Interfaces in MOF-Derived CeO$_2$–MnO$_x$ Composites as High-Activity Catalysts for Toluene Oxidation: Monolayer Dispersion Threshold

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Abstract: A series of CeO$_2$–MnO$_x$ catalysts with different Ce contents was prepared using Mn–BTC MOF as a sacrificial template for toluene oxidation. Interestingly, the performance of CeO$_2$–MnO$_x$ increased rapidly only when the Ce content lower than 5%. The 1%-, 3%- and 10%-Ce-content samples exhibited the $T_{90}$ value of 325 °C, 291 °C and 277 °C, respectively. XRD shows that the catalyst phase changes significantly before (Mn$_3$O$_4$ only) and after (Mn$_2$O$_3$, Mn$_3$O$_4$ and CeO$_2$) 3% Ce loading. All other results indicated that the Ce–Mn interface properties of different Ce content composite oxides was quite distinguishable in terms of removal and energy efficiency. XRD and XPS results further showed that there a Ce monolayer dispersion threshold existed on the interface of MnO$_x$ (3.2 wt%, confirmed by XPS), which caused the difference in performance increment. The dispersed Ce could be divided into a monolayer dispersion state (1–3%) and a crystalline phase state (>3%), according to the existence form, which corresponded to the significant and minor enhancements of toluene conversion rate. Importantly, the Ce in monolayer dispersion state obviously improved the redox properties of catalysts interface, while the Ce in crystal state not. The interfaces with monolayer dispersion Ce result in more abundant metal ion states, oxygen vacancies, better electron transfer performance and catalytic activity.

Keywords: toluene oxidation; CeO$_2$–MnO$_x$; compound oxides; interface engineering; monolayer dispersion threshold; metal–organic frameworks

1. Introduction

Volatile organic compounds (VOCs) are common harmful gases that play a key role in the conversion of other atmospheric pollutants, such as fine particles (PM$_{2.5}$) and ground-level ozone (O$_3$) [1,2], thus making a significant impact on atmospheric environment and human health. Reducing the emission of VOCs is important in sustainable development [3,4]. Catalytic oxidation—one of the current recycling and destruction technologies—has been thought to be an effective measure to control VOCs in industries [5]. High efficiency, light secondary pollution, and low risks are the prerequisites for a generalized application. Therefore, a variety of metal oxides (MO$_x$, M = Ce, Cr, Fe, Co, Cu, Mn, etc.) are considered as economical options for the compositions of the catalysts. All the above metal oxides are considered in the order of effectiveness for VOCs. Compared to others, cerium and...
manganese oxides exhibited better catalytic activities at low temperatures in previous research [6–9]. Furthermore, both CeO$_2$ and MnO$_x$ have abundant valence changes of metal cations, surface defect sites and reactive oxygen species, which exhibit excellent electron transfer ability and make them potential catalysts [10–12].

It is well known that the catalytic oxidation of VOCs is a heterogeneous charge transfer process that mostly happens on the surface of the catalysts. To some extent, the catalytic oxidation performance is determined by the interface of catalyst particles. The catalytic performance of single oxides is limited by the natures of the material itself [13], such as the types and the number of active sites. It is difficult to significantly enhance the interfacial activity of single oxides. Thus, the synthesis and regenerative mechanism of composite oxides with higher catalytic activity have attracted wide attention. A representative question for two-component catalysts arise that whether the interfaces of compound oxides can configure properly and have more available atoms [14]. According to previous research, multiple metal oxides can first be spontaneously dispersed on the surfaces of supports to form a monolayer structure, and then grow in a crystalline state [15–17]. The monolayer dispersion threshold can be extensively perceived in activities and structures of metal oxides catalysts. Monolayer-dispersed metal oxides apparently have better catalytic activity, while the traditional methods of preparing composite oxides, such as hydrothermal method, coprecipitation method, citric acid complexation method, and reduction method, etc., do not make good use of the threshold effect [18–20]. In spite of the fact that Ce–Mn mixed oxide is one of the most widely studied catalysts for VOCs oxidation, the catalysts prepared by the above methods may still exist problems. The disadvantages such as uneven dispersion of active components, uncontrollable morphology, and agglomeration of particles usually lead to unappealing outcomes [20–22]. Using metal–organic framework materials (MOFs) as a sacrificial template is expected to surmount those restrictions. The Mesoporous structure of MOFs contain interconnected, but relatively independent spaces which can be filled by Ce ions [23,24]. They provide the possibility of forming a high-dispersion Ce–Mn composite oxide interface. Moreover, the pyrolysis of MOFs template can be controlled in a mild condition, which makes the arrangement of the interface atoms more orderly [25]. The spill out process of gas molecules (CO$_2$, H$_2$O) also could be controlled by varying calcination temperature, thus regulating the quantity and size of the interior void, which make the particle size and surface area controllable [26,27]. Previous studies have only proposed the concept of the monolayer-dispersed state and the crystalline state on the catalyst surface, which can affect the catalytic activity, while less discussion has been made on how these two states affect the catalyst activity. Moreover, the research on the threshold effect of the composite oxide prepared by the sacrificial template method is still lacking. Thus, it is necessary to clarify the changes of the intrinsic natures caused by the above two states.

In this study, a series of high-dispersed CeO$_2$–MnO$_x$ with Ce contents were successfully fabricated by calcining Ce-loading MOFs (Mn–BTC) at an optimized temperature, which all presented varying activity enhancement in toluene catalytic oxidation. The influence of the Ce contents on the interface of the Mn–MOF prepared composite oxides was particularly investigated by X-ray diffraction (XRD), X-ray photoelectron spectrometry (XPS), Raman spectra and UV-Vis diffuse reflectance spectra (UV-Vis DRS) techniques. Obviously, the state of cerium changed significantly when the monolayer loading threshold was fetched, and the metal ion states of manganese, oxygen vacancies and electron transfer performance of a CeO$_2$–MnO$_x$ changed accordingly.

2. Results and Discussion

2.1. Preliminary Experiment

2.1.1. Characterization of Mn–MOF

The crystallinity of Mn–MOF template was examined by XRD. As shown in Figure S1a, the diffraction peaks of the Mn–BTC were in good agreement with the PDF#26–1233 and literature result [10]. The Mn–MOF used in this work was composed of Mn$^{2+}$ and H$_3$BTC (hence also called
Mn-BTC). One Mn$^{2+}$ and six oxygen atoms form an octahedron structure. Moreover, the octahedrons were connected to each other to form a channel-like three-dimensional network. The thermal stability of Mn–BTC was examined by thermogravimetric analysis (TGA) in air, which was showed in Figure S1b. In the range of 50–200 °C, a curve weight loss platform that could be attributed to the loss of absorbed water was detected, followed by MOF decomposition over 300 °C. The total weight loss of Mn–BTC was 70.1%, which was consistent with the theoretical value of 71.5% calculating the quantity of water and organic framework. It could be observed in Figure S1c that the sample showed a rod-like shape with smooth surface.

