

## Article

# Mesoporous Copper-Cerium Mixed Oxide Catalysts for Aerobic Oxidation of Vanillyl Alcohol

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**Abstract:** The production of vanillin from lignin-derived vanillyl alcohol poses a great deal of research interest because of the availability of renewable lignin in abundant quantities. In the present study, a series of copper-doped ceria ( $\text{CeO}_2$ ) catalysts were prepared by a modified template-assisted method, characterized by various techniques, and explored for the oxidation of vanillyl alcohol to vanillin with molecular oxygen as the oxidant at normal atmospheric pressure. Interestingly, a 10% Cu-doped ceria ( $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ ) catalyst exhibited superior catalytic activity for the oxidation of vanillyl alcohol with 95% and 100% conversions at atmospheric and moderate pressures, respectively, with 100% vanillin selectivity in both cases. A thorough characterization (XRD, BET surface area, Raman spectroscopy, SEM, TEM, XPS, and  $\text{H}_2$ -TPR) of the synthesized mesoporous oxides ( $\text{CuO}$ ,  $\text{CeO}_2$ ,  $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$ ,  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ , and  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$ ) revealed that mixed oxide catalysts exhibit more oxygen vacancies and better redox behavior in comparison to the single oxides, which lead to improved catalytic activity and selectivity. Reaction parameters, such as reaction temperature, reaction time, catalyst amount, and the solvent, were also optimized for the reaction.

**Keywords:** vanillin; vanillyl alcohol; lignin; mesoporous materials; cerium oxide; copper oxide; XRD; BET surface area; Raman spectroscopy; XPS; SEM; TEM;  $\text{H}_2$ -TPR



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## 1. Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is an essential substance in daily life, as it is used extensively in food and beverages as a flavoring agent. By virtue of its antimicrobial and antioxidant qualities, vanillin is also extensively used in pharmaceuticals, as well as in the chemical industry as an intermediate. In particular, vanillin is an important intermediate in the synthesis of popular drugs, such as L-dopa and trimethoprim [1–3]. Vanillin with two functional groups (aldehyde and phenolic-OH) can be considered as a building block for the preparation of various fine chemicals. Vanillin consumption is also extended to perfumes, cleaning products, and livestock foods more recently. Out of the estimated 12,000 tons of annual consumption, only 20 tons of vanillin is naturally produced from the extraction of vanilla pods, and the remaining has to be produced by synthetic routes. Therefore, vanillin has drawn the unprecedented attention of academia and industry for synthetic approaches [4–6]. A major portion (85%) of synthetic vanillin comes from the conversion of petroleum-derived guaiacol [7]. Nitro and glyoxylic methodologies are the traditional routes for the synthesis of vanillin from guaiacol, with good selectivity. However, the high cost, difficulty in the purification of products, and the formation of unwanted side products (p-aminodimethyl aniline and nitrile) are making these paths highly disadvantageous for practical purposes [8,9]. The remaining synthetic vanillin

demand has to come from the lignin sources. The production of vanillin from lignin-derived vanillyl alcohol presents a great deal of research interest because of its ready availability and its renewable nature. Further, the complex structured lignin sub-structure compounds to produce fine chemicals are viable alternatives to non-renewable petroleum-based feed stocks [10]. Lignin accounts for 30% of organic-based carbon residue, and more than 20% of biomass accounts for lignocellulose in the total biosphere mass on the earth. However, most of it is burned as fuel, and very small amounts are used for preparing fine chemicals due to its complexity [11]. Lignocellulosic biomass has been identified as an intriguing carbon feedstock for the environmentally friendly synthesis of fine chemicals. Large-scale production of vanillin from lignin resource requires a cost-effective manufacturing method to keep up with its continued demand.

Vanillin is normally produced by processes that are catalyzed by vanillyl alcohol oxidase and laccase [7,12]. Hu et al. synthesized vanillin by 4-methylguaiacol oxidation with homogeneous cobalt salen complex catalyst, using NaOH as an additive to obtain the total conversion with 86% product selectivity in 18 h [13]. Oxidation of 4-methylguaiacol with N-hydroxyphthalimide associated cobaltous chloride catalyst by using NaOH was also reported by Zhang et al. [14]. However, homogeneous catalysts are characterized by various disadvantages, such as heavy metal waste generation, formation of M-oxo dimers, resulting in fast deactivation of the catalyst, and difficulty in the separation of the catalyst after the reaction causing poor recyclability of the catalyst [15]. Most of these disadvantages can be overcome by the application of heterogeneous catalysts, which are easy to separate from the products thereby reusability of the catalyst becomes much easier. Therefore, a lot of research activity is inclined towards designing the most efficient heterogeneous catalysts for vanillyl alcohol oxidation. Various noble metal-based catalysts, namely, Au/CeO<sub>2</sub>, Ru/TiO<sub>2</sub>, Pt/C, and Pd, were investigated for several oxidation reactions by employing alkali [16,17]. Although catalytic systems based on noble metals show good catalytic performance, and they are not favorable due to economic and environmental implications [18]. Further, the use of NaOH causes catalyst deactivation by the formation of hydroxyl bridged metal complex in the presence of water, and large amounts of unwanted inorganic salts are generated during the product neutralization step [8,19]. Catalytic systems based on mixed oxides were reported to exhibit better activity compared to their single oxide counterparts owing to their cooperative electronic and redox characteristics [20]. Therefore, Cu-Ti composite oxide, Cu-Mn and Co-Mn mixed oxides, Co-Mn oxide promoted by graphene oxide, and some other catalysts were explored to produce vanillin from vanillyl alcohol oxidation [21–25].

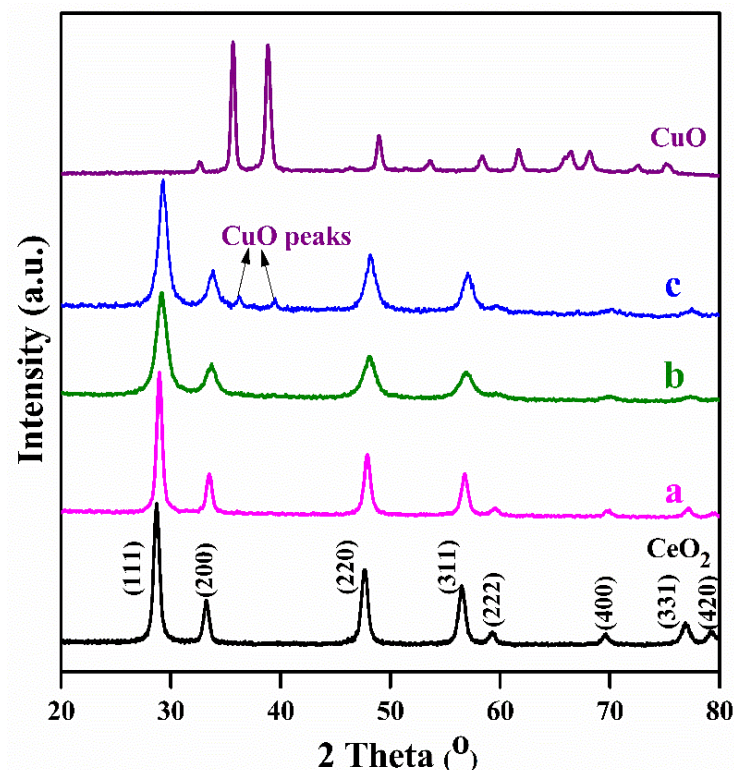
Ceria-based mixed oxide catalysts are known to exhibit very promising catalytic activity in various oxidation reactions, namely, diesel soot, ethylbenzene, benzyl alcohol, benzylamine, cyclohexene, styrene, and many other because of their superior oxygen storage/release capacity (OSC), which is attributed to the facile redox nature of the ceria ( $2\text{CeO}_2 \leftrightarrow \text{Ce}_2\text{O}_3 + \text{O}_2$ ) [26–32]. Therefore, ceria is extensively employed in three-way catalytic converters in automotive pollution control systems, where both carbon monoxide and unburnt hydrocarbons are oxidized to CO<sub>2</sub>, and NO<sub>x</sub> is reduced to harmless N<sub>2</sub> [33,34]. At high temperatures, oxygen storage capacity and redox properties of pure ceria are decreased due to poor thermal resistance and low textural stability. These drawbacks were mostly overcome by incorporating appropriate dopant cations into the ceria lattice, which increase the redox properties and a high oxygen storage and release capacity leading to better catalytic systems [35,36]. Catalytic efficiency can be fine-tuned by using an appropriate dopant such as transition or rare earth metal cation. Compared to the rare earth metals, transition elements received much research interest because of their better redox properties, variable oxidation states, low cost, and ready availability. On those lines, various ceria-based mixed oxides such as cerium-manganese, cerium-zirconium, and cerium-iron were explored for oxidation reactions at elevated temperatures and pressures [37–39]. In our quest to find an improved catalytic system for vanillyl alcohol oxidation, we have undertaken the present investigation where a series of copper-doped ceria catalysts were prepared with various

