Article

Catalytic Oxidation of Toluene over Fe-Rich Palygorskite Supported Manganese Oxide: Characterization and Performance

Shiwei Dong\(^1,2,3\), Tianhu Chen\(^1,2,3\), Fan Xu\(^1,2,3\), Haibo Liu\(^1,2,3\), Can Wang\(^1,2,3\), Yinzhen Zhang\(^1,2,3\), Minghao Ji\(^1,2,3\), Chengrui Xu\(^1,2,3\), Chengzhu Zhu\(^1,2,3\), Zhiguo Li\(^4\) and Xuehua Zou\(^1,2,3,4*,\)

1 Institute of Environmental Minerals and Materials, School of Resources and Environmental Engineering, Hefei University of Technology, Hefei 230009, China; dongshiwei@mail.hfut.edu.cn (S.D.); chentianhu@hfut.edu.cn (T.C.); xufan9@mail.hfut.edu.cn (F.X.); liuhaibosky116@hfut.edu.cn (H.L.); wangcan@mail.hfut.edu.cn (C.W.); zhangyinshe@hfut.edu.cn (Y.Z.);

2 Key Laboratory of Nano–Minerals and Pollution Control of Anhui Higher Education Institutes, Hefei University of Technology, Hefei 230009, China

3 Institute of Atmospheric Environment & Pollution Control Engineering, School of Resources and Environmental Engineering, Hefei University of Technology, Hefei 230009, China

4 Linhuan Coking Co., Ltd., Huaibei Mining Industry Group, Huaibei 235141, China; eunhyojoon@gmail.com

* Correspondence: zouxuehua1988@hfut.edu.cn

Abstract: A series of Fe–rich palygorskite supported manganese oxide (X%Mn–Pal) catalysts were prepared by co-precipitation method and used as catalysts for toluene oxidation. The components and structure of the as-prepared catalysts were characterized by XRD, Raman, TEM, XPS, and in situ DRIFTS. The results showed that the 15%Mn–Pal catalyst exhibited the highest catalytic activity (\(T_{90} = 227^\circ\)C) and excellent cycling stability for the oxidation of toluene compared with other catalysts. The characterization results indicated that remarkable activity of the 15%Mn–Pal catalyst for toluene oxidation should be ascribed to the abundant surface oxygen vacancies. In situ DRIFTS results elucidated that benzoate was the main intermediate, which can be further oxidized into \(\text{H}_2\text{O}\) and \(\text{CO}_2\). The objectives of this study are to (i) investigate the synergistic effect between Fe and Mn for toluene oxidation, (ii) develop an efficient catalyst for toluene abatement with high activity and low–cost, and (iii) promote the application of natural Fe–rich palygorskite in the control of VOCs.

Keywords: Catalytic oxidation; toluene; Fe-rich palygorskite; manganese oxide

1. Introduction

Volatile organic compounds (VOCs) are the significant precursors of photochemical smog, ozone, and secondary organic aerosols. Many countries and organizations have identified hundreds of chemicals as VOCs, which are seriously harmful to both the ecological environment and human health [1–3]. In recent years, numerous post-treatment techniques have been developed to eliminate VOCs emission, including adsorption, photocatalytic oxidation, plasma, absorption, and catalytic oxidation [4]. Among these techniques, catalytic oxidation was considered to be one of the most promising methods with the advantages of high removal efficiency, low reaction temperature, and less secondary pollutants [5].

Up to date, researchers have developed a variety of catalysts for the removal of VOCs, mainly including precious metal materials [6,7] and transition-metal oxides [8,9]. Although the noble metal catalysts display excellent properties, the problems of high cost, easy sintering, and poisoning have not been effectively solved, which limit their further practical applications [10]. Compared to noble–metal materials, transition metal oxides are considered as the candidate catalysts for VOCs oxidation due to their low cost, high thermal stability, and considerable reducibility [11–14]. Recently, the mixed metal oxide catalysts have attracted increasing attention due to their synergistic effect with many beneficial properties [15]. Of the mixed metal oxide-based catalysts, Fe–Mn oxide catalysts have

---

Citation: Dong, S.; Chen, T.; Xu, F.; Liu, H.; Wang, C.; Zhang, Y.; Ji, M.; Xu, C.; Zhu, C.; Li, Z.; et al. Catalytic Oxidation of Toluene over Fe-Rich Palygorskite Supported Manganese Oxide: Characterization and Performance. *Catalysts* 2022, 12, 763. https://doi.org/10.3390/catal12070763

Academic Editor: Jean-François Lamonier

Received: 12 June 2022
Accepted: 7 July 2022
Published: 9 July 2022

Publisher’s Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).
shown promise for the elimination of VOCs [16–18]. The strong interaction between Fe and Mn enhances the reducibility and surface oxygen vacancy of catalysts, which improve the catalytic activity at low temperatures [19,20]. Meanwhile, for the composite metal oxide catalysts, the dispersion of active components is an important factor of the catalytic properties for VOCs oxidation. However, there remains a challenge to further promote the dispersion of active components and prevent the presence of aggregation.

Supports not only improve the distribution of active ingredients, but also contribute to the enhancement of the activity through the interaction with the active species. Recently, the application of natural clay minerals (e.g., palygorskite, diatomite, montmorillonite, and halloysite) for catalytic supports have attracted great attention due to their excellent thermal stability, chemical stability, and abundant mesopores structure [21–23]. Palygorskite (Pal) is a natural rod-like clay mineral with the chemical formula of Mg$_5$Si$_8$O$_{20}$(OH)$_2$(H$_2$O)$_4$·4H$_2$O, and aluminum or iron has an obvious substitution of magnesium. Furthermore, Pal possesses a large specific surface area, strong thermal and chemical stability, and abundant nanopores, which endow it with great potential as a catalyst support [24]. In our previous work, Pal was investigated as a support for Mn–Ce, Al–Ni, and Fe–Ni oxides, and has shown effective performance in the oxidation of formaldehyde and the reforming of methane or toluene [25–27]. The high specific surface area facilitates the uniform dispersion of active components, while the plentiful nanopores favor the interaction and mass transfer of reactants. The results indicated that Pal presented excellent performance as a catalyst support. Although many researchers have investigated the effects of catalyst preparation methods, additive types, and loading amount over Pal–supported catalysts for formaldehyde oxidation, few studies have focused on the low–grade Fe–rich Pal as a support to prepare Mn–Fe/Pal catalysts for toluene oxidation.

