

Article

Mn-Modified MIL-100(Fe)-Derived FeO_x to Boost Toluene Photothermal Catalytic Degradation

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Abstract

The development of highly efficient catalysts is important for the photothermal catalytic oxidation of volatile organic compounds (VOCs). Herein, MIL-100(Fe) was used as the sacrificial template to prepare MnFeO_x catalysts with different Mn contents through the impregnation–calcination method, and their performance in photothermal catalytic oxidation of toluene was investigated. The results show that the content of Mn significantly affects the crystal phase structure, pore properties, surface chemical state, and optical response of the catalyst. Among them, 30% MnFeO_x exhibits the best photothermal catalytic activity, with T_{50} and T_{90} being 211 and 237 °C, respectively, which are significantly lower than those of FeO_x (232 and 260 °C). Characterization results suggested that the introduction of Mn caused the bandgap of FeO_x to decrease from 1.96 to 1.67 eV. Meanwhile, the surface Fe^{2+} , adsorbed oxygen (O_{ads}) species, and oxygen vacancies were increased, enhancing visible light absorption and gaseous oxygen species adsorption and activation, which promoted the photothermal catalytic oxidation of toluene. Additionally, the 30% MnFeO_x catalyst presented good thermal stability and water resistance. Furthermore, during the reaction process, the in situ activation of the catalyst's surface induced the increase in surface Fe^{2+} , Mn^{3+} , and O_{ads} species, which enhances the photothermal catalytic activity of the catalyst. Importantly, the in situ DRIFTS results further indicate that toluene is mainly oxidized along the path of toluene $\rightarrow$ benzyl alcohol $\rightarrow$ benzoate $\rightarrow$ maleic anhydride $\rightarrow$ CO_2 and H_2O . This work provides a theoretical basis for the construction of low-cost, non-precious-metal Mn–Fe-based photothermal catalysts.

Keywords: photothermal catalysis; toluene degradation; MOFs-derivative; MnFeO_x catalysts



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1. Introduction

Volatile organic compounds (VOCs) are significant pollutants in the atmospheric environment. They not only participate in the formation of ground-level ozone and secondary organic aerosols, but also some VOCs have toxic, carcinogenic, and bioaccumulation effects, posing potential threats to the ecological environment and human health [1–3]. Toluene is widely derived from petrochemicals, coatings, printing, adhesives, and the use of organic solvents, and is a common aromatic VOC in industrial exhaust gases. Due to the stable aromatic ring structure of the toluene molecule, the activation of the methyl C–H bond, the

conversion of oxygen-containing intermediates, and the fragmentation of the aromatic ring usually require a high energy barrier. Therefore, completely mineralizing it into CO₂ and H₂O still poses certain challenges. Catalytic oxidation can achieve continuous and deep purification of VOCs without transferring pollutants, and is regarded as one of the most promising treatment technologies. The key issue for catalytic oxidation still lies in catalyst design [1].

Precious metal catalysts usually have good low-temperature oxidation activity, but they are costly, have limited resources, and may undergo sintering and poisoning under high-temperature or complex gas conditions [4]. Therefore, developing inexpensive and stable transition metal oxide catalysts is of great significance. The catalytic performance of transition metal oxides is closely related to the metal valence state, oxygen vacancy concentration, metal–oxygen bond strength, lattice oxygen migration ability, and surface adsorbed oxygen content [5]. Manganese oxides have the ability of Mn²⁺/Mn³⁺/Mn⁴⁺ multi-valent state transformation, which can promote the migration and replenishment of oxygen species through reversible redox cycles [6]. Iron oxides have the advantages of abundant resources, good thermal stability, and more surface oxidation-reduction sites and adsorption sites [7]. Composing Mn and Fe together is expected to regulate the surface electronic structure through the electron exchange between Fe²⁺/Fe³⁺ and Mn²⁺/Mn³⁺/Mn⁴⁺, thereby promoting O₂ adsorption, dissociation, and the migration of reactive oxygen species. Studies have shown that the interaction between Fe and Mn can increase the content of defect-related oxygen species, accelerate the further oxidation of benzyl oxygen-containing intermediates, and promote the fragmentation and deep mineralization of the toluene aromatic ring [8–10]. Therefore, the construction of Mn-Fe composite oxide will promote the degradation of VOCs.

Recently, photothermal catalysis, by coupling the absorption of light energy with thermal catalytic reactions, had provided a new technical approach for reducing the external energy consumption in the oxidation process of VOCs [11]. During the photothermal catalytic process, the absorbed photons can be converted into local thermal energy through non-radiative relaxation of charge carriers, or generate photogenerated carriers and promote the activation of O₂ and surface oxygen species. For composite oxides, light irradiation may also enhance interfacial electron transfer, enabling the synergistic effect of the light and thermal effects. In recent years, catalysts such as CuMn₂O₄/Mn₄O₃ [12], MnO₂ [13], Mn₃O₄/Co₃O₄ [14], and Pt/N-TiO₂ [15] have all demonstrated excellent photothermal oxidation performance for toluene. The enhancement of their activity is usually attributed to wide spectral absorption, increased oxygen vacancies, enhanced lattice oxygen activity, and interface carrier migration. However, in the existing high-performance systems, a considerable portion still relies on precious metals such as Pt or complex heterostructure configurations. For non-precious-metal Mn-Fe mixed oxides, the intrinsic relationship among Mn content, crystal phase evolution, interface redox cycling, and photothermal synergy still needs to be further clarified.

Metal–organic framework materials (MOFs) possess characteristics such as adjustable composition, uniform distribution of metal nodes, and rich pore structures [16]. They can serve as ideal sacrificial templates for the preparation of porous metal oxides. Through thermal decomposition or calcination, the metal nodes in MOFs can be transformed into highly dispersed oxide nanoparticles, while retaining, to a certain extent, the porous structure and shorter mass transfer paths of the precursors. In recent years, the MOF-derived materials MnCo spinels [17] and Co/CoO_x@CN [18] have been used in VOC catalysis or photothermal catalytic oxidation, demonstrating good activity, stability, and water resistance. Herein, MIL-100(Fe) was used as the precursor to prepare FeO_x and a series of Mn-modified MnFeO_x catalysts for photothermal catalytic oxidation of toluene. The physicochemical

properties of the as-prepared catalysts were characterized by various characterization techniques, including X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Raman, N₂ adsorption–desorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The influence of Mn on the crystal structure, pore properties, morphological characteristics, surface electronic state, and optical properties of the catalyst was systematically studied. The stability, reusability, and water resistance of the catalyst were explored. Importantly, the toluene degradation pathway was also proposed *in situ* using diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), indicating that toluene degradation follows: toluene → benzyl alcohol → benzoate → maleic anhydride → CO₂ and H₂O. Meanwhile, the photothermal synergistic effect was evaluated through the comparisons between photothermal and thermal-only reactions and reversible light-on/light-off experiments.