2.1.2. Optimization of Calcination Temperature

As a synthetic template, it is vital to determine the appropriate calcination temperature of Mn–BTC. This study is meaningful not only in ensuring the complete decomposition of MOF and the formation of pure oxides, but also in avoiding particle aggregation under high calcination temperature. According to the TG results, Mn–BTCs were further calcinated at 300 °C, 400 °C, 450 °C, 500 °C and 600 °C to obtain several manganese oxides, which were denoted as Mn$_3$O$_4$–T, respectively.

The phase and crystal structure of the calcinated Mn$_3$O$_4$–T were examined by XRD, as shown in Figure S2a and Table 1. The patterns show that all diffraction peaks of the samples could be assigned to Mn$_3$O$_4$ (JCPDS 24–0734). As the calcination temperature increasing, the widths of peaks get narrower while the intensities become stronger, suggesting the high crystallinity of samples at a high temperature. Moreover, the average crystallite size of Mn$_3$O$_4$–T increased rapidly, indicating that excessively high temperature would lead to sintering of Mn$_3$O$_4$ nanoparticles. This is obviously not conducive in improving catalytic activity. Moreover, the elemental analysis of Mn$_3$O$_4$-300 (Table S1) reveals that only 1.73% organic portions remain, indicating the complete decomposition of the organic-frameworks during calcination process.

| Samples   | Average Crystallite Size $^a$ (nm) | $S_{BET}$ (m$^2$ g$^{-1}$) | Total Pore Volume (cm$^3$/g) |
|-----------|-----------------------------------|-----------------------------|------------------------------|
| Mn$_3$O$_4$-300 | 19.1                              | 19.41 ± 0.034               | 0.1425                       |
| Mn$_3$O$_4$-400 | 43.7                              | 9.44 ± 0.017                | 0.1379                       |
| Mn$_3$O$_4$-450 | 55.1                              | 7.72 ± 0.014                | 0.1351                       |
| Mn$_3$O$_4$-500 | 56.1                              | 7.69 ± 0.013                | 0.1333                       |
| Mn$_3$O$_4$-600 | 86.7                              | 6.01 ± 0.011                | 0.1281                       |

$^a$ estimated by the Scherrer equation.

The N$_2$ adsorption/desorption isotherms of Mn$_3$O$_4$–T are shown in Figure S2b. All samples showed well-developed mesoporous structure and features of the type II isotherms with hysteresis loops. The values of specific surface area ($S_{BET}$, confirmed by BET) are listed in Table 1. The proper heat-treatment was a key factor for the $S_{BET}$ and pore volume increase. Mn$_3$O$_4$-300 exhibits the highest surface area, 19.4 m$^2$ g$^{-1}$.

The morphology and nanostructure of the Mn$_3$O$_4$–T samples were investigated by SEM and HRTEM. The results are showed in Figure 1. The characterization of Mn$_3$O$_4$ calcinated at other temperatures can be found in Figure S4. It can be seen that the Mn$_3$O$_4$-300 remains a rod-like shape, even after heat treatment. However, the surface of the sample becomes rougher, which can be attributed to the formation of mesoporous caused by the loss of the organic portions. TEM reveals that nanorod is composed of numerous nanoparticles. The connection between Mn$_3$O$_4$ particles kept multiple active interfaces in the catalyst [28].
Based on the above observations, a possible procedure for the calcination was then proposed. During the calcination process, the organic ligands decomposed into CO$_2$(g) and H$_2$O(g), which spilled out from the framework afterward, leading to the formation of interior void space. Meanwhile, the metal ions Mn$^{2+}$ oxidized into Mn$_3$O$_4$ nanoparticles. Moreover, all the results show that the complete decomposition of Mn–BTC could be obtained under calcination temperature of 300 $^\circ$C, resulting in Mn$_3$O$_4$-300 sample with better features in catalysis. Therefore, we take 300 $^\circ$C as the appropriate calcination temperature in the follow-up experiments.

### 2.2. Catalytic Tests

Using Mn–BTC as templates, a series of $w$CeO$_2$–MnO$_X$-300 with different Ce contents (or $w$CeO$_2$–MnO$_X$, for short) were successfully synthesized and used for toluene oxidation. Resulted of toluene TPO were showed in Figure 2. Obviously, the catalytic activities and Ce contents were directly related. With increasing Ce contents, $w$CeO$_2$–MnO$_X$ catalysts exhibited better catalytic performance. Interestingly, when the Ce contents reached 3%, the samples no longer perform a significant increased activity. It suggests that when the amount of Ce reached a limit, the rest of the Ce cations spread on the surface of MnO$_X$, leading to no improvement of catalytic activity. Moreover, 100% conversion of toluene could be obtained at a temperature of 300 $^\circ$C for $w$CeO$_2$–MnO$_X$ ($w \geq 3\%$) catalysts. The results of the catalyst stability are shown in Figure S3. The activity of the catalysts did not decrease significantly after 30 h of continuous use.

![Figure 1](image1.png)

Figure 1. Scanning electron microscopy (SEM) (left) and high-resolution transmission electron microscope (HRTEM) (middle and right) of Mn$_3$O$_4$-300.

![Figure 2](image2.png)

Figure 2. Catalytic activities of $w$CeO$_2$–MnO$_X$-300 for toluene oxidation.
2.3. XRD and BET Analysis