Herein, the red Fe–rich Pal was used as the support to prepare Mn–Fe/Pal catalysts by co–precipitation method. The as–prepared catalysts were used for the catalytic oxidation of toluene. The catalytic behaviors for toluene oxidation of the catalysts with different Mn loadings were investigated, and the structure–activity relationships of the catalysts were discussed. The aims of this study were to (i) investigate the synergistic effect of Fe and Mn for toluene oxidation over Mn–Fe/Pal catalyst, (ii) elucidate the mechanism and the role of Pal in the process of toluene oxidation, and (iii) develop a cost–effective catalyst for toluene elimination and promote the application of the low–grade Fe–rich palygorskite in VOCs abatement.

2. Results
2.1. Material Characterization
2.1.1. XRD and Raman Analysis

The XRD patterns of the as-prepared catalysts are shown in Figure 1a. The characteristic reflections at 8.7°, 19.8°, 27.7° and 34.8° are identified as Pal, while the peaks located at 20.8°, 26.8°, 36.5°, 42.5°, 50.2°, 59.9° and 68.3° are assigned to quartz. For the X%Mn–Pal catalysts, the diffraction peaks corresponding to the bixbyite Mn$_2$O$_3$ are found at 32.9°, 38.2°, 49.4°, 55.3° and 65.9°, indicating that Mn$_2$O$_3$ was formed on the surface of Pal [12]. The peak intensity of Pal on X%Mn–Pal catalysts were decreased compared to that of Pal-Raw, which is likely due to the poor crystallinity and the high distribution of Mn oxides on Pal. The XRF result shows that roughly 7.65% of Fe$_2$O$_3$ was detected in Pal, but no XRD reflections of α–Fe$_2$O$_3$ can be observed, which should be ascribed to the low crystallinity of α–Fe$_2$O$_3$ and the detective restriction of XRD instrument.

The manganese oxides on the surface of Pal were further characterized by Raman spectroscopy. As presented in Figure 1b, all X%Mn–Pal catalysts display a strong band at ~650 cm$^{-1}$ corresponding to a characteristic symmetric stretch of Mn–O–Mn of Mn$_2$O$_3$, while a weak peak at 311 cm$^{-1}$ is consistent with the asymmetric stretch of Mn–O–Mn. These results are in good agreement with the previous reports [28,29]. The bands relating to α–Fe$_2$O$_3$ can be obviously observed in Raman spectrum, which locates at 398 cm$^{-1}$ and
1317 cm\(^{-1}\) [30]. Therefore, based on the XRD and Raman results, the Fe–rich palygorskite supported manganese oxide catalysts were successfully prepared.

![Figure 1. XRD patterns (a) and Raman spectra (b) of as–prepared catalysts.](image)

**Figure 1.** XRD patterns (a) and Raman spectra (b) of as–prepared catalysts.

2.1.2. TEM Analysis

The TEM and EDS–mapping images of 15%Mn-Pal are shown in Figure 2. Palygorskite displays the typical rod-like structure with a diameter of 20 nm in width (Figure 2a,b). Moreover, Figure 2c–e shows that the distributions of Al, Mg, and Si further confirm the rod–like structure of Pal. The EDS–mapping images show that Fe highly disperses on the surface of Pal (Figure 2f); meanwhile, Mn has the similar distribution to that of Fe (Figure 2g). This result indicated that Mn might have intimate interaction with Fe on the surface of Pal.

![Figure 2. TEM and EDS–mapping images of 15%Mn–Pal. (a, b) 15%Mn-Pal catalyst at different scales; (c–g) the distribution of Al, Mg, Si, Fe, Mn; (h) the lattice spacing image.](image)

**Figure 2.** TEM and EDS–mapping images of 15%Mn–Pal. (a,b) 15%Mn-Pal catalyst at different scales; (c–g) the distribution of Al, Mg, Si, Fe, Mn; (h) the lattice spacing image.

Furthermore, the lattice spacing of the 15%Mn–Pal catalyst was clearly calculated, and according to the previous reports, the obvious lattice fringes with the spacing of 0.27 and 0.254 nm corresponding to the (222) plane of Mn\(_2\)O\(_3\) [31] and the (110) plane of Fe\(_2\)O\(_3\) [32], respectively.

2.1.3. XPS Analysis

XPS experiments were performed to understand the surface elemental chemical state of the as–prepared catalysts. The results were shown in Figure 3 and the ratios of various elements for the as–prepared samples were summarized in Table 1. The survey spectrum demonstrated that O, Mn, and Fe species were found in the samples. In the Figure 3b, the Mn 2p\(_{3/2}\) spectra could be divided into three components corresponding to the surface Mn\(^{4+}\) (–643.4 eV), Mn\(^{3+}\) (–641.9 eV), Mn\(^{2+}\) (–640.8 eV) species, respectively [17,33,34].
Meanwhile, the 56.1% of Mn\(^{3+}\) contents for 15%Mn-Pal is higher than that of 20%Mn–Pal (49.8%) (as shown in Table 1). According to the previous reports [35,36], Mn\(^{3+}\) plays an important role in the oxidation of VOCs, and the content of Mn\(^{3+}\) is used to evaluate the concentration of oxygen vacancy, while more oxygen vacancies favored the VOCs oxidation at low temperature.

![Figure 3](image)

**Figure 3.** XPS spectra of various catalysts: (a) full spectra, (b) Mn 2p\(_{3/2}\), (c) O1s, (d) Fe 2p\(_{3/2}\).

| Catalyst     | Mn\(^{2+}\)% | Mn\(^{3+}\)% | Mn\(^{4+}\)% | Fe\(^{2+}\)% | Fe\(^{3+}\)% | O\(_{\text{latt}}\)% | O\(_{\text{abs}}\)% | O\(_{\text{OH}}\)% |
|--------------|--------------|--------------|--------------|--------------|--------------|----------------|----------------|----------------|
| 15%Mn-Pal    | 15.8         | 56.1         | 28.1         | 33.3         | 66.7         | 4.9            | 57.4           | 32.6           |
| 20%Mn-Pal    | 18.9         | 49.8         | 31.3         | 45.8         | 54.2         | 11.9           | 55.5           | 37.7           |

Three kinds of surface oxygen species were clearly observed from the O1s spectra in Figure 3c. The one peak located at ~530.1 eV was assigned to the lattice oxygen species (O\(_{\text{latt}}\)), and the peaks located at around 531.6 eV and 532.5 eV are ascribed to the surface adsorbed oxygen (O\(_{\text{ads}}\)) and surface hydroxyl oxygen (O\(_{\text{OH}}\)) species [22,37], respectively. Literature demonstrates that the surface adsorbed oxygen species play an important role in the deep oxidation of VOCs [12,38]. The higher content of surface adsorbed oxygen indicates more oxygen vacancies exist on the surface of the catalysts [39]. As shown in Table 1, 15%Mn–Pal (57.4%) shows a relatively higher surface adsorbed oxygen, which is consistent with the content of Mn\(^{3+}\).