2. Results and Discussions

2.1. Crystal Structure and Pore Properties

2.1.1. Crystal Structure

The FeO_x and corresponding MnFeO_x samples with different Mn contents were synthesized by the MOF templating method, using MIL-100(Fe) as the precursor at 350 °C. Figure 1a presents the X-ray diffraction (XRD) patterns of the as-prepared catalysts. The FeO_x displays 10 diffraction peaks at $2\theta = 24.1^\circ, 33.2^\circ, 35.6^\circ, 40.9^\circ, 49.5^\circ, 54.1^\circ, 57.6^\circ, 62.5^\circ, 64.0^\circ$ and 72.3° , which were indexed to the (012), (104), (110), (113), (024), (116), (018), (214), (300) and (119) planes of planes of rhombohedral hematite α -Fe₂O₃ (PDF#33-0664), respectively [19]. This result suggests that the MOF structure of MIL-100(Fe) was converted to Fe₂O₃ after calcination at 350 °C. After the introduction of Mn, the characteristic peaks of α -Fe₂O₃ are still clearly observed for 5%MnFeO_x and 10%MnFeO_x, and no distinct additional diffraction peaks attributable exclusively to crystalline manganese oxides were detected. This observation suggests that low-load Mn species do not markedly alter the crystalline structure of FeO_x. However, as the contents of Mn increased, the intensity of FeO_x diffraction peaks decreased, and the peak width was broadened. When the contents of Mn increased to 30%, the diffraction peaks of α -Fe₂O₃ disappeared. Meanwhile, some weak and new diffraction peaks at $2\theta = 18.0^\circ, 28.9^\circ, 31.0^\circ, 32.5^\circ, 36.0^\circ, 38.0^\circ, 44.4^\circ, 50.7^\circ, 56.1^\circ, 58.5^\circ, 59.9^\circ$, and 64.5° , corresponding to Mn₃O₄ (PDF#24-0734), appeared [20]. Furthermore, as the content of Mn improved to 50%, the diffraction peaks of Mn₃O₄ were enhanced sharply, suggesting the formation of crystalline Mn₃O₄. Notably, compared with the sharp diffraction peaks observed for 5%MnFeO_x, 10%MnFeO_x, and 50%MnFeO_x, the weakest diffraction peaks were observed in 30%MnFeO_x. Generally, the width of the diffraction peaks is related to the reduction in the coherent crystal domain size, the increase in the lattice micro-strain, or the enhancement of structural disorder [21]. Meanwhile, the crystallite size of α -Fe₂O₃ and Mn₃O₄ on the (104) and (211) crystal faces, respectively, was calculated. As shown in Table 1, the introduction of Mn caused a decrease in the α -Fe₂O₃ crystal size, suggesting that Mn incorporation inhibits the growth of hematite crystallites and increases structural disorder. With a further increase in Mn to 30% and 50%, the diffraction peaks of α -Fe₂O₃ disappeared, the diffraction peaks of Mn₃O₄ appeared, and the crystal size was increased from 8.9 nm to 13.2 nm. This indicated that the increase in Mn content may inhibit the growth of iron oxide grains and the formation of long-range ordered structures, and promote the formation of smaller-sized or less-crystalline oxide structures [22]. These results suggest that the introduction of an appropriate amount of Mn may inhibit the ordered growth of α -Fe₂O₃ grains and increase micro-strain, lattice defects, or interface disorder.

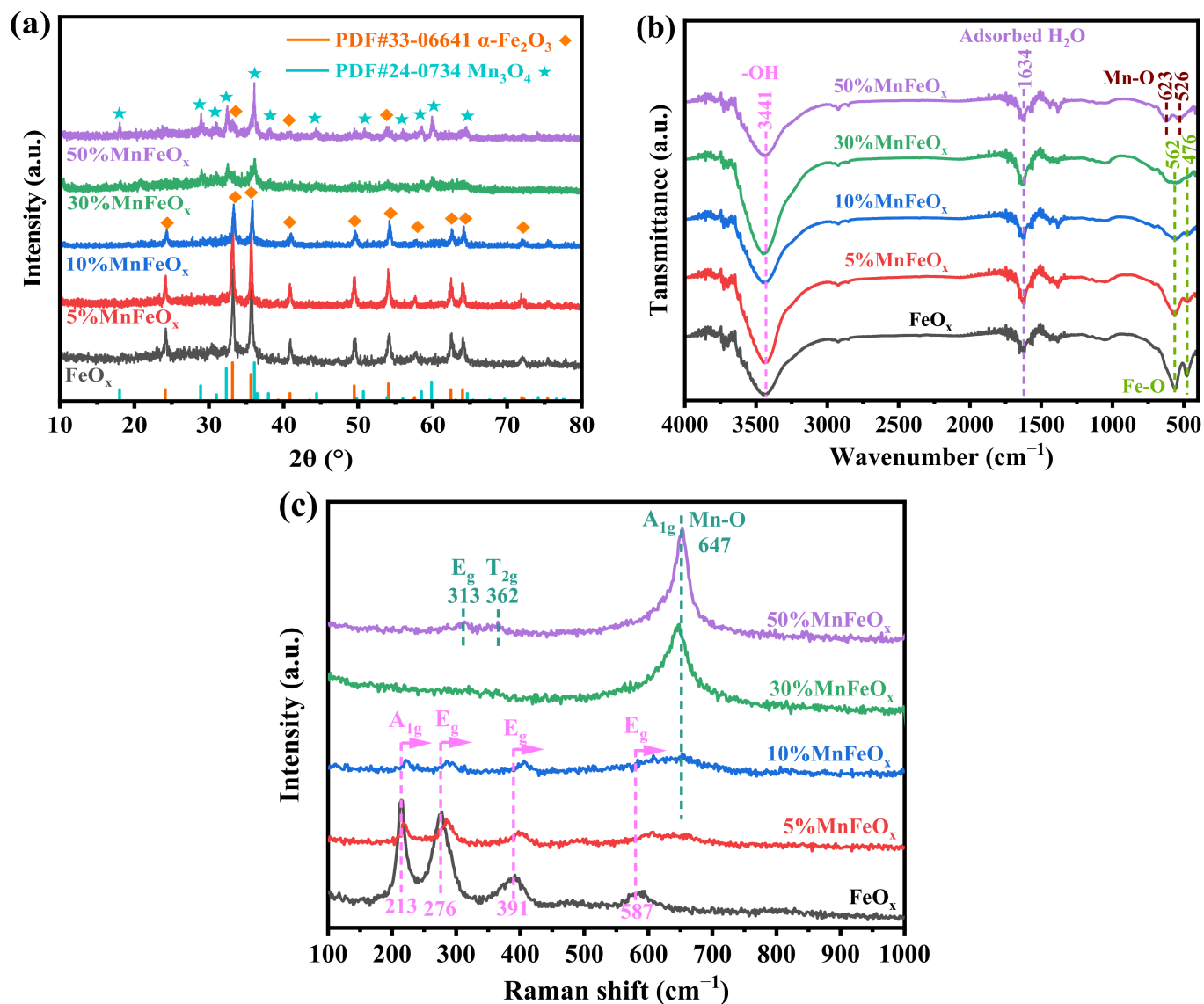


Figure 1. The (a) XRD patterns, (b) FT-IR spectra and (c) Raman spectra of MIL-100(Fe)-derived FeO_x and corresponding MnFeO_x catalysts.