The performance of catalysts is directly affected by their structures. Figure 3 presents the results of XRD and N$_2$ sorption isotherms of $\alpha$CeO$_2$–MnOX. Moreover, the textural parameters of $\alpha$CeO$_2$–MnOX are also summarized in Table 2. The XRD patterns show that the diffraction peaks which ascribed to Mn$_3$O$_4$ (JCPDS 24–0734) could be found in all samples, whereas the peaks become broader with the increasing Ce content. This may be due to the entrance of Ce$^{3+}$, which was consistent with the increasing lattice constant (Table 2). It suggests that Mn–Ce solid solution formed at the particle interfaces and expanded the size of lattice [29–31]. The phase structure of Mn–BTC nanorods had a rich and uniform pore structure, and long-term immersion ensured that Ce ions enter these pore channels. A small portion of Ce entered the Mn–MOF and formed a Ce–Mn solid solution (enters the crystal lattice of MnOX) during the subsequent pyrolysis. Most of the remaining CeO$_2$ and MnOX growth was spatially staggered. This made the Ce ions in the template have a separation effect on MnOX, which in turn provided the possibility to increase the specific surface area. From the results of BET analysis, the average crystallite size of samples did decrease with increasing Ce content, revealing that Ce cations effectively separated the MnOX and led to bigger specific surface area (Table 2). It is worth noting that the characteristic reflections of Mn$_3$O$_4$ (JCPDS 24-0508) and CeO$_2$ (JCPDS 34-0394) could also be found in $\alpha$CeO$_2$–MnOX ($w \geq 3\%$) and $\alpha$CeO$_2$–MnOX ($w \geq 5\%$), respectively. Obviously, Ce does not crystallize in $\alpha$CeO$_2$–MnOX ($w \leq 3\%$) but bind to the surface of MnOX in a highly dispersed state. The results prove that there were indeed two states of interface Ce, monolayer dispersion state and crystalline state. The existence form of Ce changes with the increase of load. It can be concluded that the threshold effect most likely to be responsible for these results [19]. To be specific, when the amount of dispersed Ce was below monolayer dispersion threshold, Ce ions interacted with the reactive site on MnOX surface to form a single layer of surface compound that scattered over the surface; when the amount of dispersive Ce exceeded the monolayer dispersion threshold, superfluous Ce existed as CeO$_2$ on the surface of catalysts. For the reason that Ce oxides generation and Mn–MOF decomposition proceed simultaneously, Ce cations could be dispersed on the surface of fine and newly formed MnOX nanoparticles, preventing aggregation of the particles and resulting in the increase of surface-specific area [17]. The turning of existence form of Ce shown by XRD was highly consistent with the toluene catalytic activity of $\alpha$CeO$_2$–MnOX. Obviously, the state of Ce was directly related to the catalytic activity of the system. To further prove the above deductions, more characterizations were used to verify the results.

(a)  
(b)  

Figure 3. (a) Powder X-ray diffraction (XRD) and (b) N$_2$ sorption isotherms of $\alpha$CeO$_2$–MnOX.
were conducted. The peak areas of Ce 3d and Mn 2p are presented (I

The fitting curve clearly shows two trends. In the lower Ce loading range (1–3%), the slope of Line 1

To determine the monolayer dispersion threshold, XPS characterizations for

The XPS extrapolation method has been developed to quantify the monolayer dispersion threshold in oxide or salt catalyst systems [38–40]. Moreover, the XPS extrapolation method has been estimated from CeO$_2$ face by Scherer equation. $^b$ total weight ratio determined by Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis.

### 2.4. SEM and TEM Analysis

The morphology and crystalline plane are examined by SEM and HRTEM. From Figure 4, it can be observed that the obtained wCeO$_2$–MnO$_x$ catalysts still remain the original rod shape, though a small fraction of the samples were cracked to pieces. The fine particles that make up the nanorods are highly crystallized and tightly connected. Crystal planes of Mn$_3$O$_4$ are easily found in all samples, while interlayer spacings of Mn$_2$O$_3$ and CeO$_2$ can only be observed in wCeO$_2$–MnO$_x$ ($w \geq 3\%$) and wCeO$_2$–MnO$_x$ ($w \geq 5\%$), respectively. The results are highly consistent with the XRD patterns. To confirm the elements distribution of wCeO$_2$–MnO$_x$, the results of EDS elemental mapping are given in Figure 5. The uniform distributions of the Ce, Mn and O elements are conducive to form highly active Ce–Mn interfaces, and offer the further possibility of improvement in toluene oxidation.

### 2.5. Raman Spectra Analysis

The Raman spectra of wCeO$_2$–MnO$_x$ are given in Figure 6. The main band centered at 645 cm$^{-1}$ is detected in all catalysts, which is generally attached to the vibration of Mn–O–Mn in Mn$_3$O$_4$ [32]. Furthermore, the band over 645 cm$^{-1}$ can be observed visible increase in bandwidth and band center blue-shifts, which can be explained by the defects formed in Mn$_3$O$_4$ and the smaller particle size of crystals. On one hand, the incorporation of cerium changes the atomic coordination of manganese and induces more defects in crystal. On the other hand, the reduction of crystal size caused the change of phonon confinement and inhomogeneous strain broadening [11]. In addition, characteristic Raman band of Mn$_2$O$_3$ (340 cm$^{-1}$) [33] and CeO$_2$ (460 cm$^{-1}$) [30,34] can also be found in wCeO$_2$–MnO$_x$ ($w \geq 3\%$) and wCeO$_2$–MnO$_x$ ($w \geq 5\%$), respectively, which agrees well with the XRD result. The existence of Mn$_2$O$_3$ is presumed to be attributed to the interaction between Ce and Mn which induced the valence of Mn$_3$O$_4$ [35,36], and the presence of CeO$_2$ demonstrates that the excess Ce is present as crystals on the catalyst surface. In general, the Raman spectra further prove the fact that Ce not only dispersed homogeneously as surface compound and oxides on the surface of MnO$_x$, but also changed the interface properties of catalysts, such as oxygen vacancy, metal valence state, etc. Moreover, this change is mainly caused by the Ce below the monolayer-dispersed threshold.

### 2.6. X-ray Photoelectron Spectroscopy (XPS) Analysis

X-ray photoelectron spectroscopy (XPS) is a common means in analyzing the surface elemental compositions and oxidation states of catalysts [37]. Moreover, the XPS extrapolation method has been developed to quantify the monolayer dispersion threshold in oxide or salt catalyst systems [38–40]. To determine the monolayer dispersion threshold, XPS characterizations for wCeO$_2$–MnO$_x$ ($w = 1–30\%$) were conducted. The peak areas of Ce 3d and Mn 2p are presented ($I_{Ce\;3d}$ and $I_{Mn\;2p}$, respectively), and the mass fractions of Ce ($w = 1–3\%$) are converted into corresponding CeO$_2$ loading (g CeO$_2$/g MnO$_x$). The relationship between ratios of $I_{Ce\;3d}/I_{Mn\;2p}$ and Ce loading contents are showed in Figure 7. The fitting curve clearly shows two trends. In the lower Ce loading range (1–3%), the slope of Line 1 is very big. At this stage, the Ce is mainly dispersed in the monolayer state on the catalysts surface and interacts with MnO$_x$ to form a high dispersed Ce–Mn surface compound [41]. When the Ce