The Fe 2p\(_{3/2}\) region is composed of two peaks, the peak at around 711.2 eV is indicative of the presence of Fe\(^{2+}\), whereas the other peak at 712.9 eV should be assigned to the surface Fe\(^{3+}\) [17,31]. The Fe\(^{3+}\) content of 15%Mn–Pal (66.7%) is higher than that of 20%Mn-Pal (54.1%). The large amount of Fe\(^{3+}\) requires the generation of free electron in the crystal matrix to achieve charge balance via the reaction of Fe\(^{2+}\) + Mn\(^{4+}\) → Fe\(^{3+}\) + Mn\(^{3+}\), which favors the total oxidation of toluene [40].

### 2.1.4. Electrochemical Property

The electrochemical properties of the as-prepared samples were also investigated. As shown in Figure 4a, the 15%Mn–Pal catalyst has higher anodic and cathodic currents, and the cyclic voltammetry (CV) curve area is larger than that of the other catalysts. The results demonstrated that 15%Mn–Pal has higher electrical activity which is beneficial to electrochemical reactions [41,42]. The Tafel curve in Figure 4b shows the similar trend with that of the CV results, in which 15%Mn–Pal shows a lower negative potential than those of the other samples. This result demonstrated the easier electron transfer occurring in
15% Mn–Pal, which is conducive to the redox reactions, and thus, enhancing its catalytic activity for toluene oxidation [43].

![Graph](image)

**Figure 4.** Electrochemical properties of all catalysts: (a) CV curves, (b) Tafel curves.

### 2.1.5. BET Analysis

It is generally believed that the catalytic activity of catalysts is closely related to their surface texture. The N₂ adsorption–desorption isotherms and pore size distributions of all samples were displayed in Figure 5. It can be seen from Figure 5a that these catalysts all showed typical type IV adsorption–desorption isotherms with H₃ hysteresis loop, and indicated that mesopores were formed in all the catalysts. Figure 5b showed the pore size distributions of each sample, which further confirmed the existence of mesoporous structure in the catalysts. Specifically, the textural parameters of the different catalysts were listed in Table 2. It was observed that the 15% Mn–Pal catalyst showed the maximum surface area (82.7 m²/g) and biggest pore volume (0.17 cm³/g), which may promote the adsorption of toluene on the surface of catalyst, and contribute to the improved catalytic performance.

![Graph](image)

**Figure 5.** N₂ adsorption–desorption isotherms (a) and pore–size distributions (b) of all catalysts.

### Table 2. Real Mn loading (wt%) and textural properties of the catalysts.

| Catalyst   | Mn Loading (wt%) | S_{BET} (m²/g) | Total Pore Volume (cm³/g) |
|------------|------------------|----------------|---------------------------|
|            | Theoretical      | Actual         |                           |
| Pal-Raw    | –                | 48.1           | 0.14                      |
| 5%Mn-Pal   | 5                | 56.2           | 0.16                      |
| 10%Mn-Pal  | 10               | 59.6           | 0.15                      |
| 15%Mn-Pal  | 15               | 82.7           | 0.17                      |
| 20%Mn-Pal  | 20               | 52.4           | 0.15                      |
2.1.6. Mechanism Analysis

In situ DRIFTS experiments were conducted to understand the reaction mechanism of toluene oxidation over 15%Mn–Pal. Figure 6a shows a typical set of temperature dependent DRIFTS spectra during the toluene oxidation process over the 15%Mn-Pal catalyst under 25−275 °C. When toluene was introduced into the reaction system at 25 °C for 30 min, a series of peaks can be observed. The peak at 3029 cm$^{-1}$ is the signal of C−H stretching vibration on aromatic ring, while two peaks at 2927 cm$^{-1}$ and 2875 cm$^{-1}$ represent the methyl and methylene species, respectively [44]. Strong broad band at 1635 cm$^{-1}$ (δ(H−O−H)) is ascribed to the isolated –OH species on the catalyst surface [45], and it gradually disappeared as the temperature increased. In addition, the peak at 1497 cm$^{-1}$ (ν(C=C)) is ascribed to the aromatic ring in-plane vibration [46]. These absorption bands indicated that the toluene was adsorbed on the surface of the 15%Mn–Pal. The adsorption and activation of toluene on the catalyst surface changed significantly as the temperature increased. The intensities of these bands at 1497 cm$^{-1}$ and 3029 cm$^{-1}$ decreased and gradually disappeared with the increase in the reaction temperature. Meanwhile, a weak and new band at 1176 cm$^{-1}$ was found, which can be assigned to the C−O stretching vibration of benzyl alcohol (C$_6$H$_5$−CH$_2$O−). This result indicates that the toluene adsorbed on the surface of catalyst can be converted into benzyl alcohol [12]. In the high wavenumber range, the peak appears at 3068 cm$^{-1}$ is attributed to the ν(CH−) stretching vibration of methyl group [12]. Additionally, two peaks appear at 1228 cm$^{-1}$ and 1257 cm$^{-1}$ may belong to the phenolate (C$_6$H$_5$−OH) species [44], and the peak located at 1535 cm$^{-1}$ can correspond to the asymmetric ν(C=O) stretching vibration of a typical carboxylate group [12]. Furthermore, the peak at 1597 cm$^{-1}$ can be ascribed to the skeleton ν(C=C) vibration of the aromatic ring [47], and the 1405 cm$^{-1}$ is a C−O symmetric stretching vibration, indicating that the formation of benzoate. The band located at 1357 cm$^{-1}$ is the characteristic of acetate species [15]. With the temperature increased from 150 to 275 °C, the intensities of 1597 and 1357 cm$^{-1}$ increased first and then decreased; meanwhile, the peak of surface maleic anhydride species at 1305 cm$^{-1}$ and 1357 cm$^{-1}$ gradually increased at 200 °C, indicating that these intermediates were gradually accumulated on the catalyst. This phenomenon can be explained by the further conversion of benzyl alcohol and benzoate to anhydride and acetate. Afterwards, these species can be deeply oxidized to CO$_2$ and H$_2$O.