Table 1. Physical parameters of MIL-100(Fe)-derived FeO_x and corresponding MnFeO_x catalysts.

Samples	Crystallite Size (nm)		BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Pore Diameter (nm)
	α-Fe ₂ O ₃ (104)	Mn ₃ O ₄ (211)			
FeO _x	16.3	/	49.2	0.271	2.0–4.2
5%MnFeO _x	14.9	/	20.1	0.277	3.4–4.2
10%MnFeO _x	14.3	/	36.9	0.351	2.0–4.9
30%MnFeO _x	/	8.9	40.2	0.361	3.0–4.9
50%MnFeO _x	/	13.2	26.3	0.288	2.0–4.2

Figure 1b shows the Fourier transform infrared (FT-IR) spectra of the MIL-Fe(100)-derived FeO_x and corresponding MnFeO_x samples. As displayed in Figure 1b, the vibration bands at 3441 and 1634 cm⁻¹ are assigned to the stretching vibrations of structural hydroxyl groups and O-H surface-adsorbed H₂O, and the bending vibration of the H-O-H in H₂O molecules, suggesting the presence of hydroxyl groups and absorbed H₂O in the catalyst surface [23,24]. The vibration bands at 700–400 cm⁻¹ are attributed to the vibration of metal–oxygen. For FeO_x, the bands at 562 and 476 cm⁻¹ are assigned to the Fe-O bond [25].

After the introduction of Mn, the vibration of Fe-O weakens and widens. Meanwhile, with the increase in Mn content, the Fe-O vibration gradually weakens and disappears with the appearance of Mn-O bond vibration in the tetrahedral and octahedral coordination environments of Mn_3O_4 at 623 and 526 cm^{-1} , respectively [26]. When the content of Mn increased to 50%, the distinct Mn-O vibrations were observed in 50% MnFeO_x , indicating the formation of Mn_3O_4 , which is consistent with the XRD results.

The structure of the as-prepared samples was further investigated via Raman spectra. As illustrated in Figure 1c, four peaks at 213, 276, 391, and 587 cm^{-1} , assigned to A_{1g} and E_g vibration modes of $\alpha\text{-Fe}_2\text{O}_3$, are observed in FeO_x [27,28]. After the introduction of Mn, the Raman peaks of FeO_x shift to higher wavenumbers. Studies have shown that Mn doping can introduce local lattice disorder, FeO_6 octahedral distortion, and controllable compressive strain in $\alpha\text{-Fe}_2\text{O}_3$ [29,30]. Therefore, the blue shift of the Raman peaks of $\alpha\text{-Fe}_2\text{O}_3$ might be related to the local lattice strain induced by Mn. As the content of Mn increased to 30%, the Raman peaks corresponding to $\alpha\text{-Fe}_2\text{O}_3$ disappeared, and new Raman peaks appeared at 313, 362, and 647 cm^{-1} . When the Mn content was further increased to 50%, the intensity of these Raman peaks was greatly enhanced. The strong peak at approximately 647 cm^{-1} can be attributed to the A_{1g} mode of the Mn-O symmetric stretching vibration in spinel Mn_3O_4 , while the other two peaks at 313 and 362 cm^{-1} are related to the E_g and T_{2g} vibration modes of Mn_3O_4 , respectively [31,32]. This further confirmed the formation of a Mn_3O_4 crystal via high Mn introduction, which is in line with the XRD results. Based on the above XRD, FT-IR, and Raman results, it could be concluded that at low Mn content, Mn mainly causes local lattice distortion of $\alpha\text{-Fe}_2\text{O}_3$ and changes in the Fe-O vibration environment. However, at higher Mn content, an independent Mn_3O_4 crystal phase appears.

2.1.2. Pore Properties

The physical parameters and pore structure of the as-prepared samples were investigated via physical adsorption. Figure 2a,b show the N_2 adsorption-desorption curves and pore size distribution of the catalysts, respectively. As shown in Figure 2a, the adsorption amounts of all the curves change relatively slowly in the low and medium relative pressure regions, but increase significantly after ($P/P_0 > 0.8$), and exhibit adsorption-desorption lag in the high relative pressure region. This indicates that the pore structure in the sample is mainly related to the irregular inter-particle mesopores formed by particle aggregation and the capillary condensation in the larger pores. Based on this feature, these adsorption-desorption isotherms can be assigned to type IV curves with an H3 hysteresis loop, suggesting the presence of mesopores in the samples [33,34]. Meanwhile, the pore size distribution of each sample in the range of 2.0–4.9 nm also indicates that the material is mainly composed of small mesopores (Figure 2b).

The specific surface area, total pore volume, and pore size of the prepared samples are summarized in Table 1. Compared with FeO_x (49.2 m^2/g , 0.271 cm^3/g , 2.0–4.2 nm), the introduction of Mn induced a decrease in specific surface area in these MnFeO_x samples, while the total pore volumes and pore diameters increased. This might be ascribed to the fact that Mn altered the nucleation and aggregation patterns of Fe_2O_3 particles, inducing the formation of a more open and interconnected mesoporous network between particles. Among these MnFeO_x catalysts, 30% MnFeO_x presents the largest surface area (40.2 m^2/g), total pore volume (0.361 cm^3/g), and large pore diameter (3.0–4.9 nm), which will be beneficial for the adsorption of toluene molecules [35].