### Table 2. Textural parameters of wCeO$_2$–MnO$_x$.

| Samples         | Average Crystallite Size $^a$ (nm) | Lattice Parameter (nm) | $S_{BET}$ (m$^2$ g$^{-1}$) | Ce Content $^b$ (wt%) |
|-----------------|----------------------------------|------------------------|-----------------------------|------------------------|
| MnO$_x$         | 19.1                             | 0.5754                 | 19.4 ± 0.034                | –                      |
| 1% CeO$_2$–MnO$_x$ | 18.9                             | 0.5793                 | 19.0 ± 0.035                | 0.91                   |
| 3% CeO$_2$–MnO$_x$ | 14.1                             | 0.5937                 | 43.8 ± 0.078                | 3.17                   |
| 5% CeO$_2$–MnO$_x$ | 12.5                             | 0.6267                 | 56.8 ± 0.099                | 4.39                   |
| 8% CeO$_2$–MnO$_x$ | 6.7                              | 0.6388                 | 51.0 ± 0.089                | 9.24                   |
| 10% CeO$_2$–MnO$_x$ | 3.9                              | 0.6411                 | 50.4 ± 0.87                 | 10.82                  |

$^a$ estimated from CeO$_2$ face by Scherer equation. $^b$ total weight ratio determined by Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis.
loading exceeds a certain value, the line 2 is obviously flattening out. It reveals the existence of Ce veers away from monolayer dispersion state and turn to the crystalline phase. At the intersection of extrapolation line 1 and extrapolation line 2 (red line in Figure 7), the value of $x$ is $0.08 \text{ g CeO}_2/\text{g MnO}_X$, which converted to the mass fraction of Ce is $3.2\%$. The intersection is the demarcation of the two forms of Ce species on the surface of the MnO$_X$ carrier, and that is the monolayer dispersion threshold of the system [38].

Figure 4. SEM (left) and HRTEM (middle and right) of $w\text{CeO}_2–\text{MnO}_X$ (From top to bottom: 1%, 3%, 5%, 8% and 10%).
The monolayer dispersion threshold (3.2%) is consistent with the turning points appeared in all the above characterization results. Catalysts with a monolayer-dispersed active component obviously show better activity. Since the Ce content is closest to the threshold, the fresh and reacted 3% CeO$_2$–MnO$_X$-300 were selected for XPS text to detect the element valence and content of the interfaces with monolayer-dispersed Ce. The results are showed in Figure 8 and Table 3. In the Mn 2p spectra, the peaks around 643 eV and 641 eV are assigned to Mn$^{4+}$ and Mn$^{3+}$ (or Mn$^{2+}$) species [42]. The ratio

Figure 5. SEM–EDS mapping of 3% CeO$_2$–MnO$_X$.

Figure 6. Visible Raman of wCeO$_2$–MnO$_X$.

Figure 7. Relationship between ratios of $I_{\text{Ce 3d}}/I_{\text{Mn 2p}}$ and the Ce content.

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of Mn⁴⁺/(Mn²⁺ + Mn³⁺) decreases from 0.32 (fresh) to 0.22 (reacted), suggesting that the Mn ions tend to get electrons in the systems (the valence of partial Mn ions dropped from +4 to +2 and +3). In the Ce 3d spectra, the peaks of 3d_{5/2} and 3d_{3/2} spin–orbit component were marked as u and v, respectively. The peaks labeled as v₁, v₂, v₃, u₁, u₂ and u₃ belong to Ce⁴⁺, and the v₁ and u₁ belong to Ce³⁺ [41,43]. The ratios of Ce⁴⁺/Ce³⁺ decreased from 9.78 to 9.33 after the catalytic reaction, decreased slightly, indicating that the part of Ce³⁺ expended in reaction irreversibly. Obviously, Ce³⁺ is helpful to the promotion of catalytic activity. The spectrum of O 1 s could be resolve into three characteristic peaks: surface oxygen (O_{surf}) at 530–532 eV, adsorbed oxygen (O_{ads}) at 533–534 eV and lattice oxygen (O_{latt}) at 529–530 eV [42,44]. The peak intensities of O_{latt}, O_{ads} and O_{surf} are all detectable changed after reaction. Furthermore, the loop of oxygen can be inferred from the increase/decrease in oxygen species ratios. The reaction consumed O_{ads} and O_{surf} directly, herein the oxygen atoms in lattice overflow and replenish to the surface, while the O₂ in the gas phase is also adsorbed to the catalyst surface to supplement the surface and crystal phase oxygen. All the above XPS results reveal that Ce⁴⁺/Ce³⁺, Mn⁴⁺/(Mn²⁺+Mn³⁺), O_{latt}, O_{ads} and O_{surf} are all involved in toluene catalytic oxidation. The monolayer-dispersed state Ce makes the valence states of elements in the system more variable. Moreover, the abundant active site number and variety are the main reason for the high activity of the wCeO₂–MnOX (w ≤ 3%).

![XPS spectra of fresh and reacted 3% CeO₂–MnOX.](image)

**Table 3.** Surface atomic compositions analysis for 3% CeO₂–MnOX.

| Samples                  | O Atom Ratio (%) | Ce⁴⁺/Ce³⁺ | Mn⁴⁺/(Mn²⁺ + Mn³⁺) |
|--------------------------|------------------|-----------|--------------------|
|                          | O_{ads}          | O_{surf}  | O_{latt}           |                   |
| 3% CeO₂–MnOX-fresh       | 1.53             | 16.42     | 82.05              | 9.78              | 0.32               |
| 3% CeO₂–MnOX-reacted     | 5.40             | 19.66     | 74.94              | 9.33              | 0.22               |

2.7. H₂-TPR Analysis

Temperature-programmed reduction (H₂-TPR) was carried out over wCeO₂–MnOX to investigate the effect of the impact of Ce–Mn interfaces with the Ce different states on the redox properties. Results are presented in Figure 9 and Table S2. The reduction of pure MnOX proceeds in two peaks at 334 °C and 472 °C, which are consistent with reduction steps: Mn₂O₃ → Mn₃O₄ → MnO [45], respectively. As compared with the pure MnOX, the wCeO₂–MnOX-300 samples also exhibit two main H₂ consumption peaks, while all peaks have shifted to a lower temperature at different extend. The position of higher temperature peaks (around 400 °C) decreases distinctly with the Ce content increase in the range of 1–5%, while basically remains stable in the range of 3–10%. The shift of the lower temperature peaks (around 285 °C) also shows the same behavior. Particularly, the samples with Ce content below or slightly above the threshold show peaks at around 210 °C, which are caused by MnO₂ → Mn₂O₃ [46]. It is well demonstrated that the monolayer-dispersed Ce induces the Mn at the interface to exhibit more abundant valence states and significantly enhances the redox activity of manganese, while the crystalline phase CeO₂ does not. In summary, the monolayer-dispersed threshold plays a key role in reducibility and activity of catalysts.
The spectrum of 1% CeO$_2$ that the interaction between Mn and monolayer-dispersed Ce increases the species and quantity of occur in monolayer-dispersed (1–3%) and low crystallinity (5%) samples. The above results indicate are 6.7 nm and 3.9 nm according to XRD. The f-size is <10 nm, the blue shift can be clearly observed in 8% and 10% CeO$_2$–MnOX, whose diameters are 6.7 nm and 3.9 nm according to XRD. The f–d transitions of Ce$^{3+}$ species at 207 and 219 nm only occur in monolayer-dispersed (1–3%) and low crystallinity (5%) samples. The above results indicate that the interaction between Mn and monolayer-dispersed Ce increases the species and quantity of metal ions at low valence states on the Ce–Mn interface. It was the Ce–Mn interface that significantly expanded the light absorption range of the integral CeO$_2$–MnOX-300, which have better electron transfer performance and catalytic activity than MnOX.