Figure 6. (a) In situ DRIFTS spectra of toluene oxidation as a function of temperature and (b) characteristic IR peak area of four intermediates versus temperature.
The characteristic IR peak of the intermediates (1176 cm\(^{-1}\) benzyl alcohol, 1535 cm\(^{-1}\) benzoate, 1305 cm\(^{-1}\) anhydride, and 1357 cm\(^{-1}\) acetate) is calculated by integral area, and the results were shown in Figure 6b. The amount of benzyl alcohol species initially increased when the temperature was lower than 225 °C, and then decreased. The formation of the four intermediates on the surface of the 15%Mn–Pal was accumulated to the maximum at the reaction temperature of 225 °C. Among them, the benzoate species has the largest amount on the surface of the 15%Mn–Pal, indicating that the aromatic ring of benzoate species is difficult to break. Based on the temperature-dependent DRIFTS results, it suggests that the toluene oxidation reaction occurs via the benzyl alcohol → benzoate → anhydride → acetate pathway, and as shown in Figure 7. The toluene adsorbed on the catalyst surface first undergoes a dehydrogenation with oxygen to form alcohols, and then oxidized into benzoate, anhydride and CO\(_2\) and H\(_2\)O. Furthermore, the deep oxidation of benzoate species or the C=C breakage of the aromatic ring could be the rate-controlling step in the toluene oxidation.

![Proposed mechanism for toluene oxidation.](image)

**Figure 7.** Proposed mechanism for toluene oxidation.

### 2.2. Evaluation of Catalytic Activity

#### 2.2.1. Catalytic Performance

The catalytic activities of as-prepared catalysts for toluene oxidation were evaluated. The component of the reaction gas mixture contains 1000 ppm toluene, the total flow was 100 mL/min, and the gas hourly space velocity (GHSV) was 20,000 mL/(g·h). The relationship between the reaction temperature and toluene conversion is shown in Figure 8, and the \(T_{50}\) and \(T_{90}\) (the temperatures for 50% and 90% conversion of toluene, respectively) are used to evaluate the catalytic performance of the catalysts. As shown in Figure 7, Pal–Raw has no obvious effect on toluene oxidation. The conversion of toluene was less than 6% in the entire temperature range, which should be due to the adsorption of toluene on the surface of Pal–Raw. Compared with Pal–Raw, the catalytic activity of 5%Mn–Pal was significantly improved, and the \(T_{50}\) and \(T_{90}\) were 223 °C and 248 °C, respectively. This result indicates that Mn plays an important role in the catalytic oxidation of toluene. With the Mn loading increased from 5% to 20%, the catalyst activity increased first and then decreased, the order of catalytic activity is 15%Mn–Pal > 20%Mn–Pal > 10%Mn–Pal > 5%Mn–Pal. Compared to 15%Mn–Pal, the lower catalytic activity of 20%Mn–Pal is likely due to the aggregation of excessive Mn on the surface of the catalyst. Based on the above results, Pal is considered as an acceptable support to synthesis the supported catalysts for toluene elimination.
2.2.2. Stability Test

It is well known that the stability of the catalyst determines its potential application to some extent. Therefore, three consecutive catalytic cycling experiments were carried out on the 15%Mn–Pal catalyst to investigate its catalytic stability, and the results are shown in Figure 9. It is found that the toluene conversion of 15%Mn–Pal catalyst keeps almost unchanged during the four-cycle tests, indicating its good stability for toluene oxidation. In addition, to further examine the possible application of catalyst in real exhaust conditions, the effect of water vapor on the catalytic performance of 15%Mn–Pal was explored at the GHSV of 20,000 mL/(g·h). As shown in Figure 10a, the toluene conversion decreased but remained above 90% after 5 vol% of water vapor was introduced into the stream at 250 °C at least for 5 h. After turning off the addition of water vapor, the toluene conversion was perfectly recovered. This result demonstrated that water vapor has little influence on the catalytic activity of 15%Mn-Pal for toluene conversion. The effect of different GHSV on the catalytic activity of the 15%Mn-Pal catalyst has also been investigated, as shown in Figure 10b. Obviously, the catalytic activity of 15%Mn–Pal is influenced by the GHSV values. With the GHSV increased from 20,000 to 60,000 mL/(g·h), the curves of toluene conversion versus reaction temperature shift to a higher temperature range. Nevertheless, the $T_{50}$ and $T_{90}$ of toluene conversion only increased by approximately 10 °C. The results indicated that the GHSV has a moderate effect on the catalytic activity of the catalyst. According to the above results, the prepared catalyst has persistent catalytic performance under the simulated real exhaust conditions.
2.2.3. Kinetic Study

The kinetics study of x%Mn–Pal catalysts for toluene oxidation were investigated in the absence of internal and external diffusion limitations. To obtain the reliable kinetic data, the toluene conversion should be controlled below 20% [37]. The apparent activation energy ($E_a$, kJ/mol) for toluene oxidation can be calculated according to the following equations:

\[
\begin{align*}
r_{\text{toluene}} &= \frac{C_{\text{in}} \times \eta \times F}{m} \\
\ln(r_{\text{toluene}}) &= \frac{E_a}{RT} + C
\end{align*}
\]

where $r_{\text{toluene}}$ denotes the reaction rate ($r_{\text{toluene}}$, mol C$_7$H$_8$/g·h), $C_{\text{in}}$ is the concentration of toluene in the gas mixture (ppm), $\eta$ is the toluene conversion, $F$ is the total flow rate (mL/min), $m$ is the catalyst weight (g), $T$ is the reaction temperature, $R$ is the gas constant, and $E_a$ (kJ/mol) is the apparent activation energy.

As can be seen from Figure 11a, the 15%Mn–Pal catalyst showed the highest toluene conversion than that of 10%Mn–Pal and 20%Mn–Pal at the same reaction temperatures. According to the toluene conversion, the $E_a$ was evaluated and shown in Figure 11b. It is evidence that the activation energy of 15%Mn–Pal (125.7 kJ/mol) was lower than those of 10%Mn–Pal (157.9 kJ/mol) and 20%Mn–Pal (142.4 kJ/mol), which indicates the excellent catalytic activity of 15%Mn–Pal for toluene oxidation.