copper contents ( $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$ ,  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ , and  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$ ) by a modified template-assisted method and explored them with molecular oxygen at normal atmospheric pressure. To our surprise, the obtained results were very promising for the title reaction under mild conditions with cheaper catalysts.

## 2. Results and Discussion

### 2.1. Characterization Studies

The X-ray powder diffraction patterns of  $\text{CuO}$ - $\text{CeO}_2$  mixed oxides, ceria, and copper oxide samples are shown in Figure 1. The observed  $2\theta$  values at 28.7, 33.2, 47.7, 56.5, 59.4, 69.5, 76.8, and 79.1, corresponding to 111, 200, 220, 311, 222, 400, 331, and 420 planes confirm the cubic fluorite structure of ceria. Peaks related to copper oxide were not found in the case of  $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$  and  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  samples that could be attributed to the formation of solid solution (incorporation of  $\text{CuO}$  ions into the ceria lattice) or small clusters of  $\text{CuO}$ , which are finely dispersed on the ceria surface and could not be detected by the XRD technique [40]. However, in the  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$  sample weak diffraction peaks of  $\text{CuO}$  were observed, which implies that at higher loadings of copper the formation of bulk  $\text{CuO}$  clusters on the ceria surface can be expected. Due to a decrease in the crystallite size, doped ceria sample peak intensities are decreased and broadened in comparison to pure ceria [41]. Average crystallite sizes of prepared samples were calculated by Scherrer equation considering full width at half maximum of the most intense peak (111 plane), and the results are presented in Table 1. It is interesting to note, from Table 1, that diffraction peaks of doped  $\text{CeO}_2$  are clearly displaced to higher Bragg angles due to lattice shrinkage caused by the replacement of  $\text{Ce}^{4+}$  (0.097 nm) with smaller  $\text{Cu}^{n+}$  ions ( $\text{Cu}^{2+}$  = 0.073 nm;  $\text{Cu}^{+}$  = 0.077 nm). These results thus confirm the formation of copper-ceria solid solutions [42,43].



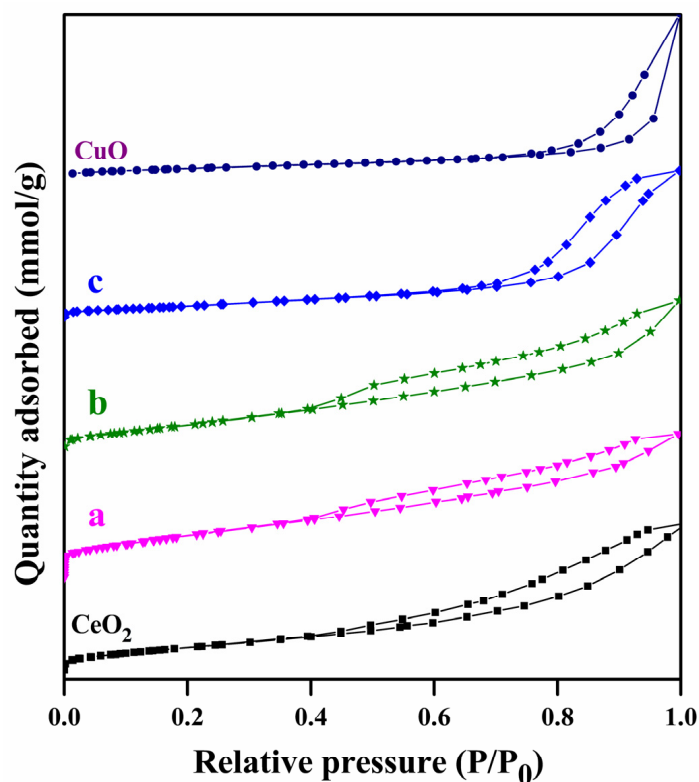
**Figure 1.** XRD patterns of  $\text{CeO}_2$ ,  $\text{CuO}$ ,  $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$  (a),  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  (b), and  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$  (c) catalysts.

**Table 1.** BET surface area (S) and mean crystallite size (D) of CeO<sub>2</sub>, CuO, Cu<sub>0.05</sub> Ce<sub>0.95</sub>O<sub>2-δ</sub>, Cu<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-δ</sub>, and Cu<sub>0.15</sub>Ce<sub>0.85</sub>O<sub>2-δ</sub> catalysts.

| Entry | Sample                                                 | S (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup> | D (nm) <sup>b</sup> |
|-------|--------------------------------------------------------|--------------------------------------------------|---------------------|
| 1     | CeO <sub>2</sub>                                       | 51                                               | 9.74                |
| 2     | CuO                                                    | 14                                               | 12.9                |
| 3     | Cu <sub>0.05</sub> Ce <sub>0.95</sub> O <sub>2-δ</sub> | 75                                               | 9.64                |
| 4     | Cu <sub>0.1</sub> Ce <sub>0.9</sub> O <sub>2-δ</sub>   | 81                                               | 6.35                |
| 5     | Cu <sub>0.15</sub> Ce <sub>0.85</sub> O <sub>2-δ</sub> | 69                                               | 7.85                |

<sup>a</sup> From BET analysis, <sup>b</sup> From XRD analysis.

The N<sub>2</sub>-physisorption isotherms of CeO<sub>2</sub>, CuO, and CuO-CeO<sub>2</sub> mixed oxides are displayed in Figure 2. The type IV isotherms with H<sub>3</sub>-type hysteresis loops positioned in the range of 0.5 to 0.98 relative pressure (P/P<sub>0</sub>) suggest that all samples are mesoporous in nature [44,45]. The BET specific surface areas and crystallite sizes are listed in Table 1. Compared to individual oxides, the mixed oxide samples show smaller crystallite sizes and a high BET surface area due to the beneficial effect of dopant ions in preventing the crystal growth of the ceria lattice, which is also revealed by XRD studies [46]. The Cu<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-δ</sub> sample shows the lowest crystallite size and a high surface area among all the other oxide catalysts prepared in this study.

