Roles of Oxygen Vacancies of CeO$_2$ and Mn-Doped CeO$_2$ with the Same Morphology in Benzene Catalytic Oxidation

Min Yang $^1$, Genli Shen $^2$, Qi Wang $^2$, Ke Deng $^2$, Mi Liu $^2$, Yunfa Chen $^3$, Yan Gong $^2$,* and Zhen Wang $^2$,*

1 School of Chemistry and Biological Engineering, University of Science and Technology, Beijing 100083, China; yangmin@ustb.edu.cn
2 CAS Key Laboratory of Standardization and Measurement for Nanotechnology, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China; shengl@nanoctr.cn (G.S.); wangy@nanoctr.cn (Q.W.); kdeng@nanoctr.cn (K.D.); liumi@nanoctr.cn (M.L.)
3 State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China; yfchen@home.ipe.ac.cn

* Correspondence: gongyan@nanoctr.cn (Y.G.); wangzh@nanoctr.cn (Z.W.); Tel.: +86-10-82545927 (Y.G.); +86-10-82545755 (Z.W.); Fax: +86-10-62525716 (Z.W.)

Abstract: Mn-doped CeO$_2$ and CeO$_2$ with the same morphology (nanofiber and nanocube) have been synthesized through hydrothermal method. When applied to benzene oxidation, the catalytic performance of Mn-doped CeO$_2$ is better than that of CeO$_2$, due to the difference of the concentration of O vacancy. Compared to CeO$_2$ with the same morphology, more oxygen vacancies were generated on the surface of Mn-doped CeO$_2$, due to the replacement of Ce ion with Mn ion. The lattice replacement has been analyzed through XRD, Raman, electron energy loss spectroscopy and electron paramagnetic resonance technology. The formation energies of oxygen vacancy on the different exposed crystal planes such as (110) and (100) for Mn-doped CeO$_2$ were calculated by the density functional theory (DFT). The results show that the oxygen vacancy is easier to be formed on the (110) plane. Other factors influencing catalytic behavior have also been investigated, indicating that the surface oxygen vacancy plays a crucial role in catalytic reaction.

Keywords: Mn-doped CeO$_2$; pure CeO$_2$; morphology; oxygen vacancy; benzene oxidation

1. Introduction

Volatile organic compounds (VOCs) are a type of low-boiling point organic matter which contains aromatic hydrocarbons, straight-chain alkane and cycloalkanes, etc. [1]. VOCs can be produced in industrial process and daily life and bring harm to human health and environment. Hence, it is particularly urgent to limit VOC emissions [2]. There are many methods to remove VOCs, in which catalytic oxidation is considered to be the most effective method due to its destructive efficiency, lower operating temperature and less by-products [3,4]. At present, two types of common catalysts have been widely researched: one is precious metal type and the other is transition metal oxide type. The application of former is limited due to the cost, sintering risk and facile poisoning. In contrast, the transition metal oxide is attracting more attention owing to the high-stability, low cost and high oxidation activity at low temperatures [5–7]. In recent years, transition metal based oxides catalysts exhibited excellent catalytic behaviors towards the removal of VOCs, such as Mn-based [8–10] and Co-based [11,12] metal oxide catalysts.

Additionally, rare-earth oxides have also attracted wide attention over the VOCs catalytic oxidation. CeO$_2$, as typical rare earth oxide has been investigated in the field of heterogeneous catalysis and exhibits enhanced performances for VOC oxidation due to its outstanding redox property and oxygen storage capacity (OSC). It is worthy to note that the microstructure of CeO$_2$ is closely related with the catalytic activity, especially crystal plane defects. Trovarelli and Llorca [13] reported different planes of CeO$_2$ possessed different
content of oxygen vacancy. The activity of CeO$_2$ for VOC oxidation is sensitive to the proportion of surface oxygen defects in the catalyst [14]. Once the surface active oxygen vacancies are covered by intermediates or carbon deposition, the catalytic behavior of CeO$_2$ will be poisoned [15,16]. In order to increase the content of active sites, transition metals are often used to be doped or composited with CeO$_2$ to produce more oxygen vacancies. Among the transition metals doped catalysts, Mn-based catalysts are widely used in the field of environmental catalysis [17,18]. It is reported that Mn-doped CeO$_2$ has been applied in the abatement of contaminants, such as the catalytic reduction of NO and diesel soot combustion, which exhibit excellent catalytic activity [19–23].

In this article, we have investigated the catalytic behavior of pure CeO$_2$ and Mn-doped CeO$_2$ with the same morphology through the complete catalytic oxidation of benzene. Their catalytic activities differences and crystal structures are analyzed in detail. Meanwhile, density function theory (DFT) was adopted to simulate crystal plane structure and calculate the formation energy of oxygen vacancies on the certain exposed plane. Although the effect of oxygen vacancy in pure CeO$_2$ on the catalytic property has been recognized, however the influence of dopants in oxygen vacancy for doped CeO$_2$ need to be described further. In addition, the difference of oxygen vacancy on the different exposed crystal plane has less been studied. Therefore, the research aims to explore the effect of crystal plane structure and dopant (Mn ion) dispersion on the formation of oxygen vacancy and analyze the roles of oxygen vacancy in the combustion of benzene further.

2. Materials and Methods

2.1. The Preparation of CeO$_2$–MnO$_x$ Composite Oxides

The chemicals used in this work, including Ce(NO$_3$)$_3$·6H$_2$O (99%), Mn(NO$_3$)$_2$ solution (50%), NaOH (98%), and ethanol, were purchased from Beijing Chemicals Company (Beijing, China). Mn-doped CeO$_2$ with different morphologies (nanofiber: NF and nanocube: NC) were synthesized by a hydrothermal process. Firstly, Ce(NO$_3$)$_3$·6H$_2$O and Mn(NO$_3$)$_2$ in given amount (Ce/Mn mole ratio = 9/1) were dissolved in a 10 mL H$_2$O and mixed with a 6 M NaOH solution. The solution was stirred for 0.5 h at room temperature then transferred to an autoclave (100 mL) and gradually heated to a certain temperature, e.g., 120 °C for NF while 160 °C for NC, respectively. The reaction at the targeting temperature was kept for 24 h. After the reaction, the precipitates in autoclaves were collected by centrifugation, washed with distilled water and ethanol several times. The obtained materials, labeled as Ce-Mn-NF and Ce-Mn-NC respectively, were dried at 80 °C overnight and calcined at 550 °C for 4 h. Pure CeO$_2$ with fiber and cube morphology were also prepared using the similar process as reference, labeled as CeO$_2$-NF and CeO$_2$-NC respectively.

2.2. Characterization

The crystal phases of the catalysts were characterized by X-ray diffraction (XRD) using Philips X'pert PRO analyzer (Philips, Amsterdam, The Netherlands) equipped with a Cu Kα radiation source (λ = 0.154187 nm) at a scanning rate of 0.03°/s (2θ from 10° to 90°).