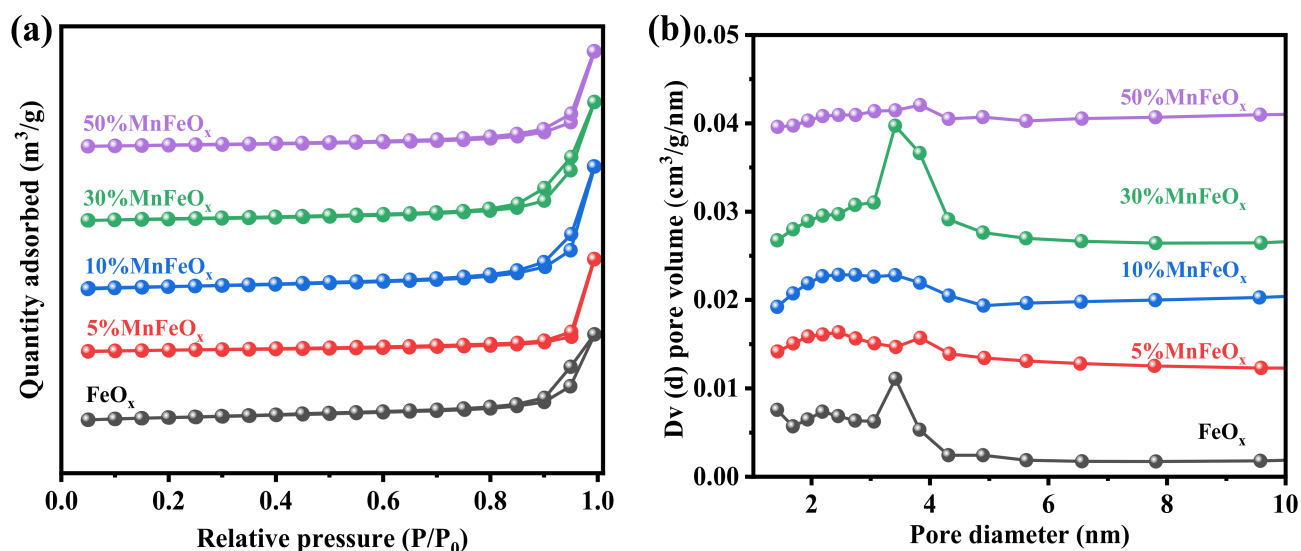


Figure 2. The (a) N₂ adsorption–desorption curves and (b) corresponding pore size distributions of MIL-100(Fe)-derived FeO_x and corresponding MnFeO_x catalysts.

2.2. Morphology and Texture

The morphology of the FeO_x and 30%MnFeO_x was investigated by scanning electron microscopy (SEM). Figure 3 presents the SEM images and corresponding element mapping of FeO_x and 30%MnFeO_x. As shown in Figure 3a, FeO_x is formed by the aggregation of primary particles with a size of several tens of nanometers, resulting in an irregular aggregate. The particle surfaces are relatively rough and retain a certain number of inter-particle pores. Some particles exhibit relatively clear particle boundaries, indicating that FeO_x has a typical nanoparticle assembly structure. Meanwhile, the element mapping suggests that Fe and O are evenly dispersed in FeO_x. Notably, Cl is also present in the catalyst, which might originate from the metal precursor during the synthesis of MIL-100(Fe). After the introduction of Mn, 30%MnFeO_x (Figure 3b) still retains its irregular agglomerated appearance composed of fine particles. Compared with FeO_x, the primary particle boundaries in 30%MnFeO_x are relatively blurred, the inter-particle contacts are more compact, and larger secondary aggregates are formed. The local open voids have decreased. This indicates that the introduction of higher Mn content has changed the nucleation, growth, and accumulation behavior of the oxide particles. Meanwhile, Fe, Mn, O, and Cl are evenly dispersed.

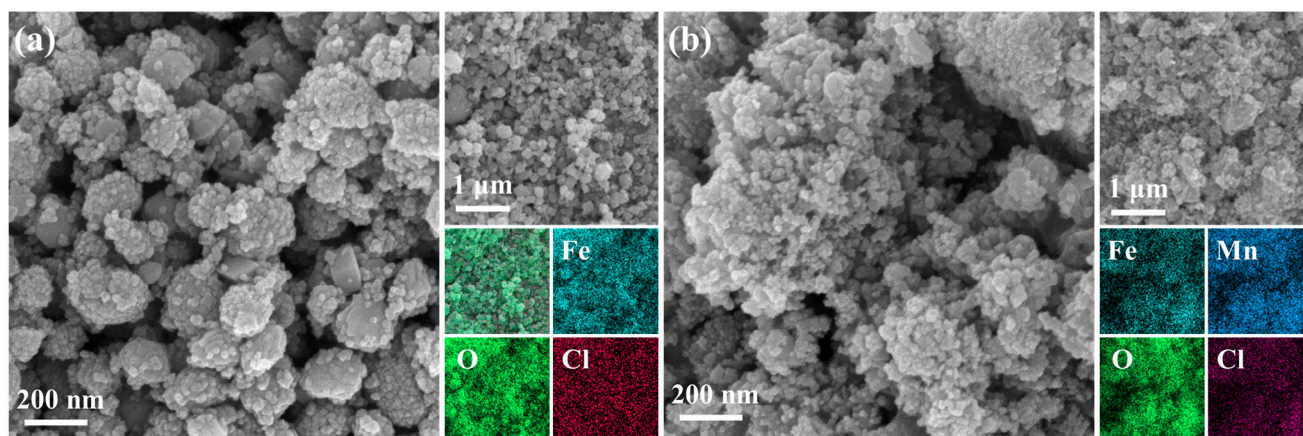


Figure 3. The SEM images and corresponding mapping of (a) FeO_x and (b) 30%MnFeO_x.

Furthermore, the texture structure of 30%MnFeO_x was studied by transmission electron microscopy (TEM). Figure 4 shows the TEM, high-resolution TEM (HRTEM), high-angle annular dark-field imaging-scanning transmission electron microscopy (HAADF-STEM) images, and corresponding element mapping of 30%MnFeO_x. As shown in Figure 4a, 30%MnFeO_x is mainly composed of irregularly shaped block-like or sheet-like nano-units, with their lateral dimensions ranging from several tens to several hundred nanometers. Different particles interlock and pile up with each other, forming distinct agglomerates, while there are still certain gaps and open spaces between the particles. This is consistent with the SEM result. As shown in Figure 4b, multiple sets of distinct and oriented crystal patterns can be observed in the HRTEM image. The crystal plane spacings of 0.270 nm and 0.252 nm can respectively be attributed to the (104) and (110) crystal planes of α -Fe₂O₃ [36,37]. The crystal plane spacing of 0.249 nm matches the (211) crystal plane of spinel Mn₃O₄ [14]. The simultaneous appearance of α -Fe₂O₃ and Mn₃O₄ lattice stripes in the same area directly proves the coexistence of the two crystal phases in 30% MnFeO_x, which is consistent with the XRD and Raman results. The HAADF-STEM image (Figure 4c) and corresponding element mapping (Figure 4d) suggest that Fe, Mn, O, and Cl are evenly dispersed in the catalyst. The mass fractions of O, Cl, Mn, and Fe are 27.86%, 0.08%, 67.21%, and 4.85%, respectively.