3. Discussion

It is well known that the catalytic activity of the Mn oxide catalysts is affected by their physical and chemical properties, such as the active component, specific surface area, the
valence state of Mn, and the surface adsorbed oxygen or lattice oxygen concentration [7]. In this work, the x%Mn–Pal catalysts were successfully obtained. It was found that Mn oxides are the main active components and the content of Mn affected the catalytic performance in toluene oxidation. The higher Mn content favors the catalytic activity of x%Mn–Pal catalyst, but excessive Mn loading inhibited the catalytic activity for toluene conversion due to the aggregation of Mn oxides [48]. The 15%Mn–Pal had the highest catalytic activity for toluene oxidation among these samples, which obtained 90% conversion of toluene at 227 °C and had excellent catalytic stability and water resistance.

In addition, the concentrations of Mn$^{3+}$ and O$_{ads}$ species of catalyst were also crucial for the deep oxidation of VOCs [49,50]. It has proved that higher Mn$^{3+}$ and O$_{ads}$ are conducive to promote the formation of oxygen vacancies, and then produce more reactive oxygen species, which is beneficial to improve the catalytic activity of samples [51]. As shown in Table 1, the 15%Mn–Pal showed a higher Mn$^{3+}$ and O$_{ads}$ species than those of the other samples, which was consistent with the results of catalytic activity in Figure 7. Generally, the catalytic mechanism of toluene over Mn–based catalysts belongs to the Mars–van Krevelen mechanism, in which the adsorbed toluene molecules can react with the surface mobile O$_{latt}$ species to form CO$_2$ and H$_2$O. Meanwhile, abundant surface adsorbed oxygen species provide the stronger oxygen mobility, which is conducive to supplementing gaseous oxygen through oxygen vacancies, thus, efficiently accelerating the replenishment of the O$_{latt}$ species in the reaction process and improving the catalytic performance [52,53]. Based on the characterization results, 15%Mn–Pal has more oxygen vacancies and stronger oxygen mobility than those of the other catalysts, exhibiting the best catalytic performance for toluene oxidation in this study.

4. Materials and Methods
4.1. Catalyst Synthesis
4.1.1. Materials

Raw palygorskite (Pal) sample used in this study was obtained from Linze, Gansu Province, China. XRF results showed that the main elemental composition of Pal is SiO$_2$ 59.61 wt%, Al$_2$O$_3$ 19.68 wt%, Fe$_2$O$_3$ 7.65 wt%, MgO 3.14 wt%, others 2.38 wt%, and the ignition loss 7.54 wt%. Ethanol, Ammonium bicarbonate (NH$_4$HCO$_3$) and Manganese nitrate (Mn(NO$_3$)$_2$) solution 50 wt% were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals used in this work were analytical reagent (AR).

4.1.2. Catalyst Preparation

The Pal–supported catalysts were synthesized via a co-precipitation method. In a typical synthesis process, 10 g of the Pal was placed into a clean 500 mL beaker, and different amounts of NH$_4$HCO$_3$ and 50 wt% Mn(NO$_3$)$_2$ solution (5, 10, 15, 20 wt% in weight percent) were dissolved into 200 mL ethanol and 100 mL deionized water to obtained clear I and II solutions, respectively. Then, the solution of I and II were added quickly to the beaker containing 10 g Pal under vigorous stirring, and the above-mixed solution was further aged at room temperature for 12 h. The formed precipitates were collected by the centrifugation method and washed several times with deionized water and ethanol. After that, the collected samples were dried at 105 °C overnight and then ground to a particle size of 40–60 mesh. The samples were calcinated at 400 °C in the air for 4 h with a heating rate of 5 °C/min. The as-prepared catalysts were labeled as X%Mn–Pal, where X denotes as the loading content of Mn in weight percent, and Pal–Raw represents the natural palygorskite. As shown in Table 2, the actual Mn loadings of the as-prepared catalysts measured by the flame atomic absorption spectrometer, which was in good agreement with the theoretical calculated value, indicating that the X%Mn–Pal catalyst was successfully prepared.

4.2. Catalyst Characterization

The X-ray diffraction (XRD) patterns of catalysts were recorded on an X–Ray diffractometer (Dandong Haoyuan-DX–2700, Dandong, China) using Cu–Kα radiation generated
at 50 kV and 100 mA in the 5 and 70° range. Raman spectra of catalysts were obtained using a LabRAM HR Evolution with a 532 nm line. Transmission electron microscopy (TEM) measurements were obtained on a JEM–2100 microscope with an energy dispersive spectrometer. The X-ray photoelectron spectroscopy (XPS) signals of catalysts were measured on a Thermo Scientific K–Alpha instrument equipped with an Al Kα source. The specific surface area was measured by N₂ adsorption–desorption at liquid nitrogen temperature using a Quantachrome NOVA 3000e analyzer. The electrochemical properties of the catalysts were obtained using an electrochemical workstation (CHI–660, Chenhua, Shanghai, China). Real Mn loading of the catalysts determined by the flame atomic absorption spectrometer (WYS2200, WAYEE, Hefei, China). In situ DRIFTS was carried on a spectrometer (VERTEX 70, Bruker, Karlsruhe, Germany) in the range of 400~4000 cm⁻¹ with a resolution of 4 cm⁻¹ and an accumulation of 64 scans.

4.3. Catalytic Activity Measurement

The dynamic activities of the as-prepared catalysts for toluene oxidation were carried out in a homemade fixed-bed quartz reactor. For each test, 0.4 g catalyst (40–60 mesh) was placed in the middle of the reactor (inner diameter 8 mm) and supported by quartz wool. The required concentration of toluene (1000 ppm) was injected by a syringe pump and balanced by pure air with a total flow of 100 mL/min. To avoid the condensation of toluene vapor, a heating tape with 60 °C was attached to the gas pipeline. A gas chromatograph (GC–9790II, FULI) equipped with an FID detector was used to monitor the trend of toluene concentration online. The toluene conversion (η, %) was calculated according to the following equation:

\[ \eta = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% \] (3)

where \( C_{\text{in}} \) and \( C_{\text{out}} \) are the influent and effluent concentration of toluene.