Scanning electron microscopy (SEM JC-Zeiss Merlin) and Transmission electron microscopy (TEM Tecnai G2 F20 U-TWIN) was used to observe the morphology and structure of samples. Aberration-corrected HAADF-STEM images, Mn L$_{2,3}$-edge and Ce M$_{4,5}$-edge electron energy loss spectroscopy (EELS) were performed from FEI Titan electron microscope equipped with a Gatan Enfnium camera system.

The surface composition and chemical states were determined by X-ray photoelectron spectroscopy (XPS ESCALAB250Xi). The binding energy (BE) was calibrated using the C1s line at 284.8 eV.

Raman spectra were measured with a Raman spectrometer (Renishaw inVia plus). The excitation source was an Ar$^+$ ion laser (λ = 514.23 nm) and the laser power was 20 mW.
Reactive oxygen species were identified by the electron paramagnetic resonance technology (EPR) at room temperature on a Bruker EMX spectrometer (Bruker Corp., Billerica, MA, USA) at a frequency of 9.8 GHz and a magnetic field of 100 kHz.

Hydrogen temperature-programmed reduction (H2-TPR) was performed on AutoChem 2920 chemisorption analyzer. Firstly, the sample (40–60 mesh) was heated to 150 °C and maintained at this temperature for 1h in 5% O2 and 95% He mixture (30 mL/min), and then cooled to 50 °C under He flow. The samples were then heated again to 900 °C in 10% H2 and 90% Ar mixture (50 mL/min). The heating rate is 10°C/min. The thermal conductivity detector signal was detected.

2.3. Catalytic Activity Tests

Activity tests for catalytic oxidation of benzene over CeO2-NF, CeO2-NC, Ce-Mn-NF and Ce-Mn-NC catalysts were performed in a continuous-flow fixed-bed reactor, containing 100 mg catalyst samples (40–60 mesh), respectively. The total reactant flow rate was 100 mL·min⁻¹, containing (100 ppm benzene + 20 vol% O2 + N2 (balance)). The weight hourly space velocity (WHSV) was typically 60,000 mL·g⁻¹·h⁻¹. The concentrations of Benzene, CO2, and CO were analyzed on-line using a gas GC/MS (Hewlett-Packard 6890N and Hewlett-Packard 5973N). 5.0 vol% water vapor was introduced to the system by a water saturator at 34 °C. Catalytic activities were characterized by two parameters (T50 and T90). For a catalyst, T50 and T90 represent the temperature of 50 and 90% benzene conversion, respectively. The benzene conversion and CO2 selectivity are calculated as following Equations (1) and (2). [Benzene]in and [Benzene]out are the inlet and outlet Benzene concentrations during catalytic reaction):

\[
\text{Benzene conversion (\%) = } \frac{[\text{Benzene}]_{\text{in}} - [\text{Benzene}]_{\text{out}}}{[\text{Benzene}]_{\text{in}}} \times 100\% 
\]

\[
\text{CO2 selectivity (\%) = } \frac{[\text{CO2}]_{\text{out}}}{([\text{CO}]_{\text{out}} + [\text{CO2}]_{\text{out}})} \times 100\% 
\]

2.4. Details of DFT + U Calculation

First-principles calculations based on density functional theory (DFT) were carried out with the Vienna Ab-initio simulation package (VASP) and PBE functional. The interaction between core electrons and valence electrons was expressed by the projector-augmented wave (PAW) method. The cutoff energy of the plane-wave basis set was set to 550 eV. To guarantee the accuracy, the convergence criteria of energy and force were set to 10⁻⁵ eV and 0.05 eV·Å⁻¹, respectively. DFT + U with U = 5eV was applied to treat Ce 4f orbital. A model was built based on a 2 × 2 × 2 CeO2 supercell. The Brillouin zone of (100) and (110) models were sampled by a 3 × 3 × 1 k-point set to acquire similar sampling densities. Before calculation, no more than half of the atomic layers from the bottom were fixed.

3. Results and Discussion

3.1. Characterization of Catalysts

The crystal structures of CeO2-NF, CeO2-NC, Ce-Mn-NF and Ce-Mn-NC was examined by XRD. As seen in Figure 1a, the diffraction peaks at 2θ = 28.5°, 33.0°, 47.4°, 56.4°, 59.2°, 69.5°, 76.6°, 79.1° and 88.6° clearly demonstrate the presence of cubic fluorite structure of CeO2 (PDF# 81-0792). For Mn-doped CeO2 (Ce-Mn-NF and Ce-Mn-NC), the patterns do not show any diffraction of manganese oxides, and only broad reflections are observed, which should be attributed to the formation of Ce-O-Mn solid solution. It is worthy to note that the characteristic diffraction peak of CeO2 (2θ = 28.5°) in the Mn-doped CeO2 moves to little bit higher value due to the decrease of the lattice parameter caused by the dopant Mn ions with smaller size, compared with the pure CeO2 (Figure 1b).
CeO$_2$ moves to little bit higher value due to the decrease of the lattice parameter caused by the dopant Mn ions with smaller size, compared with the pure CeO$_2$ (Figure 1b). The lattice parameters of all the samples have been calculated according to the XRD data and listed in Table 1. The result shows that the lattice parameters of the Mn-doped CeO$_2$ are lower than those of pure CeO$_2$ with the same morphology. The ionic radius of Mn$^{n+}$ (Mn$^{2+}$ (0.067 nm), Mn$^{3+}$ (0.066 nm) and Mn$^{4+}$ (0.053 nm)) are all smaller than that of the Ce$^{4+}$ (0.1098 nm), therefore, the incorporation of Mn$^{n+}$ into the CeO$_2$ lattice to form Ce-O-Mn solid solution could result in lattice contraction due to the doping of Mn$^{n+}$ and the consequent formation of the more oxygen vacancies.