**Figure 2.** N<sub>2</sub> adsorption–desorption isotherms of CeO<sub>2</sub>, CuO, Cu<sub>0.05</sub> Ce<sub>0.95</sub>O<sub>2-δ</sub> (a), Cu<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-δ</sub> (b), and Cu<sub>0.15</sub>Ce<sub>0.85</sub>O<sub>2-δ</sub> (c) catalysts.

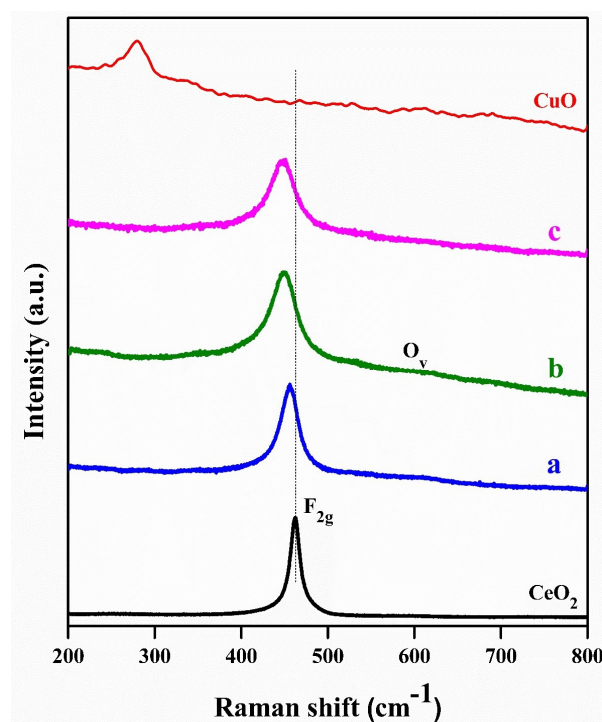
The ICP-OES analysis was undertaken to determine the Ce/Cu exact ratio in the mixed oxides, and the obtained results are presented in Table 2. The observed results are in line with the nominal values used to make the samples. These results demonstrate that the technique adopted to prepare the copper doped ceria catalysts in the present study is effective.



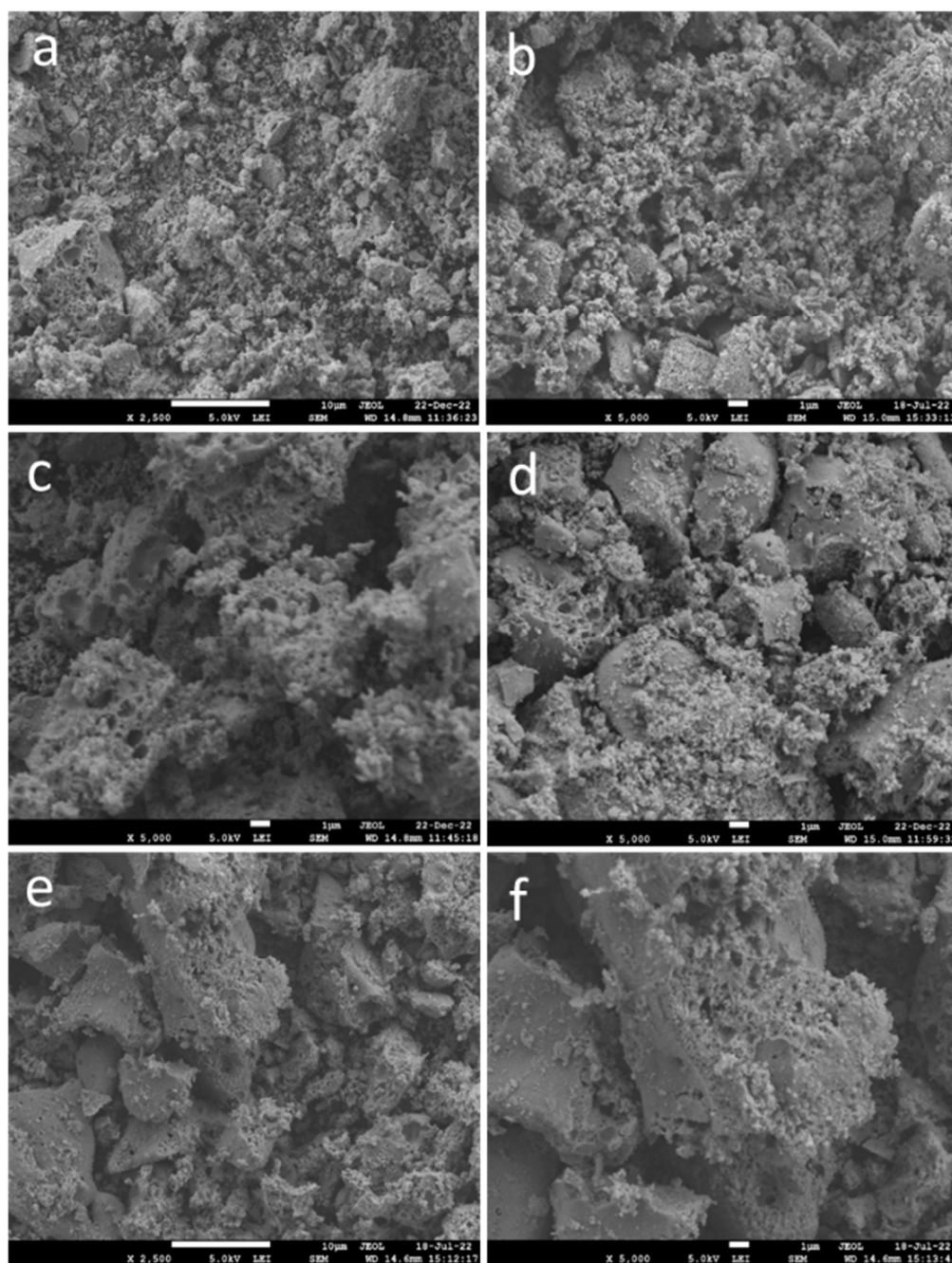
**Table 2.** ICP-OES analysis of  $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$ ,  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ , and  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$  catalysts.

| Entry | Sample                                                | Nominal Values |      | ICP-OES Analysis Values |      |
|-------|-------------------------------------------------------|----------------|------|-------------------------|------|
|       |                                                       | Ce             | Cu   | Ce                      | Cu   |
| 1     | $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$ | 0.95           | 0.05 | 0.93                    | 0.07 |
| 2     | $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$   | 0.90           | 0.10 | 0.87                    | 0.13 |
| 3     | $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$ | 0.85           | 0.15 | 0.84                    | 0.16 |

Structural changes in the  $\text{CeO}_2$  lattice that took place after the CuO doping was further investigated by Raman spectroscopy, depicted in Figure 3, which complements the XRD studies. The sharp band at  $465\text{ cm}^{-1}$  represents the  $\text{F}_{2g}$  vibrational mode related to the symmetrical breathing mode of four oxygen atoms neighboring to the  $\text{Ce}^{4+}$  ions in the  $\text{CeO}_2$ . In doped samples, as the percentage of copper increases, the  $\text{F}_{2g}$  band broadened and the peaks are shifted to lower wavelength side (peaks were red-shifted). This observation can be explained by the changes in the bonding symmetry between Ce-O atoms and the formation of extrinsic oxygen vacancies to compensate the negative charge created by introducing dopant ions [47–49]. The very broad peak (visible in expanded form) at  $595\text{ cm}^{-1}$  is attributed to oxygen vacancies [39]. It suggests that the addition of smaller sized copper ions caused a slight decrease in the lattice parameters of cubic  $\text{CeO}_2$ , creating additional oxygen vacancies, as per the earlier reports [42].