5. Conclusions

In this paper, x%Mn–Pal catalysts with different Mn contents were successfully prepared via co-precipitation method and their catalytic performance for toluene combustion was evaluated. It was found that 15%Mn–Pal catalyst exhibited the highest catalytic activity and 90% conversion of toluene was obtained at 227 °C, and exhibited practical cycle stability. Moreover, the relationship between the catalytic performance and structure was deeply investigated by various characterizations, including XRD, Raman, TEM, BET, XPS, and in situ DRIFTS. The results showed that the addition of Mn promotes the catalytic oxidation of toluene. The 15%Mn–Pal catalyst has the maximum surface area of 82.7 m²/g, which is conducive to the adsorption of toluene on the catalyst surface. In addition, 15%Mn–Pal catalyst possessed more oxygen vacancies, which were related to the higher contents of Mn³⁺ and O_ads species. The large number of oxygen vacancies lead to an increase in oxygen mobility and beneficial to the catalytic oxidation of toluene. This study implied that Fe–rich palygorskite can be used as the low cost and environmentally friendly catalyst support for catalytic oxidation of VOCs.

Author Contributions: Conceptualization, S.D. prepared the catalysts, performed catalysts characterization and catalytic oxidation tests, and wrote the manuscript. F.X. helped with the catalyst preparation, catalytic oxidation experiments. T.C. and H.L. provided constructive suggestions and had multiple discussions during the experiment. C.W. helped with the kinetic study and in situ DRIFTS experiments. Y.Z. conducted the TEM and XPS and the corresponding figures plotting. M.J. and C.X. conducted the Raman and XRD the corresponding figures plotting. C.Z. provided the experimental instruments. Z.L. provided constructive suggestions. X.Z. provided the ideas, the constructive suggestions and had discussions during the manuscript written. All authors have read and agreed to the published version of the manuscript.
**Funding:** This research was funded by the National Science Foundation of China (No. 41872040 and 42102029), the attapulgite industry development and opening issues of Linze county (No. LZFQKT-1902), Anhui Provincial Natural Science Foundation (No. 2108085QD164), and the fundamental Research Funds for the Central Universities (No. JZ2022HGTB0359).

**Data Availability Statement:** The data of this research are available within the manuscript.

**Acknowledgments:** The authors wish to acknowledge the Strategy Alliance of Attapulgite Industry Technology Innovation of Gansu Province. Many thanks the Analysis and Testing Center of Hefei University of Technology.

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

**References**

1. Liu, P.; Wei, G.; He, H.; Liang, X.; Chen, H.; Xi, Y.; Zhu, J. The catalytic oxidation of formaldehyde over palygorskite-supported copper and manganese oxides: Catalytic deactivation and regeneration. *Appl. Surf. Sci.* 2019, 464, 287–293. [CrossRef]

2. Zhu, L.; Shen, D.; Luo, K.H. A critical review on VOCs adsorption by different porous materials: Species, mechanisms and modification methods. *J. Hazard. Mater.* 2020, 389, 122102. [CrossRef] [PubMed]

3. Liu, L.; Li, J.; Zhang, H.; Li, L.; Zhou, P.; Meng, X.; Guo, M.; Jia, J.; Sun, T. In situ fabrication of highly active gamma-MnO2/SmMnO3 catalyst for deep catalytic oxidation of gaseous benzene, ethylbenzene, toluene, and o-xylene. *J. Hazard. Mater.* 2019, 362, 178–186. [CrossRef] [PubMed]

4. He, C.; Cheng, J.; Zhang, X.; Douthwaite, M.; Pattisson, S.; Hao, Z. Recent Advances in the Catalytic Oxidation of Volatile Organic Compounds: A Review Based on Pollutant Sorts and Sources. *Chem. Rev.* 2019, 119, 4471–4568. [CrossRef] [PubMed]

5. Tang, W.; Wu, X.; Li, S.; Li, W.; Chen, Y. Porous Mn–Co mixed oxide nanorod as a novel catalyst with enhanced catalytic activity for removal of VOCs. *Catal. Commun.* 2014, 56, 134–138. [CrossRef]

6. Lu, A.; Sun, H.; Zhang, N.; Che, L.; Shan, S.; Luo, J.; Zheng, J.; Yang, L.; Peng, D.-L.; Zhong, C.-J.; et al. Surface Partial-Charge-Tuned Enhancement of Catalytic Activity of Platinum Nanocatalysts for Toluene Oxidation. *ACS Catal.* 2019, 9, 7431–7442. [CrossRef]

7. Li, L.; Wahab, M.A.; Li, H.; Zhang, H.; Deng, J.; Zhai, X.; Masud, M.K.; Hossain, M.S.A. Pt-Modulated CuMnOx Nanosheets as Catalysts for Toluene Oxidation. *Appl. Nano Mater.* 2021, 4, 6637–6647. [CrossRef]

8. Wang, F.; Dai, H.; Deng, J.; Bai, G.; Ji, K.; Liu, Y. Manganese oxides with rod-, wire-, tube-, and flower-like morphologies: Highly effective catalysts for the removal of toluene. *Environ. Sci. Technol.* 2012, 46, 4034–4041. [CrossRef]

9. Chen, J.; He, Z.; Li, G.; An, T.; Shi, H.; Li, Y. Visible-light-enhanced photothermocatalytic activity of ABO3-type perovskites for the decontamination of gaseous styrene. *Appl. Catal. B Environ.* 2017, 209, 146–154. [CrossRef]

10. Kim, S.C.; Shim, W.G. Catalytic combustion of VOCs over a series of manganese oxide catalysts. *Appl. Catal. B Environ.* 2010, 98, 180–185. [CrossRef]

11. Kim, I.H.; Park, E.J.; Park, C.H.; Han, S.W.; Seo, H.O.; Kim, Y.D. Activity of catalysts consisting of Fe2O3 nanoparticles decorating entire internal structure of mesoporous Al2O3 bead for toluene total oxidation. *Catal. Today.* 2017, 295, 56–64. [CrossRef]

12. Mo, S.; Zhang, Q.; Li, J.; Sun, Y.; Ren, Q.; Zou, S.; Zhang, Q.; Lu, J.; Fu, M.; Mo, D.; et al. Highly efficient mesoporous MnO2 catalysts for the total oxidation of toluene: Oxygen-Vacancy defect engineering and involved intermediates using in situ DRIFTS. *Appl. Catal. B Environ.* 2020, 264, 118464–118479. [CrossRef]

13. Li, B.; Yang, Q.; Peng, Y.; Chen, J.; Deng, L.; Wang, D.; Hong, X.; Li, J. Enhanced low-temperature activity of LaMnO3 for toluene oxidation: The effect of treatment with an acidic KMnO4. *Chem. Eng. J.* 2019, 366, 92–99. [CrossRef]