**Table 1.** Lattice parameters and extent of expansion of synthesized samples compared with those of pure CeO$_2$.

| Samples          | Lattice Parameters (a) (Å) | Extent of Deviation ($\times 10^{-4}$) |
|------------------|----------------------------|--------------------------------------|
| CeO$_2$-NF       | 5.40864                    | 10.06                                |
| Ce-Mn-NF         | 5.40842                    | 11.94                                |
| CeO$_2$-NC       | 5.41061                    | 4.02                                 |
| Ce-Mn-NC         | 5.40878                    | 11.52                                |

The morphology and structure of samples were characterized by SEM and TEM, respectively. Figure 2a shows the SEM image of CeO$_2$-NF. It can be seen that CeO$_2$-NF with a fiber morphology has an average diameter of about 10 nm and length of about 150–300 nm. In the HRTEM of CeO$_2$-NF (Figure 2b), the exposed crystal planes (110) and (100) can be determined obviously according to the inter-planar distance 0.19 nm and 0.27 nm, respectively. Figure 2c shows the SEM image of CeO$_2$-NC. The size of CeO$_2$-NC possessing cubic morphology is about 12–25 nm. Through the HRTEM (Figure 2d), it can be acquired that the exposed crystal plane is only (100). (111) plane also exists inside the lattice. For Ce-Mn-NF and Ce-Mn-NC, the morphology has no change compared with pure CeO$_2$ with the same morphology except the change of sample size (Figure 2e–h). In order to analyze the element distribution of Mn-doped CeO$_2$, the HAADF mapping image of Ce-Mn-NF and Ce-Mn-NC were examined, respectively (Figure 2i,j). The result exhibits that both the Ce and Mn elements are homogeneously dispersed, which favors the oxygen vacancy formation.
Figure 2. SEM and HRTEM images of CeO$_2$-NF and CeO$_2$-NC (a–d); SEM and TEM images of Ce-Mn-NF and Ce-Mn-NC (e–h); HAADF mapping images of Ce-Mn-NF and Ce-Mn-NC (i,j).

Raman scattering was used to identify the solid solution phase, which can reflect indirectly the property of oxygen vacancy. Figure 3 shows visible Raman spectra of all the samples. In the pattern, a strong peak at ca. 460 cm$^{-1}$ and a weak one at ca. 610 cm$^{-1}$ are discerned, corresponding to the fluorite F$_{2g}$ mode and a defect-induced mode (D mode), respectively [24,25]. The peaks at 275 and 1163 cm$^{-1}$ are assigned to second-order transverse and longitudinal vibration modes of cubic CeO$_2$ fluoride phase [26]. These bands at ca. 610 cm$^{-1}$ are usually assigned to the presence of extrinsic oxygen vacancies created as charge compensating defects during solid solution formation [27]. For Ce-Mn-NF and Ce-Mn-NC, a band at ca. 610 cm$^{-1}$ corresponds to the second-order Raman mode attributes of O$_2^-$ vacancies formed by a low valence dopant (Mn$^{n+}$). For pure CeO$_2$, Raman band is also detected at ca. 610 cm$^{-1}$, which is also assigned to the presence of oxygen vacancies resulted from Ce$^{4+}$ transforming to Ce$^{3+}$. The ratio of integrated peak area of oxygen vacancy (~610 cm$^{-1}$) to that of main peak (460 cm$^{-1}$), defined as $A_{610}/A_{460}$, is used here to characterize the relative amount of oxygen vacancy among these samples. The $A_{610}/A_{460}$ ratio was calculated and ranked in the order of Ce-Mn-NF > Ce-Mn-NC > CeO$_2$-NF > CeO$_2$-NC (Table 2), suggesting that Ce-Mn-NF exhibits the higher concentration of oxygen vacancies.

Table 2. Physical and chemical properties of all samples.

| Sample    | $A_{610}/A_{460}$ (%) | BE (eV) | $O_\beta/(O_\alpha+O_\beta)$ (%) | Ce$^{3+}/(Ce^{3+}+Ce^{4+})$ (%) | Mn 2p$_{3/2}$ BE (eV) |
|-----------|-----------------------|---------|---------------------------------|---------------------------------|------------------------|
|           |                       | $O_\alpha$ | $O_\beta$ |                                | Mn$^{2+}$ | Mn$^{3+}$ | Mn$^{2+}$ |
| CeO$_2$-NF | 13.9                  | 529.2    | 531.5    | 21.1                       | 8.74      | -         | -         |
| Ce-Mn-NF   | 20.9                  | 529.3    | 531.7    | 25.5                       | 11.3      | 640.9     | 641.8     | 643.1     |
| CeO$_2$-NC | 11.3                  | 529.2    | 531.6    | 17.1                       | 7.32      | -         | -         |
| Ce-Mn-NC   | 19.4                  | 529.1    | 531.5    | 22.0                       | 9.71      | 640.8     | 641.8     | 643.2     |
The oxidation state of catalyst surface species was examined by XPS analysis. Figure 4a presents the XPS spectra of the Ce3d core levels for all samples. The peaks $V_0/\gamma V_0$, $V_1/\gamma V_1$ and $V_2/\gamma V_2$ refer to three pairs of spin-orbit doublets, which can be attributed to surface Ce$^{4+}$ [28], while $U_0/\gamma U_0$ and $U_1/\gamma U_1$ can be ascribed to Ce$^{3+}$ [29]. The relative amount of Ce$^{3+}$ for all the samples can be calculated according to the Equation (3) and listed in Table 2. The result shows that the relative atomic ratio of Ce$^{3+}$/(Ce$^{3+}$ + Ce$^{4+}$) in the Ce-Mn-NF is higher than that of CeO$_2$-NF. The amount of Ce$^{3+}$ in the Ce-Mn-NC is also higher than that of CeO$_2$-NC. The data indicate that the introduction of Mn ion can increase the relative amount of Ce$^{3+}$ in the Mn-doped CeO$_2$, which might arise from the charge rebalancing of oxygen vacancies and dopant Mn$^{n+}$ [30].

$$X_{\text{Ce}^{3+}} = \frac{A_{\text{Ce}^{3+}}/S_{\text{Ce}}}{\sum A_{(\text{Ce}^{3+}+\text{Ce}^{4+})}/S_{\text{Ce}}} \times 100\%$$

where $X_{\text{Ce}^{3+}}$ is the percentage content of Ce$^{3+}$, $A$ is the integrate area of characteristic peak in the XPS pattern, $S$ is sensitivity factors ($S = 7.399$).

Figure 4b depicts the O 1s XPS spectra of the CeO$_2$-NF, CeO$_2$-NC, Ce-Mn-NF and Ce-Mn-NC samples. All catalysts exhibited dominant component of lattice oxygen (O$_{\alpha}$) species, together with a shoulder of surface adsorbed oxygen (O$_{\beta}$) species on the surface vacancies. The binding energy of 529.0–530.0 eV corresponded to O$_{\alpha}$ and the binding energy of 531.0–532.0 eV was ascribed to O$_{\beta}$. The integral ratio of ($O_{\beta}/O_{\alpha} + O_{\beta}$) was applied to estimate the concentration of adsorbed oxygen species (Table 2). Ce-Mn-NF and Ce-Mn-NC samples possess more surface absorbed oxygen species compared with CeO$_2$-NF and CeO$_2$-NC, which indicate that Mn-doped CeO$_2$ contain more surface oxygen vacancy. Hence, it is inferred that the surface oxygen vacancy adsorbs and activates oxygen molecules to produce adsorbed oxygen species. This mechanism promotes the redox property of catalyst. A similar phenomenon was reported in the literature [31]. The O 1s XPS spectra results were in accordance with the XRD and Raman data.