2.8. UV-Vis DRS Analysis

To detect the surface coordination and different oxidation state of CeO$_2$–MnOX, the UV-Vis diffuse reflectance spectra were characterized and shown in Figure 10. As previously reported, crystalline Mn$_3$O$_4$ has a band gap of 2.175 eV and the corresponding absorption wavelength is 570 nm [47]. The spectrum of 1% CeO$_2$–MnOX fits this well. All samples show feeble bands at 505–509 nm and 270 nm, which are assigned to the $^6$A$_{1g}$ → $^4$T$_{2g}$ crystal field transitions of Mn$^{2+}$ and the charge transfer transition of O$^{2-}$ → Mn$^{3+}$ under the circumstance of the MnOX [12,48]. In general, the UV-Vis spectra of pure CeO$_2$ exhibits three-band centers at around 255, 285 and 340 nm. The latter two bands are caused by O$^{2-}$ → Ce$^{4+}$, whereas the vague former maxima correspond to O$^{2-}$ → Ce$^{3+}$ transitions [49]. Only the bands corresponding to O$^{2-}$ → Ce$^{3+}$ charge transfer transition appear at 238 nm in Figure 9. The absorption edge of the CeO$_2$ interband transition is sensitive to crystal size [50]. Especially, when the size is <10 nm, the blue shift can be clearly observed in 8% and 10% CeO$_2$–MnOX, whose diameters are 6.7 nm and 3.9 nm according to XRD. The f→d transitions of Ce$^{3+}$ species at 207 and 219 nm only occur in monolayer-dispersed (1–3%) and low crystallinity (5%) samples. The above results indicate that the interaction between Mn and monolayer-dispersed Ce increases the species and quantity of metal ions at low valence states on the Ce–Mn interface. It was the Ce–Mn interface that significantly expanded the light absorption range of the integral CeO$_2$–MnOX-300, which have better electron transfer performance and catalytic activity than MnOX.

![Figure 9. H$_2$-TPR of CeO$_2$–MnOX loading.](image)

![Figure 10. UV-Vis reflectance spectra of CeO$_2$–MnOX.](image)
The embedded model is a theory generally accepted by researchers in the field of catalysis [51]. The behaviors between CeO$_2$ and MnO$_X$ compounds can also be explained by an embedded model, as shown in Figure S5. Under appropriate conditions, cations of CeO$_2$ entered the lattice intervals and vacancies on the surface of Mn$_3$O$_4$, while the ortho O$^{2-}$ capped the cationic sites to dispel the excess positive charge. The lattice distortion of Mn$_3$O$_4$ is caused by Ce entering the lattice intervals and vacancies, which leads to the increase of oxygen vacancy and surface oxygen activity. Therefore, the catalyst activity promotes correlatively with the amount of Ce. It is worth noting that the surface crystal is regular when the content of Ce on the surface reaches the monolayer dispersion threshold. There are no excess efficient sites on the MnO$_X$ surface to accommodate Ce ions. Then the Ce ions begin to accumulate in the upper layer, and form CeO$_2$ crystals. Hence, the properties at the interface of the CeO$_2$–MnO$_X$ do not further change with the increase of the Ce content.

3. Materials and Methods

3.1. Synthesis of CeO$_2$–MnO$_X$

3.1.1. Starting Materials

Manganese chloride (MnCl$_2$), trimesic acid (H$_3$BTC), cerium nitrate (Ce(NO$_3$)$_3$·6H$_2$O), ethanol (CH$_3$CH$_2$OH) and triethylamine(C$_6$H$_{15}$N) were purchased from Aladdin. All the reactants were of analytical grade and were used without further purification.

3.1.2. Synthesis of Mn–MOF

In a typical procedure [52], MnCl$_2$ (15 mmol) and H$_3$BTC (10 mmol) were dissolved in ethanol solution (50 mL) under vigorous agitation at room temperature. After MnCl$_2$ is completely dissolved, 2 mL triethylamine was added into the above solution dropwise and kept stirring at medium speed. After reaction for 6 h, the white precipitate in the solution was separated using vacuum suction filtration. The white precipitate was washed with ethanol for 3 times and dried at 60 °C under vacuum for 24 h. Then the precipitate was grinded, and the resulting white powder is the sacrificial template.

3.1.3. Synthesis of CeO$_2$–MnO$_X$

Synthesis of CeO$_2$–MnO$_X$ was based on the following procedure: First, Mn–MOF (2.0 g) and Ce(NO$_3$)$_3$·6H$_2$O (0.062 g) were dissolved in ethanol solution (30 mL) under stirring at room temperature. Then let the mixture stand still for 24 h. Finally, the as-synthesized product was completely dried at 120 °C (the heating rate is 2 °C min$^{-1}$) and calcinated in the air at a particular temperature for 12 h to synthesize the 1%-CeO$_2$–MnO$_X$ nanoparticles. In addition, 3% CeO$_2$–MnO$_X$, 5% CeO$_2$–MnO$_X$, 8% CeO$_2$–MnO$_X$, 10% CeO$_2$–MnO$_X$ were prepared in the same procedure. Catalysts were coded as wCeO$_2$–MnO$_X$ (w referred to the mass fraction of Ce).