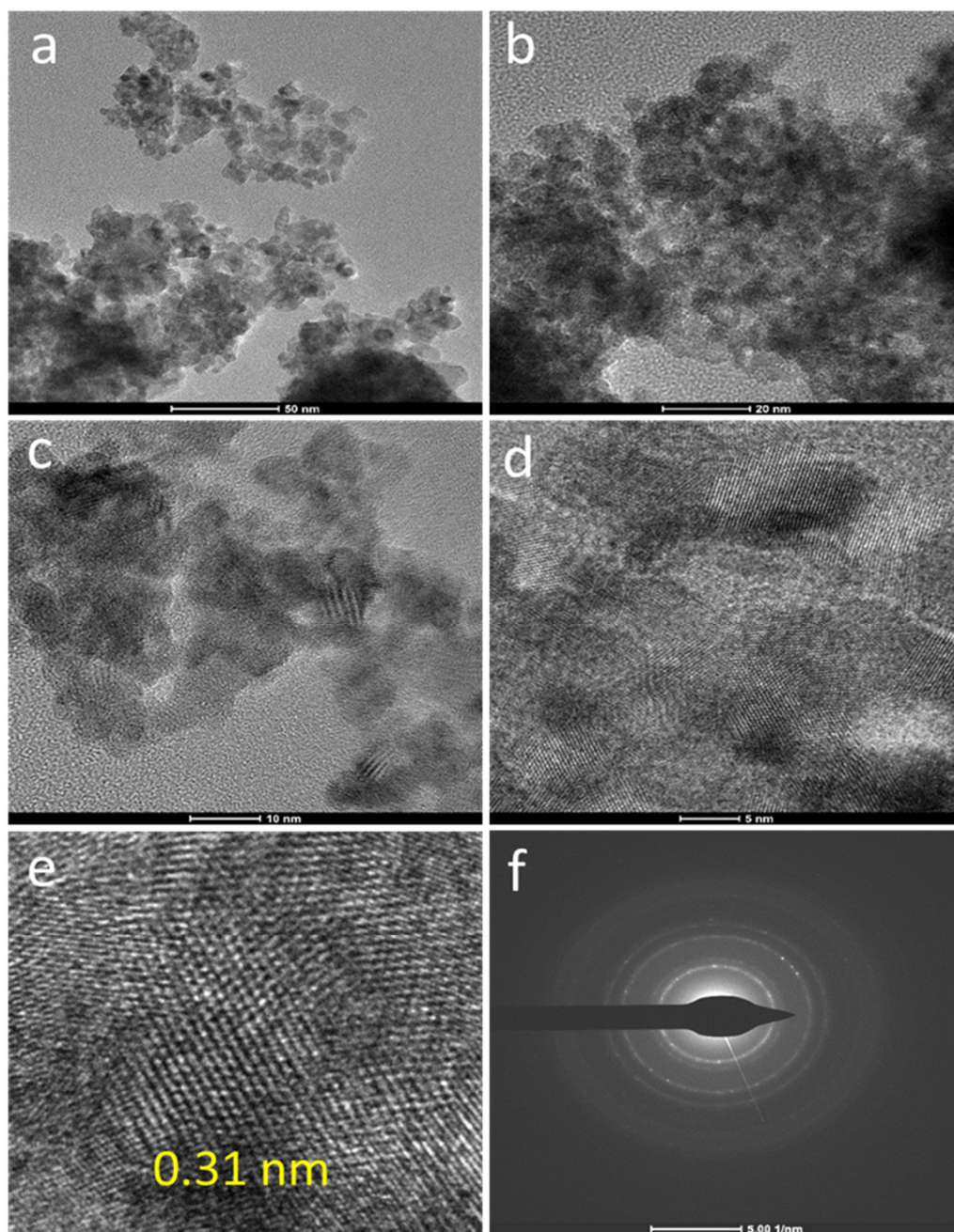
**Figure 3.** Raman spectra of  $\text{CeO}_2$ ,  $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$  (a),  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  (b),  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$  (c), and CuO catalysts.

Field Emission Scanning Electron Microscopy (FE-SEM) was used to analyze the surface morphological features of the synthesized catalysts. Figure 4 displays the FE-SEM images of pure  $\text{CeO}_2$  (a), CuO (b),  $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$  (c),  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$  (d), and  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  (e,f) samples, respectively. Nearly all samples show a definite spherical texture and morphology of the porous variety. Since all samples were prepared and processed under identical conditions, there are no significant morphological differences between different samples that can be seen in these images. However, the surface of the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  catalyst exhibits some smaller pores compared to others.



**Figure 4.** FE-SEM images of  $\text{CeO}_2$  (a),  $\text{CuO}$  (b),  $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$  (c),  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$  (d),  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  (e), and (f) catalysts.

The surface morphology of  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  sample was further studied by HRTEM and the particle size was also evaluated using the instrument software based on several images to compare with the XRD results. The representative HRTEM and SAED images of the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  sample at different areas and magnifications are shown in Figure 5. The  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  sample exhibits uniform dispersion of particles with an average particle size of about 3 to 10 nm in line with XRD results. The existence of diffraction peaks in the XRD study is clearly confirmed by all planes in the SAED spectrum. The inter-planar distance of the (111) plane in cubic fluorite structured copper doped ceria ( $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ ) is 0.31 nm.



**Figure 5.** HR-TEM images of  $(\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta})$  catalyst (a–f), enlarged d (e), and (f) SAED of the  $(\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta})$  catalyst.

The XPS technique was employed to evaluate the electronic nature of components found on the sample surface. XP spectra of CuO,  $\text{CeO}_2$ , and  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  samples are depicted in Figures 6–8, respectively. Elemental carbon 1s XP spectra at 284.5 eV were taken as references to correct the binding energies of Ce 3d, Cu 2p, and O 1s. The Ce 3d spectra of  $\text{CeO}_2$  and  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  samples exhibit two spin multiplets that are  $3d_{3/2}$  and  $3d_{5/2}$  denoted by ‘u’ and ‘v’, respectively, and, as a result, eight broad peaks are obtained in line with the literature reports and shown in Figure 6. The Ce 3d spectra of trivalent Ce compounds ( $\text{Ce}^{3+} - 3d^{10}4f^1$ ) show two peaks, namely,  $u_1$  and  $v_1$ , and the tetravalent Ce compounds ( $\text{Ce}^{4+} - 3d^{10}4f^0$ ) show six peaks that are  $u_0$ ,  $u_2$ ,  $u_3$  and  $v_0$ ,  $v_2$ ,  $v_3$ , respectively, in line with earlier reports [38,42,43]. These observations confirm the presence of both  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  ions and imply the redox nature of the synthesized catalysts. Particularly,



the presence of  $\text{Ce}^{3+}$  ions suggests the formation of oxygen vacancies in the doped ceria sample, which are crucial for the activity of the catalyst towards oxidation reactions.