Figure 3. Room temperature visible Raman spectra of all the samples.
literature data [32], the observed binding energy is tented to correspond to Mn$_2$O$_3$. It should be noted, though, that the BEs of various Mn ions are very close to each other, rendering impossible the exact identification of oxidation states due to overlap of the energy ranges for various oxidation states of Mn [33]. In the Figure 4c, the Mn 2p$_{3/2}$ XPS spectra were fitted by the presence of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$. The binding energy of 641.9–643 eV, 641.4–641.9 eV and 640.1–641.31 eV was ascribed to the peaks of Mn$^{4+}$, Mn$^{3+}$ and Mn$^{2+}$ species [34], respectively.

The distribution feature of oxygen vacancy can also be reflected through electron energy loss spectroscopy (EELS). The patterns of CeO$_2$ and Mn-doped CeO$_2$ are shown in Figure 5a, in which Mn L$_{2,3}$-edge and Ce M$_{4,5}$-edge spectra can be distinguished obviously. Through the Mn L$_{2,3}$-edge spectrum, it can be obtained that Mn ion exhibits mainly trivalent [35], which is consistent with the XPS data of Mn element. According to the literature [36–38], it can be acquired that the formation of oxygen vacancies is coupled with the localization delocalization effect of Ce 4f electrons. Therefore, the Ce M$_{4,5}$-edge EELS spectra were used to further investigate the distribution conditions of Ce$^{3+}$ and oxygen vacancies (Figure 5b). The proportions of Ce$^{3+}$ ([Ce$^{3+}$]) were calculated via the $M_5/M_4$ white-line ratios for every sample [39]. The data show that the relative proportions of Ce$^{3+}$ in Ce-Mn-NF (0.876) and Ce-Mn-NC (0.837) are more than those of CeO$_2$ with the same morphology (CeO$_2$-NF: 0.775, CeO$_2$-NC: 0.765) due to Mn$^{n+}$ replacing some Ce$^{4+}$, which indicate that abundant Ce$^{3+}$ exists on the surface of Mn-doped CeO$_2$ and more oxygen vacancies are formed. The conclusion has also been identified by the results of Raman and XPS.

Figure 4. XPS spectra of various catalysts over the spectral regions of Ce 3d (a), O 1s (b) and Mn 2p (c).
EPR is a sensitive to the paramagnetic species with unpaired electrons [40]. Thus, EPR spectra of the pure CeO2 and Mn-doped CeO2 samples were collected to study the oxygen vacancies and the species of reactive oxygen (·O2−, 1O2 and ·OH) [41,42]. As presented Figure 6a, pure-CeO2 (CeO2-NF and CeO2-NC) exhibited two types of peaks of Ce3+ in terms of the surface (g = 1.965) and bulk (g = 1.947). After Mn doping, Mn-doped CeO2 presented a strong EPR signal at g = 2.032, ascribed to the combination of Mn ion with one or two electrons [43,44]. The typical O2·− quartet spectrum, 1O2 triplet spectrum and ·OH spectrum can be detected for all the catalysts (Figure 6b–d). The intensities of peaks corresponding to ·O2− and 1O2 respectively in the Mn-doped CeO2 catalyst are far higher than those of CeO2. This may be due to more Ce3+ to Ce4+ transition on the catalyst surface of Mn-doped CeO2, which provided many electrons to O2 and accelerated the conversion O2 to active oxygen species. It is beneficial to accelerate the catalytic oxidation of benzene. It is worthy to note that CeO2 only exhibit ·OH characteristic quartet peaks, however Mn-doped CeO2 contain other peaks attributed to oxidized DMPO (radical scavenger) besides ·OH peaks, which indicate that Mn-doped CeO2 possess higher oxidation ability (Figure 6d). Therefore, it is easier to catalytic oxidize benzene for Mn-doped CeO2. The EPR patterns of oxidized DMPO, labeled as DMPO-X can be seen in the Supplementary Materials.

The reducible surface oxygen species of CeO2 and Mn-doped CeO2 were studied using H2-TPR as illustrated in Figure 7. The H2-TPR measurement of CeO2-NF exhibits two major reduction peaks at 478 °C and 725 °C. The two reduction peaks at 480 °C and 728 °C exist in the pattern of CeO2-NC. According to the literature [45–47], the former low-temperature reduction (478 °C and 480 °C) is due to the removal of surface oxygen and the latter high-temperature reduction (725 °C and 728 °C) is attributed to the release of oxygen species in bulk CeO2. For Ce-Mn-NF, the TPR profile exhibits three overlapping peaks at lower temperature and one peak at higher temperature. The lower temperature peaks at 240°C and 336°C are assigned to the two-step reduction of Mn2O3 (Mn2O3→Mn3O4; Mn3O4→MnO) [48], while the reduction peak at 400 °C is corresponded to the reduction of surface oxygen in CeO2. The higher temperature peak at 722 °C is attributed to the reduction of oxygen species in bulk CeO2. The H2-TPR pattern of Ce-Mn-NC is similar with that of Ce-Mn-NC. The lower temperature peaks (200 and 337 °C) correspond to the two-step reduction of Mn2O3. The peaks at 386 and 743 °C are attributed to the reduction of surface oxygen and bulk oxygen species in CeO2, respectively. In addition, the reduction peaks of Mn-doped CeO2 are shifted toward lower temperature compared with those of CeO2, which indicate the reducibility of Mn-doped CeO2 catalyst was increased due to Mn ion. Hence Mn-doped CeO2 should possess higher catalytic activities, which is in accordance with the result of EPR.
The reducible surface oxygen species of CeO\textsubscript{2} and Mn-doped CeO\textsubscript{2} were enhanced compared with CeO\textsubscript{2} with the same morphology. Meanwhile, the lower temperature peaks (200 and 337 °C) and one peak at higher temperature. The lower temperature reduction (478 °C and 480 °C) is due to the removal of surface oxygen and the species of reactive oxygen (·O\textsubscript{2-}, 1O\textsubscript{2} and ·OH) \[41,42\]. As previously mentioned, Mn-doped CeO\textsubscript{2} exhibits ·OH characteristic quartet peaks, however Mn-O\textsubscript{2}− or two electrons \[43, 44\]. The typical·O\textsubscript{2-} quartet spectrum, 1O\textsubscript{2} triplet spectrum and ·OH spectrum can be detected for all the catalysts (Figure 6b–d). The intensities of peaks corresponding to ·O\textsubscript{2-} and 1O\textsubscript{2} respectively in the Mn-doped CeO\textsubscript{2} catalyst are far higher than those of Ce-Mn-NC. The lower temperature peaks (200 and 337 °C) and one peak at higher temperature. The lower temperature reduction (478 °C and 480 °C) is due to the removal of surface oxygen and the species of reactive oxygen (·O\textsubscript{2-}, 1O\textsubscript{2} and ·OH) \[41,42\].