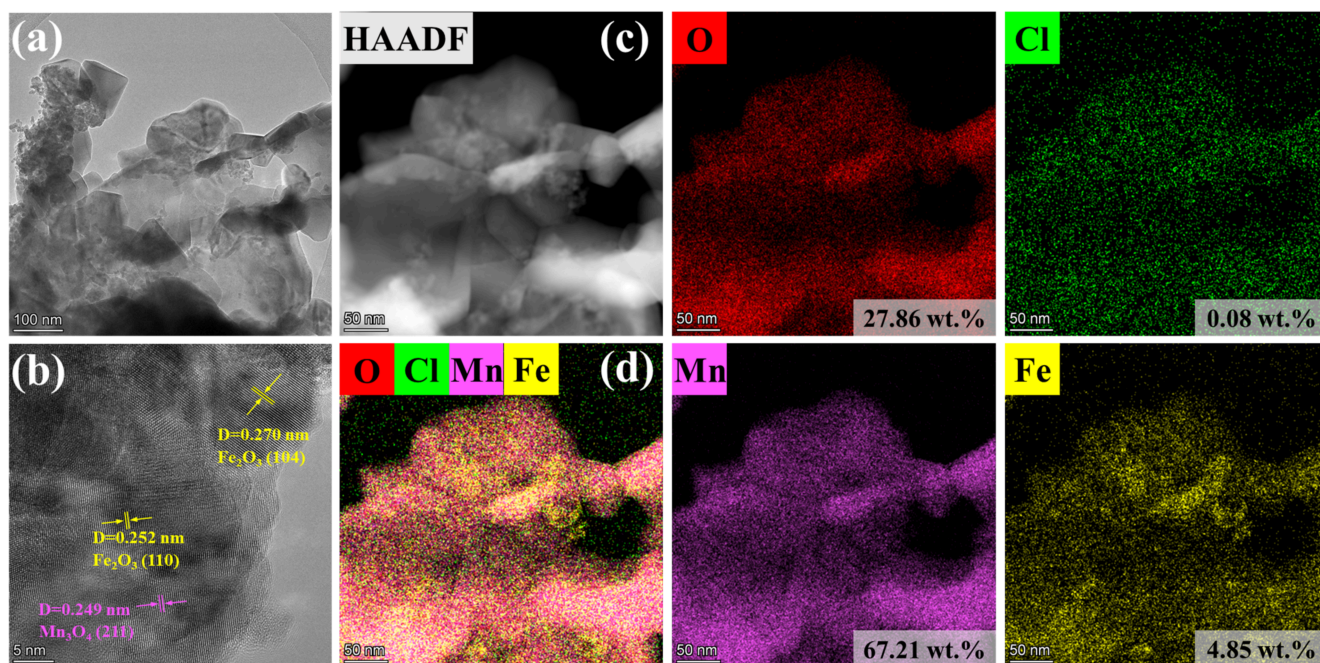


Figure 4. (a) TEM image; (b) HRTEM image; (c) corresponding HAADF-STEM image and (d) EDS elemental mappings of 30%MnFeO_x-Cl.

2.3. Surface Chemical and Optical Properties

2.3.1. Surface Chemical Properties

The surface chemical composition of FeO_x and 30%MnFeO_x was studied by X-ray photoelectron spectroscopy (XPS). Figure 5a displays the XPS spectra of the Fe 2p orbit for FeO_x and 30%MnFeO_x. The Fe 2p orbits were detected as two peaks at 710.4 and 723.7 eV, corresponding to Fe 2p_{3/2} and Fe 2p_{1/2} orbits, respectively [38,39]. The Fe 2p_{3/2} was divided into four peaks at 710.3, 711.8, 714.0 and 718.8 eV, which corresponded to Fe²⁺, Fe³⁺ and their satellite peaks, respectively [40]. Similarly, the Fe 2p_{1/2} orbit was also split into Fe²⁺ (723.5 eV), Fe³⁺ (725.1 eV) and the satellite peaks of Fe²⁺ (727.1 eV) and Fe³⁺ (732.4 eV) [41]. Meanwhile, the surface molar ratio of Fe²⁺/Fe³⁺ was calculated according to the peak area. The Fe²⁺/Fe³⁺ ratios in FeO_x and 30%MnFeO_x were calculated to be

1.24 and 1.49, respectively. This result suggests that the introduction of Mn promotes the reduction of Fe species to lower oxidation states, enriching the surface of 30%MnFeO_x with more Fe²⁺. Figure 5b shows the Mn 2p orbit of 30%MnFeO_x, in which two peaks at 641.4 and 653.4 eV are attributed to the Mn 2p_{3/2} and Mn 2p_{1/2} orbits, respectively [42]. The Mn 2p_{3/2} was deconvoluted into four peaks, Mn²⁺, Mn³⁺, Mn⁴⁺, and the satellite peak, located at 641.0, 642.3, 643.8, and 646.0 eV, respectively [43,44], suggesting the presence of multiple valence states of Mn in the catalyst surface. Meanwhile, the coexistence of Mn²⁺/Mn³⁺/Mn⁴⁺ is conducive to the formation of reversible multi-valent redox cycles, which is beneficial for the oxidation reaction [45].