3.2. Material Characterization

The crystallinity of the catalysts was studied by powder X-ray diffraction (XRD) on a D8 ADVANCE diffractometer (Bruker, Germany) with Cu-Kα radiation (40 kV, 40 mA). The patterns were obtained between 20 = 10–90° with a step size of 0.02°. Nitrogen adsorption/desorption isotherms were performed on an ASAP2020 M analyzer (Micromeritics, Norcross, GA, USA). All samples were outgassed at 150 °C in vacuum for 8 h before measurement. The thermal stability of samples was characterized by thermogravimetric analysis (TGA) on a STA449C apparatus (NETZSCH, Selb, Germany) at a heating rate of 10 °C min$^{-1}$. Elemental analysis (EA) was conducted on FLASH 2000 (Thermo Scientific, Waltham, MA, USA). The Ce contents in CeO$_2$–MnO$_X$ samples were investigated by inductively coupled plasma optical emission spectrometry (ICP-OES) on Varian 720 (USA). The morphology and structure of samples were obtained by transmission electron microscopy (TEM) (FEI f20, Hillsboro, OR, USA) and scanning electron microscopy (SEM) (Hitachi S4800/8010, Tokyo, Japan). The elemental
distribution over the selected region was acquired on an energy-dispersive X-ray spectrometer (EDS) attached to the SEM instrument. Temperature-programmed reduction (H$_2$-TPR) was performed on AutoChem (Micromeritics, Norcross, GA, USA) under 10% H$_2$/Ar mixture gas at a rate of 10 °C min$^{-1}$ up to 900 °C. Moreover, the outlet exhaust was detected by TCD. The valence states of Mn, Ce and O were studied by EscaLab 250Xi X-ray photoelectron spectrometry (XPS) (Thermo Scientific, Waltham, MA, USA). The Raman spectra of the catalysts were recorded in a LabRAM HR Evolution Laser Raman Spectrometer (HYJ, Arras, France) with a He–Ne laser and a CDD detector. Visible Raman spectra were collected using the exciting line at 532 cm$^{-1}$ from 300–800 cm$^{-1}$. UV-Vis diffuse reflectance spectra (DRS) measurements were taken in the range of 200–800 nm using a UV–2700 spectrophotometer (Shimadzu, Kyoto, Japan).

3.3. Catalytic Activity Evaluation

An evaluation of catalytic activities was performed on a toluene temperature-programmed oxidation (TPO) apparatus with a continuous flow microreactor made quartz (8 mm i.d., 500 mm length). Per 200 mg sample mixed into 800 mg of silica to avoid reaction runaway. All the particles were packed at the bed of the reactor. The reactant mixture gas (1000 ppm Toluene, 20% O$_2$/N$_2$) flowed through the reactor at a rate of 160 mL min$^{-1}$, corresponding to the weight hourly space velocity (WHSV) at 48,000 mL g$^{-1}$ h$^{-1}$. The effluent gases were monitored online by gas chromatography (GC-2014C, Shimadzu, Japan) equipped with FID. The toluene conversion (X$_{\text{toluene}}$) was analyzed by the inlet and outlet concentration, which was calculated based on the following equation:

$$X_{\text{toluene}}(\%) = 100 \times \frac{(C_{\text{in}} - C_{\text{out}})}{C_{\text{in}}}$$  

(1)

where X$_{\text{toluene}}$ denotes the toluene conversion at a certain temperature; C$_{\text{in}}$ (ppm) and C$_{\text{out}}$ (ppm) denotes the concentrations of toluene in the inlet and outlet gas, respectively.

4. Conclusions

In summary, a series of porous composite oxides (wCeO$_2$–MnO$_x$) with high dispersity and activity were successfully prepared via a simple Mn–MOFs templated pyrolytic transformation at 300 °C. The MOF sacrificial template with immersion treatment helps to synthesize the composite oxide with high dispersion and controllable interface. These as-prepared wCeO$_2$–MnO$_x$ catalysts exhibited novel morphologies and two-stage performance improvement in toluene oxidation. This was mainly because the Ce had two-dispersed states on the MnO$_x$ interface. The monolayer dispersion threshold (3.2% wt.) was the sign of the monolayer dispersion state turning to crystalline and the key indicator of system activity. The Ce–Mn interfaces with monolayer dispersion feature were crucial for efficient catalytic activity. The monolayer dispersion state Ce changed the chemical property of pure Mn$_3$O$_4$ surface, which significantly improved the reducibility, oxygen mobility, metal ion valence state abundance and electron transfer ability of catalysts. And the crystal Ce was much more like a fence, separating the particles and only enhanced the activity by changing physical structure parameters, such as particle size and specific surface area. Obviously, the monolayer-dispersed Ce was more efficient in improving the catalytic activity.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/6/681/s1, Figure S1: (a) XRD, (b) TG and (c) SEM of Mn–BTC, Figure S2: (a) XRD and (b) N2 sorption isotherms of Mn3O4 derived from Mn–BTC, Figure S3: Long-term durability test over wCeO$_2$–MnO$_x$, Figure S4: SEM (left) and HRTEM (middle and right) of Mn3O4 calcinated from Mn–BTC, Figure S5: Diagram of CeO2 supported on the surface of MnOX (112), Table S1: The elemental analysis of Mn3O4 calcinated from Mn–BTC, Table S2: Position of main reduction peaks and H2 consumption for wCeO$_2$–MnOX-300.
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References
1. Duan, J.; Tan, J.; Yang, L.; Wu, S.; Hao, J. Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing. Atmos. Res. 2008, 88, 25–35. [CrossRef]
2. Rao, G.; Vejerano, E.P. Partitioning of volatile organic compounds to aerosols: A review. Chemosphere 2018, 212, 282–296. [CrossRef] [PubMed]
3. Kim, Y.M.; Harrad, S.; Harrison, R.M. Concentrations and sources of VOCs in urban domestic and public microenvironments. Environ. Sci. Technol. 2001, 35, 997–1004. [CrossRef] [PubMed]
4. Tan, B.; Wang, T.-Y.; Pang, B.; Zhu, Z.-Y.; Wang, D.-H.; Lü, Y.-L. [Pollution characteristics and health risk assessment of atmospheric volatile organic compounds (VOCs) in pesticide factory]. Environ. Sci. 2013, 34, 4577–4584.
5. An, H.T.Q.; Huu, T.P.; Le Van, T.; Cormier, J.; Khacef, A. Application of atmospheric non thermal plasma-catalysis hybrid system for air pollution control: Toluene removal. Catal. Today 2011, 176, 474–477. [CrossRef]
6. Yu, D.; Yue, L.; Wu, Z. Low-temperature catalytic oxidation of toluene over mesoporous MnOx–CeO2/TiO2 prepared by sol–gel method. Catal. Commun. 2010, 11, 788–791. [CrossRef]
7. Zhang, Y.; Deng, J.; Zhang, L.; Dai, H. Preparation and catalytic performance of Fe-SBA-15 and FeO x /SBA-15 for toluene combustion. Chin. Sci. Bull. 2014, 59, 4093–4002. [CrossRef]
8. Bai, G.; Dai, H.; Liu, Y.; Ji, K.; Li, X.; Xie, S. Preparation and catalytic performance of cylinder- and cake-like Cr2O3 for toluene combustion. Catal. Commun. 2013, 36, 43–47. [CrossRef]
9. Chiang, K.-H.; Liu, Z.-S.; Chang, Y.-H.; Lu, C.-Y.; Wey, M.-Y. Study of SBA-15 supported catalysts for toluene and NO removal: The effect of promoters (Co, Ni, Mn, Ce). React. Kinet. Mech. Catal. 2010, 99, 409–420. [CrossRef]
10. Taylor-Pashow, K.M.L.; Rieter, W.J.; Lin, W. Manganese-Based Nanoscale Metal–Organic Frameworks for Magnetic Resonance Imaging. J. Am. Chem. Soc. 2008, 130, 14358–14359. [CrossRef]
11. Wu, Z.; Li, M.; Howe, J.; Meyer, H.M.; Overbury, S.H. Probing Defect Sites on CeO2 Nanocrystals with Well-Defined Surface Planes by Raman Spectroscopy and O2 Adsorption. Langmuir 2010, 26, 16595–16606. [CrossRef] [PubMed]
12. Narayana, B.L.; Mukri, B.D. Mn Ion substituted CeO 2 Nano spheres for Low Temperature CO Oxidation: The Promoting Effect of Mn Ions. ChemistrySelect 2016, 1, 3150–3158. [CrossRef]
13. Heyes, C.J.; Irwin, J.G.; Johnson, H.A.; Moss, R.L. The catalytic oxidation of organic air pollutants part 1. Single metal oxide catalysts. J. Chem. Technol. Biotechnol. 2007, 82, 1025–1033. [CrossRef]
14. Wang, J.; Yoshida, A.; Wang, P.; Yu, T.; Wang, Z.; Hao, X.; Abudula, A.; Guan, G. Catalytic oxidation of volatile organic compound over cerium modified cobalt-based mixed oxide catalysts synthesized by electrodeposition method. Appl. Catal. B Environ. 2020, 271, 118941. [CrossRef]
15. Wang, X.; Zhao, B.; Jiang, D.-E.; Xie, Y. Monolayer dispersion of MoO3, NiO and their precursors on γ-Al2O3. Appl. Catal. A Gen. 1999, 188, 201–209. [CrossRef]
16. Gao, Y.; Zhao, H.; Zhao, B. Monolayer dispersion of oxide additives on SnO2 and their promoting effects on thermal stability of SnO2 ultrafine particles. J. Mater. Sci. 2000, 35, 917–923. [CrossRef]
17. Wang, C.; Zhao, B.; Xie, Y. Advances in the Studies of Spontaneous Monolayer Dispersion of Oxides and Salts on Supports. Chin. J. Catal. 2003, 24, 475–482.
18. Hou, Z.; Feng, J.; Lin, T.; Zhang, H.; Zhou, X.; Yao-Qiang, C. The performance of manganese-based catalysts with Ce0.6Zr0.35O2 as support for catalytic oxidation of toluene. Appl. Surf. Sci. 2018, 434, 82–90. [CrossRef]
19. Lin, X.; Fu, M.; He, H.; Wu, J.; Chen, L.; Ye, D.; Hu, Y.; Wang, Y.; Wen, W. Synthesis of MnOx-CeO2 Using Metal-Organic Framework as Sacrificial Template and Its Performance in the Toluene Catalytic Oxidation Reaction. *Acta Phys. Chim. Sin.* 2018, 34, 719–730.