The typical·O\textsubscript{2-} quartet spectrum, 1O\textsubscript{2} triplet spectrum and ·OH spectrum can be detected for all the catalysts (Figure 6b–d). The intensities of peaks corresponding to ·O\textsubscript{2-} and 1O\textsubscript{2} respectively in the Mn-doped CeO\textsubscript{2} catalyst are far higher than those of Ce-Mn-NC. The lower temperature peaks (200 and 337 °C) and one peak at higher temperature. The lower temperature reduction (478 °C and 480 °C) is due to the removal of surface oxygen and the species of reactive oxygen (·O\textsubscript{2-}, 1O\textsubscript{2} and ·OH) \[41,42\].

The reducible surface oxygen species of CeO\textsubscript{2} and Mn-doped CeO\textsubscript{2} were enhanced compared with CeO\textsubscript{2} with the same morphology. Meanwhile, the lower temperature peaks (200 and 337 °C) and one peak at higher temperature. The lower temperature reduction (478 °C and 480 °C) is due to the removal of surface oxygen and the species of reactive oxygen (·O\textsubscript{2-}, 1O\textsubscript{2} and ·OH) \[41,42\]. As previously mentioned, Mn-doped CeO\textsubscript{2} exhibits ·OH characteristic quartet peaks, however Mn-O\textsubscript{2}− or two electrons \[43, 44\]. The typical·O\textsubscript{2-} quartet spectrum, 1O\textsubscript{2} triplet spectrum and ·OH spectrum can be detected for all the catalysts (Figure 6b–d). The intensities of peaks corresponding to ·O\textsubscript{2-} and 1O\textsubscript{2} respectively in the Mn-doped CeO\textsubscript{2} catalyst are far higher than those of Ce-Mn-NC. The lower temperature peaks (200 and 337 °C) and one peak at higher temperature. The lower temperature reduction (478 °C and 480 °C) is due to the removal of surface oxygen and the species of reactive oxygen (·O\textsubscript{2-}, 1O\textsubscript{2} and ·OH) \[41,42\].

Figure 6. Electron paramagnetic resonance signals of all the samples (a), superoxide radical (b), singlet oxygen (c) and hydroxyl radical (d).

Figure 7. H\textsubscript{2}-TPR profiles of CeO\textsubscript{2}-NF, CeO\textsubscript{2}-NC, Ce-Mn-NF and Ce-Mn-NC.
3.2. Catalytic Oxidation Activity towards Benzene

The catalytic activities of Mn-doped CeO$_2$ and pure CeO$_2$ with the same morphology were evaluated by their oxidation performance towards benzene (Figure 8a). It can be seen that the catalytic activity decreases in the order of Ce-Mn-NF, Ce-Mn-NC, CeO$_2$-NF and CeO$_2$-NC, which is consistent with that of oxygen vacancy concentration. The oxygen vacancy is closely related with the catalytic activity. $T_{50}$ and $T_{90}$ on Ce-Mn-NF is 278 and 395 °C respectively, which are much lower than those on Ce-Mn-NC (304/450 °C) and pure phase oxide. The catalytic activities of the catalysts were also compared based on the yield of CO$_2$. From the Figure 8b, it can be also obtained that the catalytic properties of Mn-doped CeO$_2$ are enhanced compared with CeO$_2$ with the same morphology. Meanwhile benzene has almost been converted into CO$_2$ completely without the detection of any other gas. Water vapor is a common component of industrial waste gas, therefore the impact of water vapor on catalytic activity is requisite. The impact of 5.0 vol% water vapor introduction on catalytic activities of Ce-Mn-NC and Ce-Mn-NF at 400 °C was conducted (Figure 8c,d). As a result, the introduction of 5.0 vol% water vapor leads to benzene conversion dropping from 91% to 77% for Ce-Mn-NC and 83% to 67% for Ce-Mn-NF, respectively. After 10 h of continuous 5.0 vol% water vapor injection, the benzene percent conversion for Ce-Mn-NC and Ce-Mn-NF is completely recovered upon the cutting off of the water vapor feeding. The competitive adsorption between H$_2$O and benzene molecules onto the active sites is the main reason causing the decrease of benzene conversion. The result above indicated both of Ce-Mn-NC and Ce-Mn-NF having good water-resistant ability.

![Figure 8. Benzene conversion (%), CO$_2$ yield (%) over CeO$_2$-NF, CeO$_2$-NC, Ce-Mn-NF and Ce-Mn-NC. Effect of water vapor on the catalytic activities of Ce-Mn-NF(c) and Ce-Mn-NC (d). Water concentration = 5 vol%.

\[ E_f = E_{SV} - E_{O_2} \]

where $E_{SV}$ and $E_{O_2}$ are the total energies of the supercell with and without an oxygen vacancy, and $E_{O_2}$ is the total energy of an O$_2$ molecule [49].
3.3. DFT Calculations

Through the analysis above, we have recognized that the oxygen vacancy has an important effect on their catalytic activities; however enough theory evidences are still needed. In this article, the density functional theory (DFT) is adopted to calculate the formation energy of oxygen vacancy so that identifying its role in the catalytic reaction further (Figure 9). The defect formation energy \( E_f \) of oxygen vacancy is defined as Equation (4):

\[
E_f = E_{S,V_O} + \frac{1}{2}E_{O_2} - E_S
\]

where \( E_{S,V_O} \) and \( E_S \) are the total energies of the supercell with and without an oxygen vacancy, and \( E_{O_2} \) is the total energy of an \( O_2 \) molecule [49].

We compare the oxygen vacancy formation energies \( E_f \) on the (110) and (100) crystal planes of Mn-doped CeO\(_2\). The calculated \( E_f \) corresponding to (110) plane is -0.48 eV. In contrast, the \( E_f \) on the (100) plane increases to 4.46 eV. The result means that the oxygen vacancy is easier to be formed on the (110) plane than (100) plane, which also indicate Mn ion is easier to be doped on the (110) plane. Given the central role of oxygen vacancy in catalyst [50,51], the Ce-Mn-NF [exposed (110) and (100) planes] is therefore expected to show better performance than Ce-Mn-NC [exposed (100) plane] and pure CeO\(_2\) (CeO\(_2\)-NF and CeO\(_2\)-NC), which is consistent with the results of benzene catalytic degradation. In addition, the distances of Ce-O near the oxygen vacancy in the Mn-doped CeO\(_2\), whether (110) or (100) planes, have only slight differences compared with those of CeO\(_2\) which may be caused by the substitution of Mn ion. The distance data of Ce-O bond can be seen in Supplementary Materials.