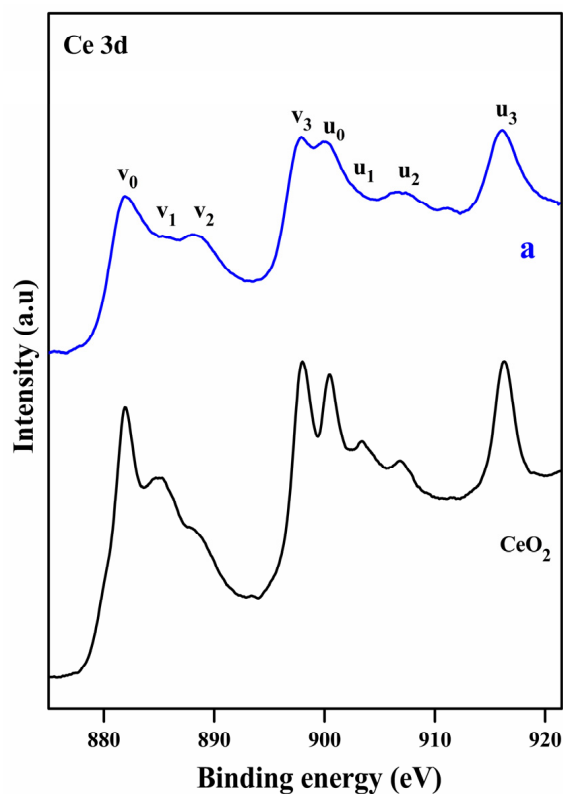


Figure 6. Ce 3d XP spectra of  $\text{CeO}_2$  and  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  (a) catalysts.

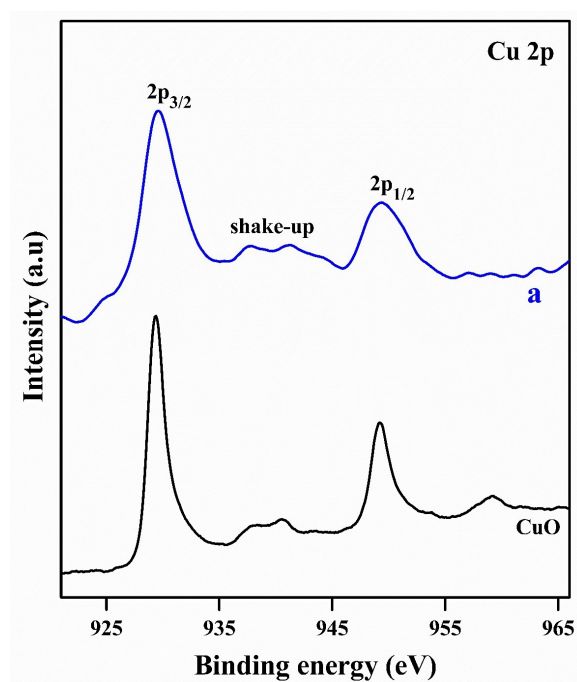


Figure 7. Cu 2p XP spectra of  $\text{CuO}$  and  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  (a) catalysts.

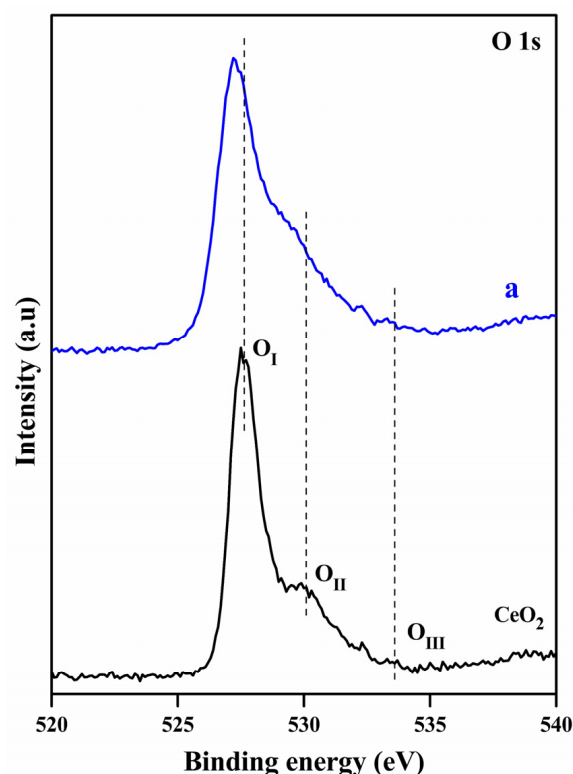


Figure 8. O 1s XP spectra of  $\text{CeO}_2$  and  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  (a) catalysts.

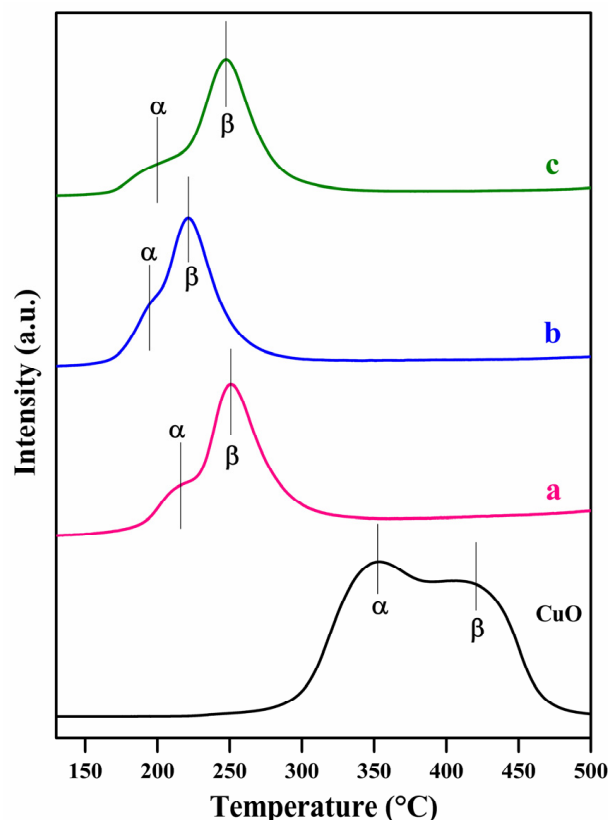
The XP spectra of Cu 2p for  $\text{CuO}$  and  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  samples are depicted in Figure 7. It can be clearly observed that the Cu  $2p_{3/2}$  XP spectrum of the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  sample shows two peaks at 949.3 eV and 929.6 eV binding energies corresponding to  $\text{Cu}^{2+}$  and  $\text{Cu}^{+1}$  oxidation states, respectively. Compared to  $\text{CuO}$ , in the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  sample, the amount of  $\text{Cu}^{2+}$  state is decreased, and the  $\text{Cu}^{+1}$  state is increased. The  $\text{Cu}^{2+}$  state is the final state, and the  $\text{Cu}^{+1}$  species is thought to be the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  catalysts' active ingredient. It is reported that copper-ceria catalyst prepared via calcination in air is more likely to include  $\text{Cu}^{+1}$  ions [39,40,50].