20. Hu, F.; Chen, J.; Zhao, S.; Li, K.; Si, W.; Song, H.; Li, J. Toluene catalytic combustion over copper modified Mn0.5Co0.5Ox solid solution sponge-like structures. *Appl. Catal. A Gen.* 2017, 540, 57–67. [CrossRef]

21. Liao, Y.; Fu, M.; Chen, L.; Wu, J.; Huang, B.-C.; Ye, D. Catalytic oxidation of toluene over nanorod-structured Mn–Ce mixed oxides. *Catal. Today* 2013, 216, 220–228. [CrossRef]

22. Jiang, Z.; Chen, C.; Ma, M.; Guo, Z.; Yu, Y.; He, C. Rare-earth element doping-promoted toluene low-temperature combustion over mesostructured CuMnCeOx (M = Y, Eu, Ho, and Sm) catalysts: The indispensable role of in situ generated oxygen vacancies. *Catal. Sci. Technol.* 2018, 8, 5933–5942. [CrossRef]

23. Zhang, X.; Yang, Y.; Lv, X.; Wang, Y.; Cuia, L. Effect of Preparation Method on the Structure and Catalytic Activity of Ag–Fe2O3 Catalysts Derived from MOFs. *Catalysts* 2017, 7, 382. [CrossRef]

24. Chen, X.; Cai, S.; Yu, E.; Chen, J.; Jia, H. MnOx/Cr2O3 composites prepared by pyrolysis of Cr-MOF precursors containing in situ assembly of MnOx as high stable catalyst for toluene oxidation. *Appl. Surf. Sci.* 2019, 475, 312–324. [CrossRef]

25. Khramenkov, E.V.; Polynski, M.V.; Vinogradov, A.V.; Pidko, E.A. Degradation paths of manganese-based MOF materials in a model oxidative environment: A computational study. *Phys. Chem. Chem. Phys.* 2018, 20, 20785–20795. [CrossRef] [PubMed]

26. Chen, X.; Cai, S.; Chen, J.; Xu, W.; Jia, H.; Chen, J. Catalytic combustion of toluene over mesoporous Cr2O3-supported platinum catalysts prepared by in situ pyrolysis of MOFs. *Chem. Eng. J.* 2018, 334, 768–779. [CrossRef]

27. Zhang, W.; Jiang, X.; Zhao, Y.; Carné-Sánchez, A.; Malgras, V.; Kim, J.; Kim, J.H.; Wang, S.; Liu, J.; Jiang, J.-S.; et al. Hollow carbon nanobubbles: Monocrystalline MOF nanobubbles and their pyrolysis. *Chem. Sci.* 2017, 8, 3538–3546. [CrossRef] [PubMed]

28. Zhang, W.; Sun, C.; Huo, F.; Liu, H.; Li, L.; Yang, Z.; Feng, X.; Lu, X. CuO/Cu2O porous composites: Shape and composition controllable fabrication inherited from metal organic frameworks and further application in CO oxidation. *J. Mater. Chem. A* 2015, 3, 5294–5298. [CrossRef]

29. Spassova, I.; Tsontcheva, T.; Velichkova, N.; Khristova, M.; Nihitianova, D. Catalytic reduction of NO with decomposed methanol on alumina-supported Mn–Ce catalysts. *J. Colloid Interface Sci.* 2012, 374, 267–277. [CrossRef]