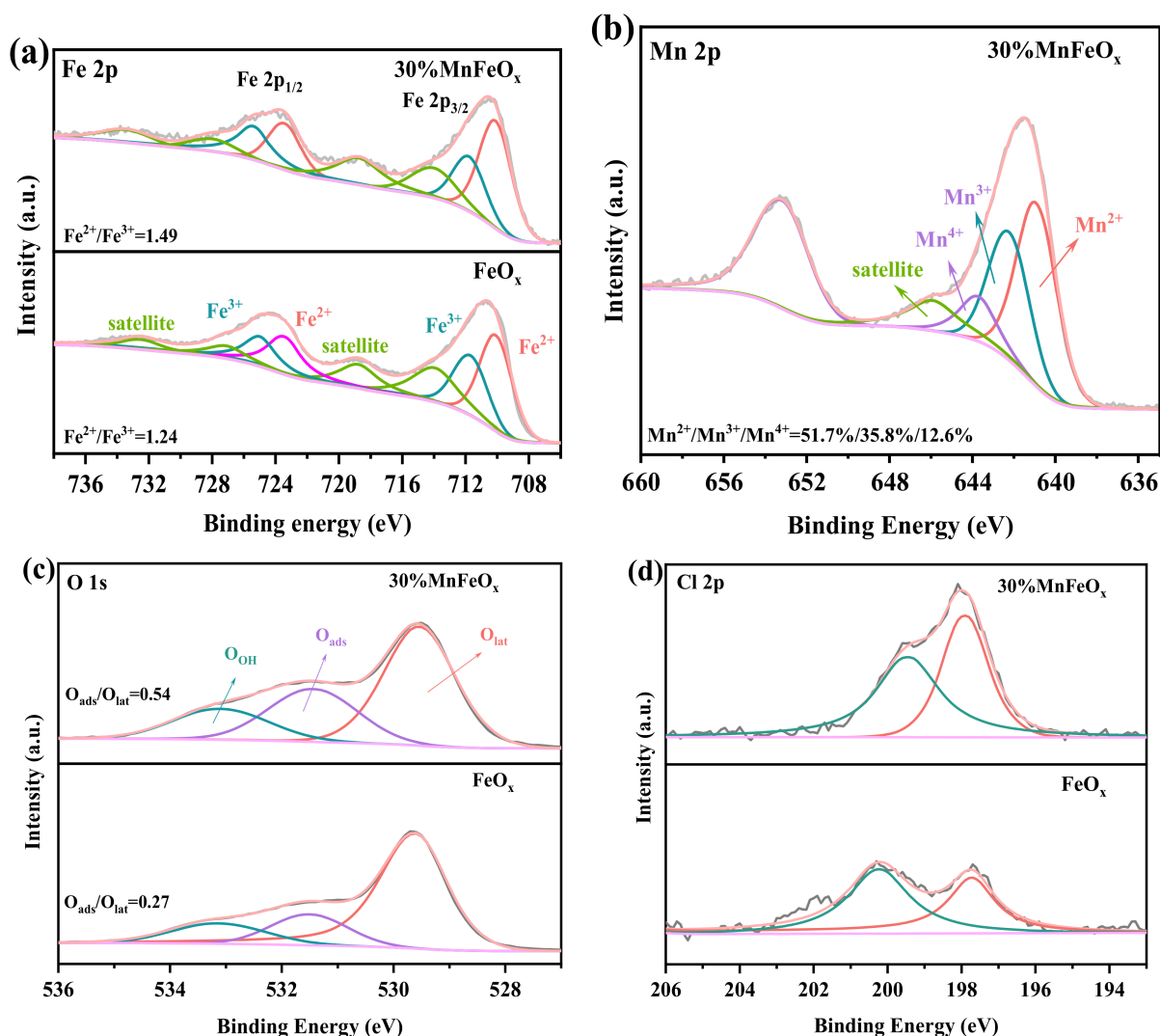


Figure 5. XPS spectra of FeO_x and 30%MnFeO_x: (a) Fe 2p; (b) Mn 2p; (c) O 1s and (d) Cl 2p orbits.

The O 1s spectra (Figure 5c) were divided into three peaks. The lattice oxygen (O_{lat}) species can be found at 529.5 eV [46]. Two other peaks at 531.5 and 533.2 eV are assigned to surface adsorbed oxygen (O_{ads}) species and adsorbed surface hydroxyl (O_{OH}), respectively [47–49]. Similarly, the molar ratio of O_{ads}/O_{lat} was also calculated according to the peak area. The values of O_{ads}/O_{lat} for FeO_x and 30%MnFeO_x are 0.27 and 0.54, respectively. Compared with FeO_x, the introduction of Mn induced a great increase in the content of O_{ads} species. Generally, the surface O_{ads} species has higher mobility and reactivity compared to the O_{lat} species, which is conducive to the adsorption and activation of reactants and the interface oxidation-reduction process [50]. Meanwhile, the surface O_{ads} originates from the oxygen species generated by the adsorption and activation of gaseous

oxygen species at oxygen vacancies. Therefore, the content of O_{ads} is directly proportional to the content of oxygen vacancies. Specifically, the introduction of Mn induced the formation of more oxygen vacancies in 30%MnFeO_x. As presented in Figure 5d, the Cl 2p XPS spectra of FeO_x and 30%MnFeO_x were divided into Cl 2p_{3/2} and Cl 2p_{1/2}, located at 197.7 and 200.2 eV, respectively, which corresponded to the Cl[−] or metal-chloride-type surface species [51]. These Cl species may originate from the minor residues of chlorine-containing precursors during the preparation and heat treatment process, or from surface chemical adsorption. According to the above, it can be concluded that the introduction of Mn significantly alters the surface electronic structure of FeO_x, resulting in an increase in the Fe²⁺/Fe³⁺ ratio from 1.24 to 1.49, and an increase in the $O_{\text{ads}}/O_{\text{lat}}$ ratio from 0.27 to 0.54. Additionally, a mixed valence state surface composed of Mn²⁺, Mn³⁺, and Mn⁴⁺ was formed, and the content of oxygen vacancies also improved, which would enhance the catalytic activity of the catalysts.

2.3.2. Optical Properties

Figure 6 presents the UV-vis diffuse-reflectance spectra (DRS) and corresponding Tauc's band-gap plots (b) of FeO_x and 30%MnFeO_x. As shown in Figure 6a, FeO_x exhibits strong absorption in the ultraviolet region and a broadened absorption band at approximately 300 nm. As the wavelength increases, its absorbance gradually decreases, and a significant absorption attenuation occurs after approximately 550 nm. This absorption feature is mainly related to the charge transfer from O 2p to Fe 3d in α -Fe₂O₃ and the Fe³⁺ crystal field transition [52]. For 30%MnFeO_x, the absorption characteristics of 30%MnFeO_x in the ultraviolet region are similar to those of FeO_x in general, but it maintains a higher absorption intensity in the range of approximately 500–800 nm, indicating that the introduction of Mn has shifted the absorption edge of the material towards the long-wavelength direction and significantly broadened its spectral response range in the visible light and even near-infrared regions. Furthermore, the bandgap energies (E_g) of FeO_x and 30%MnFeO_x were calculated via the Kubelka–Munk method. As illustrated in Figure 6b, the apparent direct optical band gaps of FeO_x and 30%MnFeO_x are 1.96 eV and 1.67 eV, respectively. The decrease in the band gap in 30%MnFeO_x suggests that the introduction of Mn effectively broadened the visible light response range of the material, which might improve the absorption of low-energy photons and the electron transition, promoting the photothermal oxidation reaction [53].

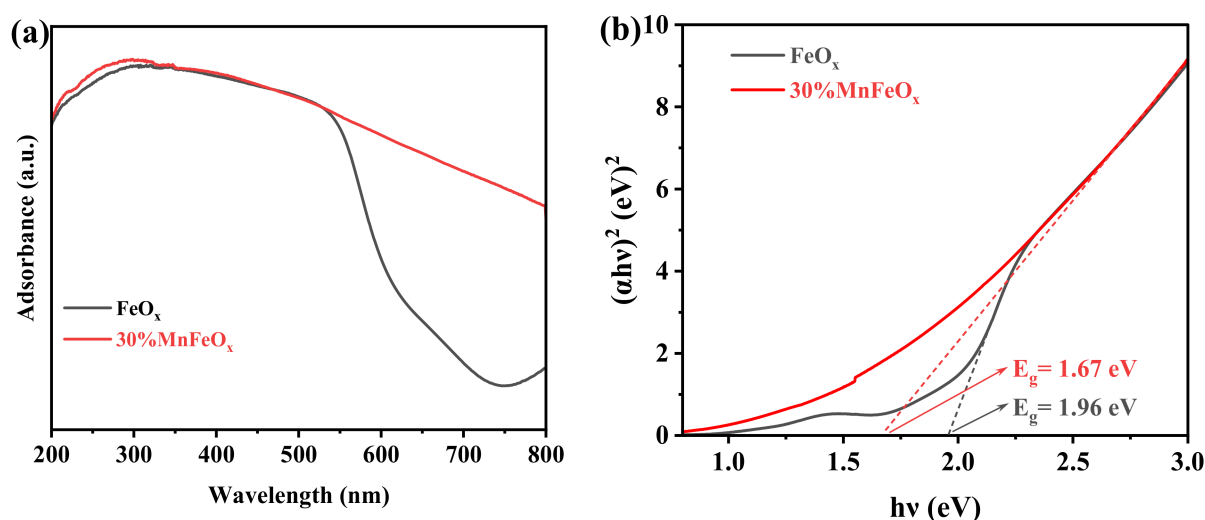


Figure 6. (a) The UV-vis DRS spectra and (b) corresponding Tauc's band-gap plots of FeO_x and 30%MnFeO_x.