The XP spectrum of O 1s for the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  sample is presented in Figure 8. In the spectrum, at least three types of peaks are noticed, and the peak at 527.6 eV is ascribed to lattice oxygen ( $\text{O}_I$ ) of the metal oxide, and another peak at 530.1 eV is related to chemisorbed oxygen ( $\text{O}_{II}$ ) or poorly bonded oxygen atoms to the surface of metal oxides, and the largest binding energy peak at 533.5 eV may be attributed to water and carbonate species ( $\text{O}_{III}$ ) [41,51]. Compared to  $\text{CeO}_2$ , in the case of the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  sample, the binding energies are decreased, and peaks are broadened because of the overlapping of peaks related to the different nature of Ce and Cu atoms in the mixed oxides [39]. According to the earlier observations, surface-adsorbed oxygen species ( $\text{O}_{II}$ ) show high mobility and are responsible for oxidation processes.

The catalytic activity of ceria-based catalysts for oxidation reactions is known to be directly related to the redox properties. Therefore, the reducibility of catalysts was investigated by  $\text{H}_2$ -TPR measurements and displayed in Figure 9. According to prior studies, pure ceria exhibits two reduction peaks, one at around 500 °C of surface oxygen and the other at around 800 °C of bulk oxygen in the ceria lattice [52]. In contrast, the pure  $\text{CuO}$  reduction peaks may be seen in the  $\text{H}_2$ -TPR profile at around 350 °C and 430 °C. In copper-doped ceria samples, the presence of overlapped two-step reduction peaks at 150–350 °C suggests that the catalyst is having at least two types of copper ions. A low intensity peak at a lower temperature may be due to the reduction of  $\text{CuO}$  that is strongly bound to the  $\text{CeO}_2$  phase, which is well dispersed. Another peak with high intensity at a relatively high temperature can be attributed to the reduction of bulk  $\text{CuO}$  that is poorly bound to



the  $\text{CeO}_2$  [40,47]. Compared to the pure CuO sample, the reduction temperatures of CuO in the mixed oxides are decreased. This can be explained by the synergetic interaction between CuO and  $\text{CeO}_2$  that can improve the reducibility of CuO. Among the mixed oxide samples, the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  exhibited the lowest reduction temperature, suggesting that this catalyst shows better redox properties and consequently good catalytic activity is anticipated.

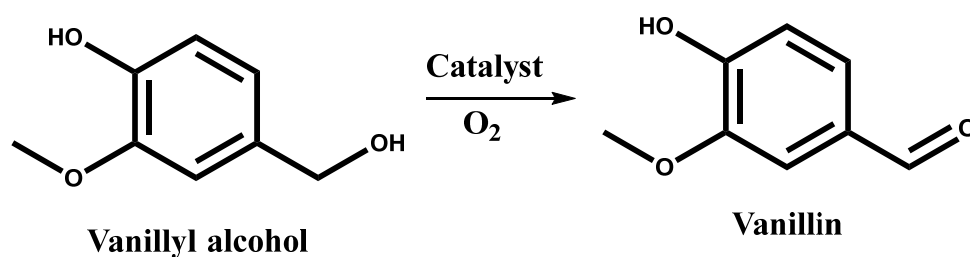


**Figure 9.**  $\text{H}_2$ -TPR of  $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$  (a),  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  (b), and  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$  (c) catalysts.

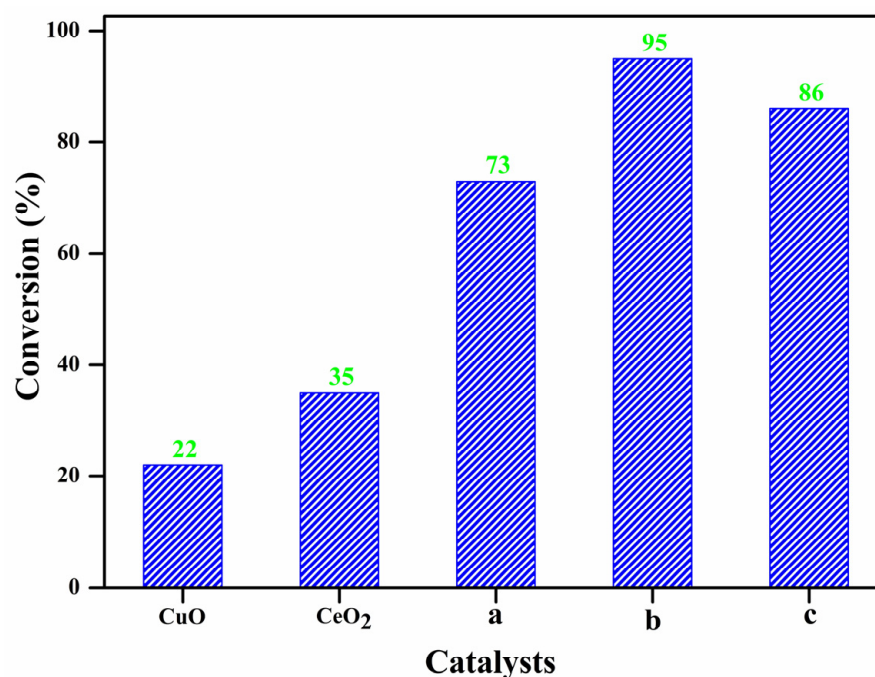
## 2.2. Catalytic Activity

The catalytic efficiency of  $\text{CeO}_2$ , CuO, and CuO- $\text{CeO}_2$  mixed oxide catalysts ( $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$ ,  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ , and  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$ ) was evaluated for oxidation of vanillyl alcohol with molecular oxygen at atmospheric pressure under base-free conditions (Scheme 1). The reaction was performed by taking vanillyl alcohol (200 mg), catalyst (50 mg), and N, N-dimethyl formamide (10 mL) into a 25 mL round bottom flask. A molecular oxygen bladder was fitted to the flask and contents were stirred for 12 h on a magnetic stirrer at 130 °C temperature. After the fixed reaction time, the contents were cooled to room temperature, catalyst was separated by centrifugation, and the liquid contents were analyzed by GC and GCMS. The obtained results are presented in Figure 10. The presence of products after the reaction were confirmed by both NMR and MS techniques, as established in the literature. Compared to the individual oxides of Ce and Cu, their mixed oxides show a high catalytic activity. The activity order among various catalysts is as follows:  $\text{CuO} < \text{CeO}_2 < \text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta} < \text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta} < \text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ . All the investigated oxide catalysts exhibited different specific surface areas. The normalized activity based on specific areas is presented in Table S1 (Supporting Information). The activity trend reveals that the specific surface area is not the primary contributor for the observed results. Therefore, the diverse activities can be explained by a strong synergetic interaction between the Ce and Cu ions to induce oxygen activation process, which is important for oxidation reactions. In general, the oxygen transfers between  $\text{Cu}^{1+}/\text{Cu}^{2+}$  and  $\text{Ce}^{3+}/\text{Ce}^{4+}$  redox cycles promote the oxygen activation, which consequently results

in good catalytic activity. Among the CuO-CeO<sub>2</sub> mixed oxide catalysts investigated, the Cu<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-δ</sub> combination catalyst shows superior catalytic activity towards vanillyl alcohol oxidation with 95% conversion and 100% selectivity to vanillin. These results provide an indication that the Ce/Cu ratio plays a key role in the modification of the structural changes in the ceria lattice. Doping of 10% CuO into CeO<sub>2</sub> lattice results in favorable changes in the physicochemical properties of ceria, which is evidenced by a high BET surface area, a greater number of oxygen vacancies, and low temperature reducibility in comparison to other samples. Therefore, the effect of various reaction parameters, such as temperature, pressure, amount of catalyst, and the reaction time on vanillyl alcohol oxidation, was thoroughly investigated using the Cu<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-δ</sub> catalyst.



