysts at Nanoscale: How Do Crystal Shapes Shape Catalysis? *ACS Catal.* 2017, 7, 4716–4735. [CrossRef]

193. Lei, W.; Zhang, T.; Gu, L.; Liu, P.; Rodriguez, J.A.; Liu, G.; Liu, M. Surface-Structure Sensitivity of CeO$_2$ Nanocrystals in Photocatalysis and Enhancing the Reactivity with Nanogold. *ACS Catal.* 2015, 5, 4385–4393. [CrossRef]

194. Sehar, S.; Naz, I.; Rehman, A.; Sun, W.; Alhewairini, S.S.; Zahid, M.N.; Younis, A. Shape-controlled synthesis of cerium oxide nanoparticles for efficient dye photodegradation and antibacterial activities. *Appl. Organomet. Chem.* 2020, 35, e6069. [CrossRef]

195. Dong, F.; Meng, Y.; Han, W.; Zhao, H.; Tang, Z. Morphology effects on surface chemical properties and lattice defects of Cu/CeO$_2$ catalysts applied for low-temperature CO oxidation. *Sci. Rep.* 2019, 9, 12056. [CrossRef]

196. Li, J.; Liu, Z.; Cullen, D.A.; Hu, W.; Huang, J.; Yao, L.; Peng, Z.; Liao, P.; Wang, R. Distribution and Valence State of Ru Species on CeO$_2$ Supports: Support Shape Effect and Its Influence on CO Oxidation. *ACS Catal.* 2019, 9, 11088–11103. [CrossRef]

197. Mori, K.; Jida, H.; Kuwahara, Y.; Yamashita, H. CoOx-decorated CeO$_2$ heterostructures: Effects of morphology on their catalytic properties in diesel soot combustion. *Nanoscale* 2019, 12, 1779–1789. [CrossRef]

198. Ibrahim, I.M. The effect of rear earth doping CdS nanostructure on structural, optical and photoconductivity properties. *Iraqi J. Phys.* 2019, 17, 108–118. [CrossRef]