3.4. Factor Influencing the Catalytic Activity

Through the analysis, it has been acquired that Mn-doped CeO\(_2\) performs higher activity than pure CeO\(_2\) with the same morphology over catalytic oxidation of benzene. Oxygen vacancy is considered to be a critical factor in catalytic performances. For Mn-doped CeO\(_2\), the existence of Ce-Mn solid solution results in the formation of more oxygen vacancies compared with CeO\(_2\) due to incorporate Mn into CeO\(_2\) crystal lattice, which can provide more surface active sites to adsorb active oxygen species. This phenomenon has also been identified through the analysis of TPR, in which Mn-doped CeO\(_2\) possesses more highly reducible surface species closely related with surface oxygen vacancy. In addition, exposed crystal plane can also influence the catalytic activity, which is also attributed to the oxygen vacancy due to the different formation energy of oxygen vacancy on the exposed crystal planes. Based on this, Ce-Mn-NF exhibits higher catalytic ability than Ce-Mn-NC.
As we known, the oxidation of organic molecules over transition metal oxide or mixed metal oxide catalysts involves two identical mechanisms: a Langmuir-Hinshelwood mechanism and a Mars-van Krevelen mechanism [52,53]. At lower temperature, the adsorbed oxygen species with higher activity can enhance the adsorption and oxidation of VOCs, which match with Langmuir-Hinshelwood mechanism. It mainly contains four steps: (1) benzene molecule is adsorbed on the exposed crystal plane to form π-complex of benzene due to the interaction of benzene ring with catalyst; (2) gas-phase oxygen molecule is activated on the crystal plane to adsorb in surface vacancies; (3) the attack of active surface oxygen species to benzene ring; (4) benzene ring breakage and the formation of final products. When the reaction temperature rises, the adsorbed organic molecules are oxidized by the oxygen of metal oxides, which is consistent with the Mars-van Krevelen mechanism. It involves a similar process: (1) adsorption of benzene molecule; (2) the attack of lattice oxygen released from the catalyst to benzene ring; (3) benzene ring breakage and deep oxidation to final products. In addition, there are also two key elements involved in this process: (i) oxygen vacancies formed are replenished by the surface active oxygen species; (ii) active oxygen species are transported and delivered through the bulk oxygen vacancy (Figure 10). In summary, oxygen vacancy as transport medium, is the link of the whole reaction, therefore it has an important role in determining the catalytic activity.

4. Conclusions

Pure CeO$_2$ and Mn-doped CeO$_2$ with the same morphology (nanofiber and nanocube) were synthesized through hydrothermal method and the complete catalytic oxidation of benzene was examined. The results showed that Mn-doped CeO$_2$ possessed higher activity than pure CeO$_2$ with the same morphology due to the formation of more oxygen vacancies. In the Mn-doped CeO$_2$, Ce-Mn-NF exhibited better catalytic behavior than Ce-Mn-NC, which was closely related the exposed crystal planes. Ce-Mn-NF exposed (110) and (100) planes, while Ce-Mn-NC exposed only (100) plane. According to theoretical calculation, the formation energy of oxygen vacancy on the (110) plane is much less than that on (100),

![Provisional figure showing proposed mechanism for benzene oxidation over Mn-doped CeO$_2$ on different crystal planes.](image-url)
which indicate that oxygen vacancy is easier formed and more surface active species is adsorbed on the (110) plane resulting in the higher catalytic property of Ce-Mn-NF. In general, the effect of crystal plane on the activity is also attributed to the oxygen vacancy. Therefore, oxygen vacancy is a key factor in the process of catalytic reaction.

Supplementary Materials: The following are available online, Figure S1. Electron paramagnetic resonance signals of DMPO-X: (a) Ce-Mn-NF, (b) Ce-Mn-NC; Figure S2. The distances of Ce-O on the surface and in bulk: (a) CeO$_2$ (100) plane, (b) Mn-doped CeO$_2$ (100) plane, (c) CeO$_2$ (110) plane, (d) Mn-doped CeO$_2$ (110) plane.

Author Contributions: Conceptualization: M.Y., Q.W., Z.W.; methodology: M.Y., G.S.; software: K.D.; validation: M.Y., Y.G., Z.W.; formal analysis: M.Y., M.L.; resources: Z.W., Q.W.; data curation: M.Y., G.S.; writing—original draft preparation: M.Y.; writing—review and editing: Y.G., Z.W.; visualization: M.L.; supervision: Y.G., Z.W.; project administration: Y.C., K.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the National Key R&D Program of China (No. 2016YFC0207100) and the National Basic Research Program of China (No. 2017YFA0205000).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: Thanks for many constructive suggestions given by Lan Chen.

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

References

1. Kong, J.J.; Xiang, Z.W.; Li, G.Y.; An, T.C. Introduce oxygen vacancies into CeO$_2$ catalyst for enhanced coke resistance during photothermocatalytic oxidation of typical VOCs. Appl. Catal. B Environ. 2020, 269, 118755. [CrossRef]

2. Zhang, C.H.; Huang, H.; Li, G.Q.; Wang, L.; Song, L.; Li, X.B. Zeolitic acidity as a promoter for the catalytic oxidation of toluene over MnO$_x$ /HZSM-5 catalysts. Catal. Today 2019, 327, 374–381. [CrossRef]

3. Ma, C.Y.; Mu, Z.; Li, J.J.; Jin, Y.G.; Cheng, J.; Lu, G.Q.; Hao, Z.P.; Qiao, S.Z. Mesoporous Co$_3$O$_4$ and Au/Co$_3$O$_4$ Catalysts for Low-Temperature Oxidation of Trace Ethylene. J. Am. Chem. Soc. 2010, 132, 2608–2613. [CrossRef]

4. Wang, Y.F.; Zhang, C.B.; Liu, F.D.; He, H. Well-dispersed palladium supported on ordered mesoporous Co$_3$O$_4$ for catalytic oxidation of o-xylene. Appl. Catal. B Environ. 2013, 142, 72–79. [CrossRef]

5. Zhang, C.H.; Wang, C.; Zhan, W.C.; Guo, Y.L.; Guo, Y.; Lu, G.Z.; Baylet, A.; Giror-Fendler, A. Catalytic oxidation of vinyl chloride emission over LaMnO$_3$ and La$_{1.5}$Mg$_{0.5}$O$_3$ (B = Co, Ni, Fe) catalysts. Appl. Catal. B Environ. 2013, 129, 509–516. [CrossRef]

6. Kolodziej, A.; Lojewska, J.; Tyczkowski, J.; Jodlowski, P.; Redzynia, W.; Iwaniszyn, M.; Zapotoczny, S.; Kustrowski, P. Coupled engineering and chemical approach to the design of a catalytic structured reactor for combustion of VOCs: Cobalt oxide catalyst on knitted wire gauzes. Chem. Eng. J. 2012, 200, 329–337. [CrossRef]