**Scheme 1.** Vanillyl alcohol oxidation.



**Figure 10.** Catalytic activity of the prepared samples: Cu<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2-δ</sub> (a), Cu<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-δ</sub> (b), Cu<sub>0.15</sub>Ce<sub>0.85</sub>O<sub>2-δ</sub> (c). Reaction conditions: vanillyl alcohol (200 mg), catalyst (50 mg), O<sub>2</sub> (balloon), time (12 h), temperature (130 °C), and *N,N*-dimethylformamide (10 mL).

The impact of reaction time was investigated by performing the reaction for 3, 6, 9, and 12 h at a constant temperature of 130 °C, and the obtained results are shown in Figure S1 (SI). At 3 h time duration, the conversion of vanillyl alcohol was 41% and at 6, 9, and 12 h of reaction time the conversion was 65, 83, and 95%, respectively. After 12 h of reaction time, there was no further increase in the conversion. Therefore, a 12 h reaction time duration was found to be the optimum for the vanillyl oxidation under the experimental conditions used in this study.

The temperature effect on vanillyl alcohol oxidation was studied by varying the temperature from 70 to 130 °C, and the results are depicted in Figure S2 (SI). At 70 °C, the

conversion of vanillyl alcohol was less (24%), and, by increasing the temperature to 90 °C and 110 °C, this resulted in 39% and 62% conversion, respectively. A steep increase in conversion up to 95% with a 100% selectivity to vanillin was obtained when the temperature was increased to 130 °C. However, by raising the temperature to 140 °C, it was observed that there is no positive impact. Therefore, it can be concluded that 130 °C reaction temperature is the optimum for the oxidation of vanillyl alcohol under the investigated conditions in this study.

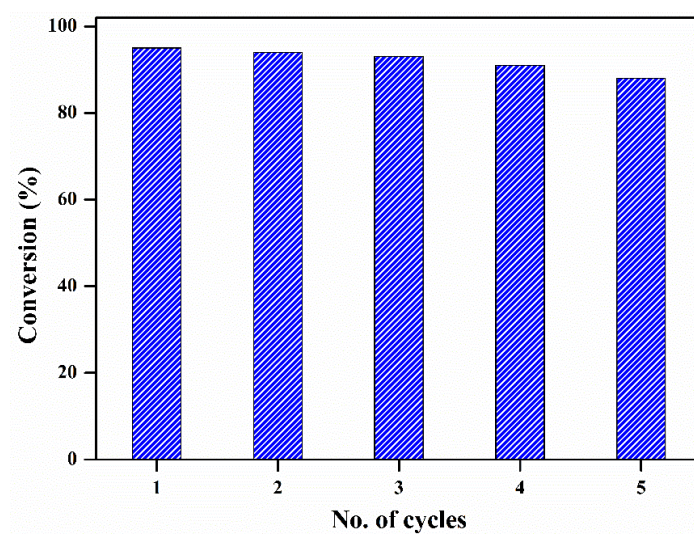
The results shown in Figure S3 (SI) explain the effect of reaction time duration at different temperatures (90, 110, 130 °C) on vanillyl alcohol oxidation. At 90 °C, the conversion of vanillyl alcohol is much less (13%) in the time frame of 3 h. By increasing the time from 3 to 12 h, the conversion increased gradually from 13 to 29%. A similar trend is observed at the investigated 110 and 130 °C temperatures, respectively. Based on these observations, we have estimated the rate constants ( $\ln(1 - X_A)$  versus reaction time) and drawn the Arrhenius plot ( $\ln(k)$  versus  $1/T$ ) for oxidation of the vanillyl alcohol reaction.

The plot between  $\ln(1 - X_A)$  and the reaction time depicted in Figure S4 (SI) shows that the rate constants are 0.02685, 0.07911, and 0.2404 h<sup>-1</sup> at 90, 110, and 130 °C temperatures, respectively, for vanillyl alcohol conversion. The reaction appears to be pseudo-first order, and the Arrhenius plot (Figure S5 of SI) based on the given  $k$  values shows an activation energy of 66.63 kJ/mol.

The impact of the catalyst amount on the reaction at 130 °C for 12 h of reaction time was examined by varying the catalyst quantity from 25 to 75 mg, and the outcomes are displayed in Figure S6 (SI). Blank (without catalyst) reaction shows very little conversion, and, with 25 mg of catalyst amount, the conversion of vanillyl alcohol was 59%. With 50 and 75 mg of catalyst amounts, the obtained conversions were 95 and 100% respectively. It is apparent, from these results, that a 50 mg of catalyst amount is adequate for vanillyl alcohol oxidation reaction under the investigated conditions.

Figure S7 (SI) illustrates the effect of various solvents on vanillyl alcohol oxidation in the presence of a Cu<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2- $\delta$</sub>  catalyst. Since some solvents have low boiling points, the reaction was carried out in 100 mL autoclave at 20 bar oxygen pressure. As observed from the results, the activity of the catalyst depends on the nature of the solvent. The conversion of vanillyl alcohol was low when non-polar solvents, such as hexane and toluene, were used as the reaction medium, while the conversion was increased with polar solvents. It is primarily due to the fact that vanillyl alcohol dissolves more readily in polar solvents than nonpolar ones. *N,N*-dimethylformamide (DMF) demonstrated superior conversion than other polar organic solvents, such as isopropanol and acetonitrile. At 20 bar pressure, the vanillyl alcohol conversion was 100% in 4 h reaction time compared to the atmospheric pressure where the conversion was 95% in 12 h reaction time.

The reusability of the Cu<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2- $\delta$</sub>  catalyst was tested for five cycles, and the results are depicted in Figure 11. After every cycle, the catalyst and reaction mixture were separated by centrifugation. The catalyst was then dried at 150 °C for 5 h after being repeatedly washed with methanol to remove impurities. The activity of the catalyst was not significantly decreased up to five cycles. However, the conversion gradually declines from the first to the fifth cycle, indicating a small deactivation of the catalyst. The selectivity of vanillin, however, remains unchanged until the fifth cycle. The used catalyst was characterized by XRD and BET surface area measurements. There was no change in the XRD patterns in comparison to the fresh catalyst, indicating that the catalyst is quite stable. However, there was a small decrease in the surface area after the catalytic experiments, indicating that there is some insignificant pore blocking during the catalytic runs.



**Figure 11.** The reusability test of the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  catalyst. Reaction conditions: vanillyl alcohol (200 mg), catalyst (50 mg),  $\text{O}_2$  (balloon), time (12 h), temperature (130 °C), and *N,N*-dimethylformamide (10 mL).

To appreciate the significance of the present catalyst, a comparison is made with some of the reported catalysts for oxidation of vanillyl alcohol to vanillin, and the reported results are presented in Table S2 (SI). As can be noted from this table, the reaction was carried out mostly under pressure at different temperatures and using different catalysts with different solvents. Only one study (entry 7) was conducted at atmospheric pressure with the same solvent. A simple comparison of the present catalyst (entry 8) with other reported catalysts reveals that it is superior in terms of conversion and product selectivity at relatively milder conditions. Further studies are under active progress to extend the reaction to longer hours (catalyst life study) with larger quantities of the catalyst for possible commercial utilization.