14. Luo, M.; Cheng, Y.; Peng, X.; Pan, W. Copper modified manganese oxide with tunnel structure as efficient catalyst for low-temperature catalytic combustion of toluene. *Chem. Eng. J.* 2019, 369, 758–765. [CrossRef]

15. Dong, C.; Qu, Z.; Qin, Y.; Fu, Q.; Sun, H.; Duan, X. Revealing the Catalytically Performance of Spinel CoMnO4 for Toluene Oxidation: Involvement and Replenishment of Oxygen Species Using In Situ Designed-TP Techniques. *ACS Catal.* 2019, 9, 6698–6710. [CrossRef]

16. Wang, Y.; Wu, J.; Wang, G.; Yang, D.; Ishihara, T.; Guo, L. Oxygen vacancy engineering in Fe doped akhtenskite-type MnO2 for low-temperature toluene oxidation. *Appl. Catal. B Environ.* 2021, 285, 119873–119888. [CrossRef]

17. Wang, Y.; Zhang, L.; Guo, L. Enhanced Toluene Combustion over Highly Homogeneous Iron Manganese Oxide Nanocatalysts. *ACS Appl. Nano Mater.* 2018, 1, 1066–1075. [CrossRef]

18. Wang, Y.; Wang, G.; Deng, W.; Han, J.; Qin, L.; Zhao, B.; Guo, L.; Xing, F. Study on the structure-activity relationship of Fe-Mn oxide catalysts for chlorobenzene catalytic combustion. *Chem. Eng. J.* 2020, 395, 125172–1125184. [CrossRef]

19. Chen, J.; Chen, X.; Xu, W.; Xu, Z.; Chen, J.; Jia, H.; Chen, J. Hydrolysis driving redox reaction to synthesize Mn-Fe binary oxides as highly active catalysts for the removal of toluene. *Chem. Eng. J.* 2017, 330, 281–293. [CrossRef]

20. Yusuf, S.; Haribal, V.; Jackson, D.; Neal, L.; Li, F. Mixed iron-manganese oxides as redox catalysts for chemical looping–oxidative dehydrogenation of ethane with tolerable heat of reactions. *Appl. Catal. B Environ.* 2019, 257, 117885–117893. [CrossRef]
21. Wang, C.; Zou, X.; Liu, H.; Chen, T.; Suib, S.L.; Chen, D.; Xie, J.; Li, M.; Sun, F. A highly efficient catalyst of palygorskite-supported manganese oxide for formaldehyde oxidation at ambient and low temperature: Performance, mechanism and reaction kinetics. *Appl. Surf. Sci.* **2019**, *486*, 420–430. [CrossRef]

22. Han, Z.; Wang, C.; Zou, X.; Chen, T.; Dong, S.; Zhao, Y.; Xie, J.; Liu, H. Diatomite-supported bimessite-type MnO₂ catalytic oxidation of formaldehyde: Preparation, performance and mechanism. *Appl. Surf. Sci.* **2020**, *502*, 144201–144210. [CrossRef]

23. Deng, L.; Yuan, P.; Liu, D.; Annabi-Bergaya, F.; Zhou, J.; Chen, F.; Liu, Z. Effects of microstructure of clay minerals, montmorillonite, kaolinite and halloysite, on their benzene adsorption behaviors. *Applied Clay Sci.* **2017**, *143*, 184–191. [CrossRef]

24. Liu, P.; Wei, G.; Liang, X.; Chen, D.; He, H.; Chen, T.; Xi, Y.; Chen, H.; Han, D.; Zhu, J. Synergetic effect of Cu and Mn oxides supported on palygorskite for the catalytic oxidation of formaldehyde: Dispersion, microstructure, and catalytic performance. *Applied Clay Sci.* **2018**, *161*, 265–273. [CrossRef]

25. Wang, C.; Liu, H.; Chen, T.; Qiong, C.; Zou, X.; Xie, J.; Zhang, X. Synthesis of palygorskite-supported Mn₁₋ₓCeₓO₂ clusters and their performance in catalytic oxidation of formaldehyde. *Applied Clay Sci.* **2018**, *159*, 50–59. [CrossRef]

26. Wang, Y.; Chen, T.; Liu, H.; Zhang, P.; Wang, C.; Dong, S.; Chen, D.; Xie, J.; Zou, X.; Suib, S.L.; et al. High catalytic performance of the Al-promoted Ni/Palygorskite catalysts for dry reforming of methane. *Applied Clay Sci.* **2020**, *188*, 105498–105508. [CrossRef]

27. Zou, X.; Chen, T.; Zhang, P.; Chen, D.; He, J.; Dang, Y.; Ma, Z.; Chen, Y.; Toloueiinia, P.; Zhu, C.; et al. High catalytic performance of Fe-Ni/Palygorskite in the steam reforming of toluene for hydrogen production. *Appl. Energy*. **2018**, *226*, 827–837. [CrossRef]

28. Han, Y.; Chen, F.; Zhong, Z.-Y.; Ramesh, K.; Widjaja, E.; Chen, L.-W. Synthesis and characterization of MnₓOᵧ and Mn₂O₃ nanocrystals on SBA-15: Novel combustion catalysts at low reaction temperatures. *Catal. Commun.* **2006**, *7*, 739–744. [CrossRef]

29. Pan, H.; Jian, Y.; Chen, C.; He, C.; Hao, Z.; Shen, Z.; Liu, H. Sphere-Shaped MnₓOᵧ Catalyst with Remarkable Low-Temperature Activity for Methyl-Ethyl-Ketone Combustion. *Environ. Sci. Technol.* **2017**, *51*, 6288–6297. [CrossRef]

30. Liang, X.; Wang, L.; Wen, T.; Liu, H.; Zhang, J.; Liu, Z.; Zhu, C.; Long, C. Mesoporous poorly crystalline alpha-FeₓOᵧ with abundant oxygen vacancies and acid sites for ozone decomposition. *Sci. Total Environ.* **2022**, *804*, 150161. [CrossRef]

31. Li, X.; He, G.; Ma, J.; Shao, X.; Chen, Y.; He, H. Boosting the Dispersity of Metallic Ag Nanoparticles and Ozone Decomposition Performance of Ag-Mn Catalysts via Manganese Vacancy-Dependent Metal-Support Interactions. *Environ. Sci. Technol.* **2021**, *55*, 16143–16152. [CrossRef] [PubMed]