7. Mo, S.P.; Li, S.D.; Li, W.H.; Li, J.Q.; Chen, J.Y.; Chen, Y.F. Excellent low temperature performance for total benzene oxidation over mesoporous CoMnAl composite oxides from hydroxalites. J. Mater. Chem. A. 2016, 4, 8113–8122. [CrossRef]

8. Zhao, L.L.; Zhang, Z.P.; Li, Y.S.; Leng, X.S.; Zhang, T.R.; Yuan, F.L.; Niu, X.Y.; Zhu, Y.J. Synthesis of Ce$_x$MnO$_x$ hollow microsphere with hierarchical structure and its excellent catalytic performance for toluene combustion. Appl. Catal. B Environ. 2019, 245, 502–512. [CrossRef]

9. Chang, Y.F.; McCarty, J.G. Novel oxygen storage components for advanced catalysts for emission control in natural gas fueled vehicles. Catal. Today 1996, 30, 163–170. [CrossRef]

10. Zhang, X.D.; Lv, X.T.; Bi, F.K.; Lu, G.; Wang, Y.X. Highly efficient Mn$_2$O$_3$ catalysts derived from Mn-MOFs for toluene oxidation: The influence of MOFs precursors. Mol. Catal. 2020, 482, 110701. [CrossRef]

11. Zhou, G.L.; He, X.L.; Liu, S.; Xie, H.M.; Fu, M. Phenyl VOCs catalytic combustion on supported CoMn/AC oxide catalyst. J. Ind. Eng. Chem. 2015, 21, 932–941. [CrossRef]

12. Xie, X.W.; Li, Y.; Liu, Z.Q.; Haruta, M.; Shen, W.J. Low-temperature oxidation of CO catalysed by Co$_3$O$_4$ nanorods. Nature 2009, 458, 746–749. [CrossRef]

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

14. Lopez, J.M.; Gilbank, A.L.; Garcia, T.; Solsona, B.; Agouram, S.; Torrente-Murciano, L. The prevalence of surface oxygen vacancies over the mobility of bulk oxygen in nanostructured ceria for the total toluene oxidation. Appl. Catal. B Environ. 2015, 174, 403–412. [CrossRef]

15. Yang, C.T.; Miao, G.; Pi, Y.H.; Xia, Q.B.; Wu, J.L.; Li, Z.; Xiao, J. Abatement of various types of VOCs by adsorption/catalytic oxidation: A review. Chem. Eng. J. 2019, 370, 1128–1153. [CrossRef]
16. Weon, S.; Choi, W. TiO<sub>2</sub> Nanotubes with Open Channels as Deactivation-Resistant Photocatalyst for the Degradation of Volatile Organic Compounds. *Environ. Sci. Technol.* 2016, *50*, 2556–2563. [CrossRef] [PubMed]

17. Lin, R.; Liu, W.P.; Zhong, Y.J.; Luo, M.F. Catalyst characterisation and activity of Ag-Mn complex oxides. *Appl. Catal. A Gen.* 2001, *220*, 165–171. [CrossRef]

18. Quirioz, J.; Giraudon, J.M.; Gervasio, A.; Dujardin, C.; Lancelot, C.; Trentesaux, M.; Lamonier, J.F. Total Oxidation of Formaldehyde over MnO<sub>x</sub>-CeO<sub>x</sub> Catalysts: The Effect of Acid Treatment. *Acad. Catal.* 2013, *5*, 2260–2269. [CrossRef]

19. Qi, G.S.; Yang, R.T.; Chang, R. MnO<sub>x</sub>-CeO<sub>x</sub> mixed oxides prepared by co-precipitation for selective catalytic reduction of NO with NH<sub>3</sub> at low temperatures. *Appl. Catal. B Environ.* 2004, *51*, 93–106. [CrossRef]

20. Qi, G.S.; Yang, R.T. Performance and kinetics study for low-temperature SCR of NO with NH<sub>3</sub> over MnO<sub>x</sub>-CeO<sub>x</sub> catalyst. *J. Catal.* 2003, *217*, 434–441. [CrossRef]

21. Guo, Z.Y.; Liang, Q.H.; Yang, Z.Y.; Liu, S.; Huang, Z.H.; Kang, F.Y. Modifying porous carbon nanofibers with MnO<sub>x</sub>-CeO<sub>x</sub> mixed oxides for NO catalytic oxidation at room temperature. *Catal. Sci. Technol.* 2016, *6*, 422–425. [CrossRef]

22. Zhang, J.; Cao, Y.D.; Wang, C.A.; Ran, R. Design and Preparation of MnO<sub>2</sub>/CeO<sub>2</sub>-MnO<sub>2</sub> Double-Shelled Binary Oxide Hollow Spheres and Their Application in CO Oxidation. *ACS Appl. Mater. Inter.* 2016, *8*, 8670–8677. [CrossRef] [PubMed]

23. Xing, L.L.; Yang, X.Y.; Cao, C.M.; Zhao, D.Y.; Gao, Z.N.; Ren, W.; Tian, Y.; Ding, T.; Li, X.G. Decorating CeO<sub>2</sub> Nanoparticles on MnO<sub>2</sub>Nanosheets to Improve Catalytic Soot Combustion. *ACS Sustain. Chem. Eng.* 2018, *6*, 16544–16554. [CrossRef]

24. Weber, W.H.; Hass, K.C.; Mcbride, J.R. Raman-Study of CeO<sub>2</sub>Molecules. *Electrodeposited Films for the Oxygen Evolution Reaction of Water.*

25. Hu, F.Y.; Chen, J.J.; Peng, Y.; Song, H.; Li, K.Z.; Li, J.H. Novel nanowire self-assembled hierarchical CeO<sub>2</sub> microspheres for low temperature toluene catalytic combustion. *Chem. Eng. J.* 2018, *331*, 425–434. [CrossRef]

26. Du, X.J.; Zhang, D.S.; Shi, L.Y.; Gao, R.H.; Zhang, J.P. Morphology Dependence of Catalytic Properties of Ni/CeO<sub>2</sub>Nanostructures for Carbon Dioxide Reforming of Methane. *J. Phys. Chem. C.* 2012, *116*, 10009–10016. [CrossRef]

27. Souza, E.C.C.; Brito, H.F.; Muccillo, E.N.S. Optical and electrical characterisation of samaria-doped ceria. *J. Alloys Compd.* 2010, *491*, 460–464. [CrossRef]

28. Pfau, A.; Schierbaum, K.D. The electronic-structure of stoichiometric and reduced CeO<sub>2</sub> surfaces-an XPS, UPS and HREELS study. *Surf. Sci.* 1994, *321*, 71–80. [CrossRef]

29. Du, X.S.; Wang, X.M.; Chen, Y.R.; Gao, X.; Zhang, L. Supported metal sulfates on Ce-TiO<sub>x</sub>Nanotubes with Open Channels as Deactivation-Resistant Photocatalyst for the Degradation of Volatile Organic Compounds. *Environ. Sci. Technol.* 2016, *50*, 2556–2563. [CrossRef] [PubMed]