### 3. Experimental

#### 3.1. Catalyst Preparation

Copper doped ceria mixed oxides (denoted as  $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$ ,  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ , and  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$ ),  $\text{CeO}_2$ , and  $\text{CuO}$  catalysts were prepared by a modified template-assisted method [53]. Cerium(III) nitrate hexahydrate and copper(II) nitrate trihydrate were used as metal precursors (AR grade of Sigma-Aldrich) and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123) polymer as the template. In a typical method, required amounts of metal precursors ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) were dissolved in *n*-butanol at room temperature, to this solution appropriate amount of P123 (equal to precursors weight) was added and stirred continuously for 3 h to dissolve the contents completely, then the desired amount (precursor to nitric acid mole ratio = 1:7.5) of concentrated  $\text{HNO}_3$  was added slowly. After 30 min, the temperature was raised to 120 °C and maintained until obtaining a dry black powder. To remove the anion impurities and residual surfactant, the obtained black powder was washed with ethanol and centrifuged several times and dried at 120 °C overnight. Finally, the samples were calcined at different temperatures at various periods of time in the temperature range of 250 to 550 °C (at 250 °C for 4 h, 350 °C for 3 h, 450 °C for 2 h, and 550 °C for 1 h with 5 °C/min ramping).

#### 3.2. Catalyst Characterization

The X-ray diffraction patterns of the synthesized samples were obtained on a Rigaku Multiflex diffractometer (Rigaku, Tokyo, Japan), which was equipped with a radiation source (1.5418 Å) of nickel-filtered  $\text{Cu K}\alpha$  and a scintillation counter detector. Diffractograms were collected at the  $2\theta$  values in the range of 10–80° scale with a step size of 0.021 and a step time of 1 s per point. By using Scherrer equation, the average crystallite size (*D*)



was calculated by taking the most intense peak's full width at half maximum. The BET surface areas and pore volume distribution were measured by BELSORP II (Osaka, Japan) instrument at  $-196\text{ }^{\circ}\text{C}$  temperature. The average pore size of the samples was determined from the desorption isotherm by using the Barrett-Joyner-Halenda (BJH) method, and their specific surface areas were determined using the multipoint BET technique. The samples were degassed under a vacuum at  $250\text{ }^{\circ}\text{C}$  before analysis to remove residues that are adsorbed on the sample surface. The elemental content of the prepared samples was confirmed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICPOES) (Thermo Jarrell Ash model IRIS Intrepid II XDL, Waltham, MA USA). Raman studies were performed by using a Horiba Jobin-Yvon Labram HR Evolution confocal Raman spectrometer equipped with a liquid-nitrogen cooled charge-coupled device (CCD) detector. Samples of about  $1\text{ }\mu\text{m}$  in diameter were excited by a  $632\text{ nm}$  emission line of a  $\text{Ar}^+$  ion laser. Based on the intensity of Raman scattering, the acquiring time was adjusted, and the deviation of the wavenumber values was  $<2\text{ cm}^{-1}$ . The surface morphology of the samples was analysed by using the JEOLJSM-7610F instrument using FE-SEM. The TEM and HRTEM images of the  $\text{Ce}_{0.9}\text{Cu}_{0.1}\text{O}_2$  sample were obtained on a TECNAIG2 TEM instrument operated at  $160\text{--}200\text{ kV}$  and having a slow-scan CCD camera. Before analysis, the sample was sonicated in ethanol, and deposited a drop of it on a carbon-coated copper grid. XPS data were collected using ESCA3400 for excitation at room temperature.  $\text{Mg K}\alpha$  radiation ( $1253.6\text{ eV}$ ) was used. By keeping samples under vacuum to eliminate the contamination, the spectral noise of the contamination was minimized. The peak at  $284.6\text{ eV}$  of carbon  $1s$  ( $\text{C }1s$ ) was taken as a reference to correct the obtained binding energies of the samples. Reducibility of the prepared samples was assessed by the  $\text{H}_2$ -TPR technique, which has a temperature-programmed reactor associated with a gas chromatograph mounted with TCD. Around  $50\text{ mg}$  of the sample was loaded into a tubular reactor, pretreated at  $200\text{ }^{\circ}\text{C}$  with helium gas, and then the sample was subjected to TPR from room temperature to  $850\text{ }^{\circ}\text{C}$  with the continuous flow of  $5\%$   $\text{H}_2$  balanced in Ar.

### 3.3. Catalytic Activity Measurements

The activity of synthesized catalysts was evaluated for vanillyl alcohol oxidation with molecular oxygen as the oxidant. Typically, a  $25\text{ mL}$  round bottom flask was loaded with vanillyl alcohol ( $200\text{ mg}$ ),  $N,N$ -dimethylformamide solvent ( $10\text{ mL}$ ), and the catalyst ( $50\text{ mg}$ ). An oxygen bladder was connected to the flask, and the reaction mixture was continuously stirred ( $600\text{ rpm}$ ) at  $130\text{ }^{\circ}\text{C}$  temperature for  $12\text{ h}$ . After the specified reaction time, the catalyst was separated by centrifugation, and liquid contents were analyzed using GC with a capillary column (BP-20 wax) and GC-MS equipped with a DB-5 capillary column.

## 4. Conclusions

A series of mesoporous  $\text{CeO}_2$ ,  $\text{CuO}$ , and copper-cerium mixed oxide ( $\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$ ,  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ , and  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$ ) catalysts were prepared through a modified template-assisted method. The prepared catalysts were characterized by various techniques and evaluated for vanillyl alcohol oxidation with molecular oxygen as the oxidant. A  $10\%$  Cu-doped ceria ( $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ ) catalyst showed superior catalytic activity for vanillyl alcohol oxidation with  $95\%$  conversion and  $100\%$  vanillin selectivity at ambient pressure. The influence of the Ce/Cu mole ratio on the physicochemical properties of catalysts, as well as on their catalytic activity, was probed. XRD measurements revealed that Cu-doped catalysts had a cubic  $\text{CeO}_2$  phase and formation of solid solution with  $10\%$  and below copper content. Raman analysis confirmed a higher number of oxygen vacancies in the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  sample.  $\text{N}_2$ -adsorption and desorption measurements and the TEM study confirmed the mesoporous nature of the catalysts. The TPR results revealed that the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  sample exhibits a high redox nature. These favorable characteristics play a key role in the observed, better activity of the  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  catalyst towards vanillyl alcohol oxidation. The DMF was found to be the suitable solvent for this reaction.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13071058/s1>, Table S1: Normalized activity of catalysts with respect to BET surface area. Figure S1: Effect of reaction time over  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  catalyst; Figure S2: Effect of temperature over  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  catalyst; Figure S3: Effect of reaction time duration at various temperatures over  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  catalyst; Figure S4:  $\ln(1 - X_A)$  versus reaction time duration for oxidation of vanillyl alcohol; Figure S5: Arrhenius plot:  $\ln(k)$  versus  $1/T$  ( $T$  is in Kelvin); Figure S6: Effect of catalyst amount over  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ ; Figure S7: Effect of various solvents over  $\text{Ce}_{0.9}\text{Cu}_{0.1}\text{O}_2$  catalyst. Table S2: Comparison of present results with previously reported studies.

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