2.4. Catalytic Performance for Photothermal Toluene Oxidation

2.4.1. Photothermal Catalytic Performance

The catalytic activity of the as-prepared catalysts was estimated by the photothermal catalytic degradation using toluene as the model molecule. Figure 7a shows the toluene conversion of FeO_x and different Mn-content MnFeO_x catalysts under photothermal conditions. All samples exhibited typical S-shaped ignition curves: the toluene conversion was generally low within the range of 80–180 °C, and the reaction gradually accelerated after heating to 200 °C and then rapidly increased in the range of 220–260 °C. Among the different samples, the ignition curve of 30%MnFeO_x shifted significantly towards lower temperatures, demonstrating the best low-temperature photothermal catalytic activity. Meanwhile, the temperatures at which toluene conversion reached 10%, 50% and 90% (T₁₀, T₅₀ and T₉₀) are calculated in Table 2. As listed in Table 2, 30%MnFeO_x shows the lowest T₅₀ and T₉₀ values of 211 and 237 °C, respectively, followed by 10%MnFeO_x (225 and 251 °C), 5%MnFeO_x (229 and 255 °C), FeO_x (232 and 260 °C), and 50%MnFeO_x (236 and 260 °C), suggesting its optimal photothermal activity for toluene degradation. Figure 7b presents the corresponding CO₂ yield over these catalysts for toluene photothermal oxidation. The tendency of the CO₂ yield is similar to that of toluene conversion. However, at the same temperatures, the CO₂ yield was lower than that of toluene conversion, indicating the formation of intermediates during toluene oxidation. Additionally, the 30%MnFeO_x catalyst is compared with other Mn-Fe-based or other catalysts for toluene oxidation in Table 3. Compared with the reported catalysts in the literature [12,54–59] for toluene oxidation, the prepared 30%MnFeO_x catalyst also possesses better catalytic performance at lower light intensity.

Table 2. Catalytic performance of the as-prepared catalysts for toluene photothermal oxidation.

Samples	Photothermal Catalytic Performance (°C)			Thermal Catalytic Performance (°C)		
	T ₁₀	T ₅₀	T ₉₀	T ₁₀	T ₅₀	T ₉₀
FeO _x	156	232	260	180	245	280
5%MnFeO _x	200	229	255	/	/	/
10%MnFeO _x	190	225	251	/	/	/
30%MnFeO _x	151	211	237	174	231	259
50%MnFeO _x	200	236	260	/	/	/

Table 3. The performance comparison of catalysts for toluene degradation reported in the literature.

Catalysts	Toluene Concentration (ppm)	Catalytic Type	Space Velocity (mL/(g h))	Irradiance (mW/cm ²)	Activity (T ₉₀ , °C)	Ref.
30%MnFeO _x	300	Photothermal	30,000	330	237	This work
CeO ₂ /LaMnO ₃	200	Photothermal	32,320	280	275	[54]
CMO-5	100	Photothermal	30,000	700	220	[12]
LaCoO ₃ /BC-1	500	Photothermal	20,000	350	375	[55]
0.65Pt/Mn-TiO ₂	200	Photothermal	56,250	625	192	[56]
MnFO _x	1000	Thermal	40,000	-	270(T ₁₀₀)	[57]
15Mn/ARM	1000	Thermal	60,000	-	268	[58]
Mn ₃ O ₄ -Fe ₂ O ₃	1000	Thermal	48,000	-	279	[59]

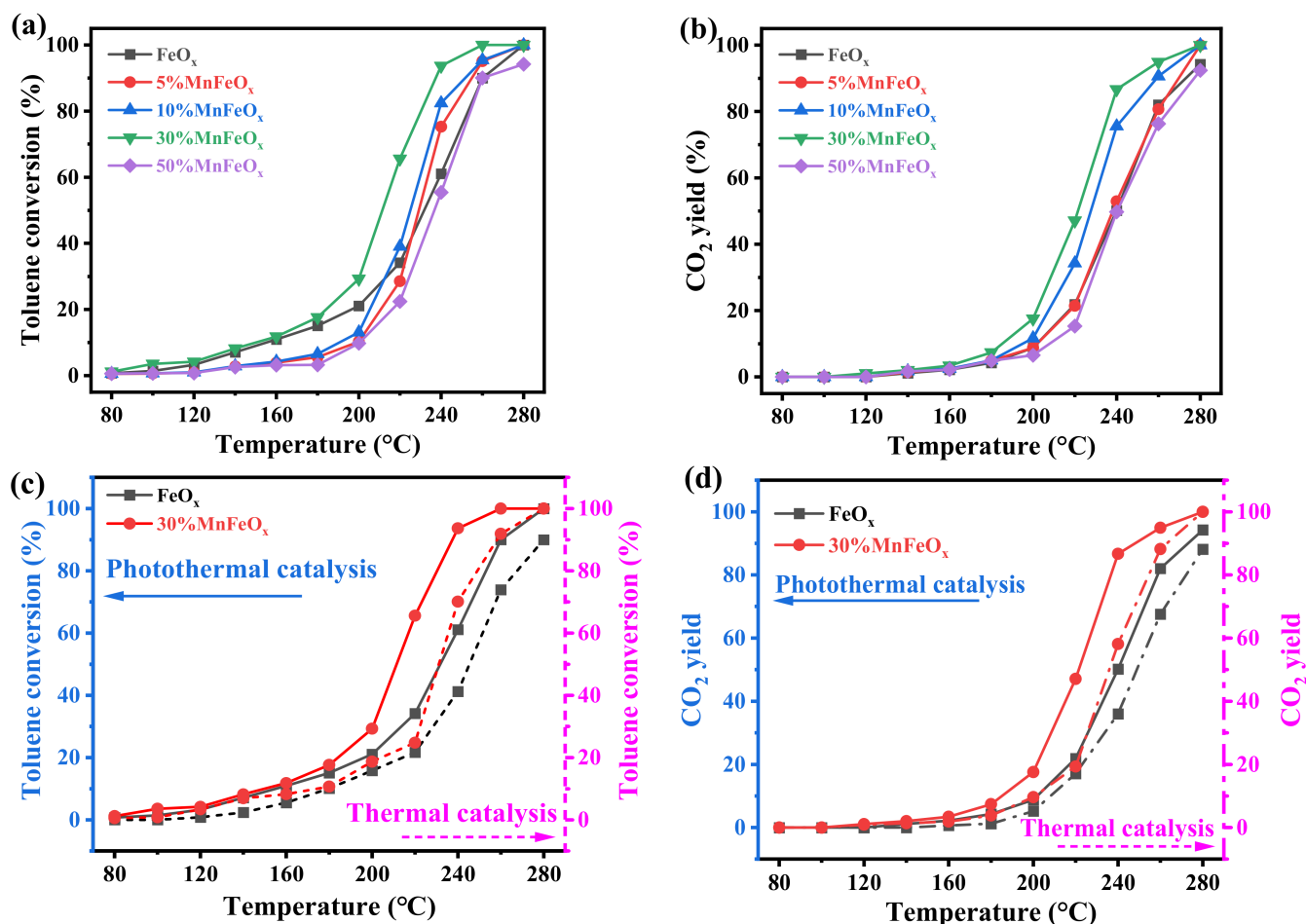


Figure 7. Photothermal catalytic performance for toluene degradation over the as-prepared catalysts: (a) toluene conversion and (b) CO₂ yield. Catalytic performance of 30%MnFeO_x for toluene oxidation under thermal and photothermal catalysis: (c) toluene conversion and (d) CO₂ yield.