30. Lee, S.M.; Park, K.H.; Hong, S.C. MnO<sub>x</sub>/CeO<sub>2</sub>-TiO<sub>2</sub> mixed oxide catalysts for the selective catalytic reduction of NO with NH<sub>3</sub> at low temperature. *Chem. Eng. J.* 2012, *195*, 325–331. [CrossRef]

31. Yang, W.H.; Su, Z.A.; Xu, Z.H.; Yang, W.N.; Peng, Y.; Li, J.H. Comparative study of α-, β-, γ- and δ-MnO<sub>2</sub> on toluene oxidation: Oxygen vacancies and reaction intermediates. *Appl. Catal. B Environ.* 2020, *260*, 118150. [CrossRef]

32. Machida, M.; Uto, M.; Kurogi, D.; Kijima, T. MnO<sub>x</sub>-CeO<sub>2</sub> binary oxides for catalytic NO<sub>x</sub> sorption at low temperatures. Sorptive removal of NO<sub>x</sub>. *Chem. Mater.* 2000, *12*, 3158–3164. [CrossRef]

33. Ra, T.; Shen, M.Q.; Jia, L.W.; Hao, J.J.; Wang, J. Oxidation of ethanol over Mn-Ce-O and Mn-Ce-Zr-O complex compounds synthesized by sol-gel method. *Catal. Today.* 2007, *118*, 1743–1747. [CrossRef]

34. Ramirez, A.; Hillebrand, P.; Stellmach, D.; May, M.M.; Bogdanoff, P.; Fiechter, S. Evaluation of MnO<sub>x</sub>, MnO<sub>y</sub>, and MnO<sub高于x</sub>Electrodeposited Films for the Oxygen Evolution Reaction of Water. *J. Phys. Chem. C.* 2014, *118*, 14073–14081. [CrossRef]

35. Marris, H.; Deboudt, K.; Flamant, P.; Grobety, B.; Gire, R. Fe and Mn Oxidation States in the Bulk and Surface of CeO<sub>2</sub> for Toluene Catalytic Combustion. *Environ. Sci. Technol.* 2020, *54*, 12684–12692. [CrossRef]

36. Zhang, H.; Cai, J.M.; Wang, Y.T.; Wu, M.Q.; Meng, M.; Tian, Y.; Li, X.G.; Zhang, J.; Zheng, L.R.; Jiang, Z.; et al. Insights into the effects of surface/bulk defects on photocatalytic hydrogen evolution over TiO<sub>2</sub> with exposed [001] facets. *Appl. Catal. B Environ.* 2018, *220*, 126–136. [CrossRef]

37. Ren, S.; Liang, W.J.; Li, Q.L.; Zhu, Y.X. Effect of Pd/CE loading on the performance of Pd-Ce/gamma-Al<sub>2</sub>O<sub>3</sub>catalysts for toluene abatement. *Chemosphere.* 2020, *251*, 126382. [CrossRef]

38. Xia, D.H.; Xu, W.J.; Wang, Y.C.; Yang, J.L.; Huang, Y.J.; Hu, L.L.; He, C.; Shu, D.; Leung, D.Y.C.; Pang, Z.H. Enhanced Performance and Conversion Pathway for Catalytic Ozonation of Methyl Mercaptan on Single-Atom Ag Deposited Three-Dimensional Ordered Mesoporous MnO<sub>x</sub>. *Environ. Sci. Technol.* 2018, *52*, 13399–13409. [CrossRef]

39. Qi, G.S.; Yang, R.T. Characterization and FTIR studies of MnO<sub>x</sub>-CeO<sub>2</sub>catalyst for low-temperature selective catalytic reduction of NO with NH<sub>3</sub>. *J. Phys. Chem. B.* 2004, *108*, 15738–15747. [CrossRef]
44. Yu, X.L.; Wu, X.M.; Chen, Z.Y.; Huang, Z.W.; Jing, G.H. Oxygen vacancy defect engineering in Mn-doped CeO$_2$ nanostructures for nitrogen oxides emission abatements. *Mol. Catal.* 2019, 476, 110512. [CrossRef]

45. Trovarelli, A. Catalytic properties of ceria and CeO$_2$-containing materials. *Catal. Rev.* 1996, 38, 439–520. [CrossRef]

46. Aneggi, E.; Boaro, M.; de Leitenburg, C.; Dolcetti, G.; Trovarelli, A. Insights into the redox properties of ceria-based oxides and their implications in catalysis. *J. Alloys Compd.* 2006, 408, 1096–1102. [CrossRef]

47. Tao, Zhang, M.L.; Li, J.; Li, H.J.; Li, Y.; Shen, W.J. Morphology-dependent redox and catalytic properties of CeO$_2$ nanostructures: Nanowires, nanorods and nanoparticles. *Catal. Today* 2009, 148, 179–183. [CrossRef]

48. Wang, Z.; Shen, G.L.; Li, J.Q.; Liu, H.D.; Wang, Q.; Chen, Y.F. Catalytic removal of benzene over CeO$_2$-MnO$_x$ composite oxides prepared by hydrothermal method. *Appl. Catal. B Environ.* 2013, 138, 253–259. [CrossRef]

49. Wang, Z.; Deng, Y.Z.; Shen, G.L.; Akram, S.; Han, N.; Chen, Y.F.; Wang, Q. Catalytic Degradation of Benzene over Nanocatalysts containing Cerium and Manganese. *ChemistryOpen* 2016, 5, 495–504. [CrossRef]

50. Blochl, P.E. Projector Augmented-Wave Method. *Phys. Rev. B.* 1994, 50, 17953–17979. [CrossRef]

51. Chang, S.J.; Li, M.; Hua, Q.; Zhang, L.J.; Ma, Y.S.; Ye, B.J.; Huang, W.X. Shape-dependent interplay between oxygen vacancies and Ag-CeO$_2$ interaction in Ag/CeO$_2$ catalysts and their influence on the catalytic activity. *J. Catal.* 2012, 293, 195–204. [CrossRef]

52. Santos, V.P.; Pereira, M.F.R.; Orfao, J.J.M.; Figueiredo, J.L. The role of lattice oxygen on the activity of manganese oxides towards the oxidation of volatile organic compounds. *Appl. Catal. B Environ.* 2010, 99, 353–363. [CrossRef]

53. Tang, W.X.; Wu, X.F.; Li, D.Y.; Wang, Z.; Liu, G.; Liu, H.D.; Chen, Y.F. Oxalate route for promoting activity of manganese oxide catalysts in total VOCs’ oxidation: Effect of calcination temperature and preparation method. *J. Mater. Chem. A.* 2014, 2, 2544–2554. [CrossRef]