30. Wu, X.; Liu, S.; Weng, D.; Lin, F. Textural–structural properties and soot oxidation activity of MnOx-CeO2 mixed oxides. *Catal. Commun.* 2011, 12, 345–348. [CrossRef]

31. Wu, X.; Liu, S.; Weng, D.; Lin, F.; Ran, R. MnOx–CeO2–Al2O3 mixed oxides for soot oxidation: Activity and thermal stability. *J. Hazard. Mater.* 2011, 187, 283–290. [CrossRef] [PubMed]

32. Kaliaguine, S.; Van Neste, A.; Szabo, V.; Gallot, J.; Bassir, M.; Muzychuk, R. Perovskite-type oxides synthesized by reactive grinding. *Appl. Catal. A Gen.* 2001, 209, 345–358. [CrossRef]

33. Luo, Y.; Deng, Y.-Q.; Mao, W.; Yang, X.-J.; Zhu, K.-K.; Xu, J.; Han, Y.-F. Probing the Surface Structure of α-Mn2O3 Nanocrystals during CO Oxidation by Operando Raman Spectroscopy. *J. Phys. Chem. C* 2012, 116, 20975–20981. [CrossRef]

34. Sato, T.; Komanoya, T. Selective oxidation of alcohols with molecular oxygen catalyzed by Ru/MnOx/CeO2 under mild conditions. *Catal. Commun.* 2009, 10, 1095–1098. [CrossRef]

35. Radhakrishnan, R.; Oyama, S.T.; Ohminami, Y.; Asakura, K. Structure of MnOx/Al2O3 Catalyst: A Study Using EXAFS, In Situ Laser Raman Spectroscopy and ab Initio Calculations. *J. Phys. Chem. B* 2001, 105, 9067–9070. [CrossRef]

36. Xu, J.; Li, P.; Song, X.; He, C.; Yu, J.; Han, Y.-F. Operando Raman Spectroscopy for Determining the Active Phase in One-Dimensional Mn1±xCeOx2+y Nanorod Catalysts during Methane Combustion. *J. Phys. Chem. Lett.* 2010, 1, 1648–1654. [CrossRef]

37. Hungria, A.; Fernández-Garcia, M.; Anderson, J.; Martínez-Arias, A. The effect of Ni in Pd–Ni/(Ce,Zr)O4/Al2O3 catalysts used for stoichiometric CO and NO elimination. Part 2: Catalytic activity and in situ spectroscopic studies. *J. Catal.* 2005, 235, 262–271. [CrossRef]

38. Xie, Y.-C.; Tang, Y.-Q. Spontaneous Monolayer Dispersion of Oxides and Salts onto Surfaces of Supports: Applications to Heterogeneous Catalysis. *Adv. Catal.* 1990, 37, 1–43. [CrossRef]
39. Deo, G.; Wachs, I. Reactivity of Supported Vanadium Oxide Catalysts: The Partial Oxidation of Methanol. J. Catal. 1994, 146, 323–334. [CrossRef]
40. Dong, L.; Hu, Y.; Shen, M.; Jin, T.; Wang, J.; Ding, W.; Chen, Y.D.A.N. Dispersion behaviors of copper oxide on the mixed “CeO2+gamma-Al2O3” support. Chem. Mater. 2001, 13, 4227–4232. [CrossRef]
41. Larachi, F.; Pierre, J.; Adnot, A.; Bernis, A. Ce 3d XPS study of composite CexMn1−xO2−y wet oxidation catalysts. Appl. Surf. Sci. 2002, 195, 218–226. [CrossRef]
42. Li, H.; Qi, G.; Zhang, X.; Huang, X.; Li, W.; Shen, W. Low-temperature oxidation of ethanol over a Mn0.6Ce0.4O2 mixed oxide. Appl. Catal. B Environ. 2011, 103, 54–61. [CrossRef]
43. Li, Y.; Sun, Q.; Kong, M.; Shi, W.; Huang, J.; Tang, J.; Zhao, X. Coupling Oxygen Ion Conduction to Photocatalysis in Mesoporous Nanorod-like Ceria Significantly Improves Photocatalytic Efficiency. J. Phys. Chem. C 2011, 115, 14050–14057. [CrossRef]
44. Wang, X.; Kang, Q.; Li, D. Low-temperature catalytic combustion of chlorobenzene over MnOx–CeO2 mixed oxide catalysts. Catal. Commun. 2008, 9, 2158–2162. [CrossRef]
45. Chen, H.; Sayari, A.; Adnot, A.; Larachi, F. Composition–activity effects of Mn–Ce–O composites on phenol catalytic wet oxidation. Appl. Catal. B Environ. 2001, 32, 195–204. [CrossRef]
46. Torres, J.Q.; Giraudon, J.-M.; Lamonier, J.-F. Formaldehyde total oxidation over mesoporous MnOx catalysts. Catal. Today 2011, 176, 277–280. [CrossRef]
47. Zhao, J.; Nan, J.; Zhao, Z.; Li, N.; Liu, J.; Cui, F. Energy-efficient fabrication of a novel multivalence Mn3O4-MnO2 heterojunction for dye degradation under visible light irradiation. Appl. Catal. B Environ. 2017, 202, 509–517. [CrossRef]
48. Parida, K.; Dash, S.; Singha, S. Structural properties and catalytic activity of Mn-MCM-41 mesoporous molecular sieves for single-step amination of benzene to aniline. Appl. Catal. A Gen. 2008, 351, 59–67. [CrossRef]
49. Reddy, B.M.; Bharali, P.; Thrimurthulu, G.; Saikia, P.; Katta, L.; Park, S.-E. Catalytic Efficiency of Ceria–Zirconia and Ceria–Hafnia Nanocomposites for Soot Oxidation. Catal. Lett. 2008, 123, 327–333. [CrossRef]
50. Rao, G.R.; Sahu, H.R. XRD and UV-Vis diffuse reflectance analysis of CeO2-ZrO2 solid solutions synthesized by combustion method. J. Chem. Sci. 2001, 113, 651–658. [CrossRef]
51. Xu, B.; Dong, L.; Chen, Y. Influence of CuO loading on dispersion and reduction behavior of CuO/TiO2 (anatase) system. J. Chem. Soc. Faraday Trans. 1998, 94, 1905–1909. [CrossRef]
52. Zhang, B.; Zhang, J.; Liu, C.; Peng, L.; Sang, X.; Han, B.; Ma, X.; Luo, T.; Tan, X.; Yang, G. High-internal-phase emulsions stabilized by metal-organic frameworks and derivation of ultralight metal-organic aerogels. Sci. Rep. 2016, 6, 21401. [CrossRef] [PubMed]