32. Wang, C.; Cheng, X.; Zhou, X.; Sun, P.; Hu, X.; Shimano, K.; Lu, G.; Yamazoe, N. Hierarchical alpha-FeₓOᵧ/NiO composites with a hollow structure for a gas sensor. *ACS Appl Mater Interfaces* **2014**, *6*, 12031–12037. [CrossRef] [PubMed]

33. Huang, X.; Li, L.; Liu, R.; Li, H.; Lan, L.; Zou, W. Optimized Synthesis Routes of MnOₓ-ZrO₂ Hybrid Catalysts for Improved Toluene Combustion. *Catalysts* **2021**, *11*, 1037–1050. [CrossRef]

34. Dong, Y.; Zhao, J.; Zhang, J.-Y.; Chen, Y.; Yang, X.; Song, W.; Wei, L.; Li, W. Synergy of Mn and Ni enhanced catalytic performance for toluene combustion over Ni-doped α-MnO₂ catalysts. *Chem. Eng. J.* **2020**, *388*, 124244–124255. [CrossRef]

35. Awaya, K.; Koyanagi, Y.; Hatakeyama, K.; Ohyama, J.; Guo, L.; Masui, T.; Ida, S. Catalytic Toluene Combustion over Metastable Layered Manganese Cobalt Oxide Nanosheet Catalysts. *Ind. Eng. Chem. Res.* **2021**, *60*, 16930–16938. [CrossRef]

36. Dong, C.; Qu, Z.; Jiang, X.; Ren, Y. Tuning oxygen vacancy concentration of MnO₂ through metal doping for improved toluene oxidation. *J. Hazard. Mater.* **2020**, *391*, 122181. [CrossRef]

37. Chen, B.; Wu, B.; Yu, L.; Crocker, M.; Shi, C. Investigation into the Catalytic Roles of Various Oxygen Species over Different Crystal Phases of MnO₂ for C₆H₆ and HCHO Oxidation. *ACS Catal.* **2020**, *10*, 6176–6187. [CrossRef]

38. Wu, M.; Chen, S.; Xiang, W. Oxygen vacancy induced performance enhancement of toluene catalytic oxidation using LaFeO₃ pervoskite oxides. *Chem. Eng. J.* **2020**, *387*, 124101–124112. [CrossRef]

39. Song, W.; Poyraz, A.S.; Meng, Y.; Ren, Z.; Chen, S.-Y.; Suib, S.L. Mesoporous CoO₄ with Controlled Porosity: Inverse Micelle Synthesis and High-Performance Catalytic CO Oxidation at −60 °C. *Chem. Mater.* **2014**, *26*, 4629–4639. [CrossRef]

40. Peng, P.; Wang, J.; An, X.; Shi, J.; Shangguan, W.; Hao, X.; Xu, G.; Tang, B.; Abudula, A.; Guan, G. Generation of abundant defects in Mn-Co mixed oxides by a facile agar-gel method for highly efficient catalysis of total toluene oxidation. *Appl. Catal. B Environ.* **2021**, *282*, 119560–119571. [CrossRef] [PubMed]

41. Liu, F.; Song, S.; Zhang, P.; Gao, L. One-step synthesis of nanocarbon-decorated MnO₂ with superior activity for indoor formaldehyde removal at room temperature. *Appl. Catal. B Environ.* **2018**, *235*, 158–167. [CrossRef]

42. Hao, L.; Ning, J.; Luo, B.; Wang, B.; Zhang, Y.; Tang, Z.; Yang, J.; Thomas, A.; Zhi, L. Structural evolution of Nitrogen Oxides and Toluene over the Bifunctional CeO₂-TiO₂ Mixed Oxide Catalyst. *Environ. Sci. Technol.* **2022**, *56*, 4467–4476. [CrossRef] [PubMed]

43. Hernández-Alonso, M.D.; Tejedor-Tejedor, I.; Coronado, J.M.; Anderson, M.A. Operando FTIR study of the photocatalytic oxidation of methlycyclohexane and toluene in air over TiO₂–ZrO₂ thin films: Influence of the aromaticity of the target molecule on deactivation. *Appl. Catal. B Environ.* **2011**, *101*, 283–293. [CrossRef]
46. Yang, W.; Su, Z.a.; Xu, Z.; Yang, W.; Peng, Y.; Li, J. Comparative study of α-, β-, γ- and δ-MnO₂ on toluene oxidation: Oxygen vacancies and reaction intermediates. *Appl. Catal. B Environ.* **2020**, *260*, 118150–118159. [CrossRef]

47. Chen, Z.; Peng, Y.; Chen, J.; Wang, C.; Yin, H.; Wang, H.; You, C.; Li, J. Performance and Mechanism of Photocatalytic Toluene Degradation and Catalyst Regeneration by Thermal/UV Treatment. *Environ. Sci. Technol.* **2020**, *54*, 14465–14473. [CrossRef] [PubMed]

48. Huang, J.; Zhang, Y.; Zhang, Y. Preparation and characterization of manganese oxides supported on functionalized halloysite nanotubes with enhanced catalytic oxidation for toluene. *Appl. Clay Sci.* **2021**, *209*, 106147–106155. [CrossRef]

49. Li, K.; Chen, C.; Zhang, H.; Hu, X.; Sun, T.; Jia, J. Effects of phase structure of MnO₂ and morphology of δ-MnO₂ on toluene catalytic oxidation. *Appl. Surf. Sci.* **2019**, *496*, 143662–143671. [CrossRef]

50. Zhang, X.; Zhao, H.; Song, Z.; Liu, W.; Zhao, J.; Ma, Z.a.; Zhao, M.; Xing, Y. Insight into the effect of oxygen species and Mn chemical valence over MnO on the catalytic oxidation of toluene. *Appl. Surf. Sci.* **2019**, *493*, 9–17. [CrossRef]

51. Delimaris, D.; Ioannides, T. VOC oxidation over MnOₓ–CeO₂ catalysts prepared by a combustion method. *Appl. Catal. B Environ.* **2008**, *84*, 303–312. [CrossRef]

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

53. Deng, J.; He, S.; Xie, S.; Yang, H.; Liu, Y.; Guo, G.; Dai, H. Ultralow Loading of Silver Nanoparticles on Mn₂O₃ Nanowires Derived with Molten Salts: A High-Efficiency Catalyst for the Oxidative Removal of Toluene. *Environ. Sci. Technol.* **2015**, *49*, 11089–11095. [CrossRef] [PubMed]