Generally, the catalytic performance of a catalyst is closely related to its physicochemical properties. Firstly, the excellent photothermal catalytic performance of 30%MnFeO_x is attributed to its enhanced light-capture ability. The UV-vis DRS results show that after the introduction of Mn, the material's absorption in the 500–800 nm range significantly increases. The surface photonic band gap decreases from 1.96 eV of FeO_x to 1.67 eV, enabling 30%MnFeO_x to absorb more visible light and a portion of near-infrared light. The absorbed light energy can be converted into lattice heat through non-radiative carrier relaxation, thereby increasing the local temperature on the catalyst surface and accelerating the toluene oxidation reaction [12]. Secondly, the XPS results show that after the introduction of Mn, the ratio of Fe²⁺/Fe³⁺ increased from 1.24 to 1.49. Meanwhile, on the 30%MnFeO_x surface, there are mixed valence states of Mn²⁺, Mn³⁺, and Mn⁴⁺. These reversible redox pairs are conducive to the formation of interface electron circulation and the rapid conversion of Fe²⁺/Fe³⁺ and Mn²⁺/Mn³⁺/Mn⁴⁺, promoting the adsorption, dissociation, and electron transfer of oxygen molecules, thereby increasing the generation and replenishment rate of surface-active oxygen [57,58]. Meanwhile, the O 1s XPS results further indicate that the O_{ads}/O_{lat} ratio of 30%MnFeO_x increased from 0.27 of FeO_x to 0.54, suggesting that its surface has more chemically adsorbed or defect-related oxygen species. During the complete oxidation of toluene, toluene can first adsorb at the metal–oxygen sites and be gradually oxidized by surface-adsorbed oxygen or active lattice oxygen; after the oxygen is consumed, the defect sites are replenished by gaseous O₂, thus completing the Mars–van Krevelen-type oxidation cycle. Therefore, the higher O_{ads}/O_{lat} ratio and mixed valence

metal centers collectively enhance the generation, migration, and cycling ability of reactive oxygen species, thereby promoting the aromatic ring cleavage and deep mineralization of toluene and its oxygen-containing intermediates. According to the above, 30%MnFeO_x exhibited the lowest toluene ignition temperature, the highest conversion rate of toluene at medium and low temperatures, and the highest CO₂ yield in catalysts with different Mn contents. Its excellent performance can be attributed to the following synergistic effects: (1) enhanced visible–near-infrared absorption improves the photothermal conversion ability; (2) the mixed valence states of Fe and Mn accelerate the redox cycle; and (3) more abundant surface-adsorbed oxygen and defect sites enhance the activation of O₂ and the migration of lattice oxygen.

To further investigate the role of light during photothermal catalysis, the catalytic performance of FeO_x and 30%MnFeO_x for toluene oxidation under photothermal conditions and thermal conditions was compared. Figure 7c and d illustrate toluene conversion and the corresponding CO₂ yield for toluene degradation under different conditions, respectively. At the sample temperature, toluene conversion and the CO₂ yield of the FeO_x and 30%MnFeO_x under photothermal conditions were both higher than those under pure thermal conditions, and this promoting effect was most obvious in the ignition range of 200–240 °C. For example, at approximately 220 °C, the photothermal toluene conversion of 30%MnFeO_x was about 65%, while under pure thermal conditions it was only about 25%. Meanwhile, the corresponding photothermal CO₂ yield was about 47%, which is also significantly higher than the approximately 20% under pure thermal conditions. These results indicate that light may activate oxygen species through photogenerated carriers or interface electrons, thereby generating a light–heat synergy effect.

2.4.2. Reusability, Stability and Water Resistance

To evaluate the reusability, long-term stability, water resistance, and light response characteristics of 30%MnFeO_x in the photothermal catalytic oxidation of toluene, cyclic activity, continuous operation, water vapor switching, and light–dark switching experiments were conducted. The results are shown in Figure 8. As shown in Figure 8a, the three cycles all exhibited typical S-shaped ignition behavior and reached a toluene conversion rate of approximately 95–100% within the range of 240–280 °C, indicating that the catalyst has good reusability in the high conversion range. Notably, after the cycle process, the activity of the catalyst has significantly improved, which suggests that 30%MnFeO_x underwent a certain degree of in situ activation during the initial reaction process, rather than being deactivated through cycling. This activation process may be related to the removal of weakly adsorbed water on the surface, the rebalancing of Fe/Mn valence states, the exposure of defect sites, and the redistribution of surface-active oxygen species. Zhang et al. [13] also found that manganese oxide photothermal catalysts can form stable active surfaces during the reaction process through the migration of surface oxygen species and the adjustment of redox states. Meanwhile, 30%MnFeO_x exhibited good thermal stability for 24 h.

Figure 8c presents the water resistance of 30%MnFeO_x for photothermal toluene oxidation. After introducing 1 vol.% of H₂O, the catalytic activity remained basically unchanged, indicating that the low concentration of water vapor had a relatively minor impact on the reaction. When the water vapor concentration was increased to 3 vol.%, the toluene conversion rate experienced a brief drop at the beginning of the switching process, but then gradually recovered to a level close to the initial one. Similarly, under the condition of 5 vol.% water vapor, only slight and brief fluctuations in activity were observed, and the conversion rate after stabilization still remained above approximately 95%. After each interruption of water vapor supply, the toluene conversion rate could quickly recover, indicating that the inhibition caused by water vapor was reversible, rather than causing

the destruction of the catalyst crystal phase or the permanent deactivation of the active components. The instantaneous inhibition of water vapor may result from the competitive adsorption of H_2O , toluene, and O_2 at the metal center, surface hydroxyl sites, and oxygen vacancies. After the adsorption of water or hydroxyl species temporarily occupies the active sites, the adsorption rate of toluene and the activation rate of O_2 can be reduced. When the water vapor is removed, or the surface reaches the adsorption equilibrium again, the occupied sites are released, and the catalytic activity is restored accordingly [58]. In short, $30\%\text{MnFeO}_x$ possesses great water resistance for the photothermal catalytic oxidation of toluene.

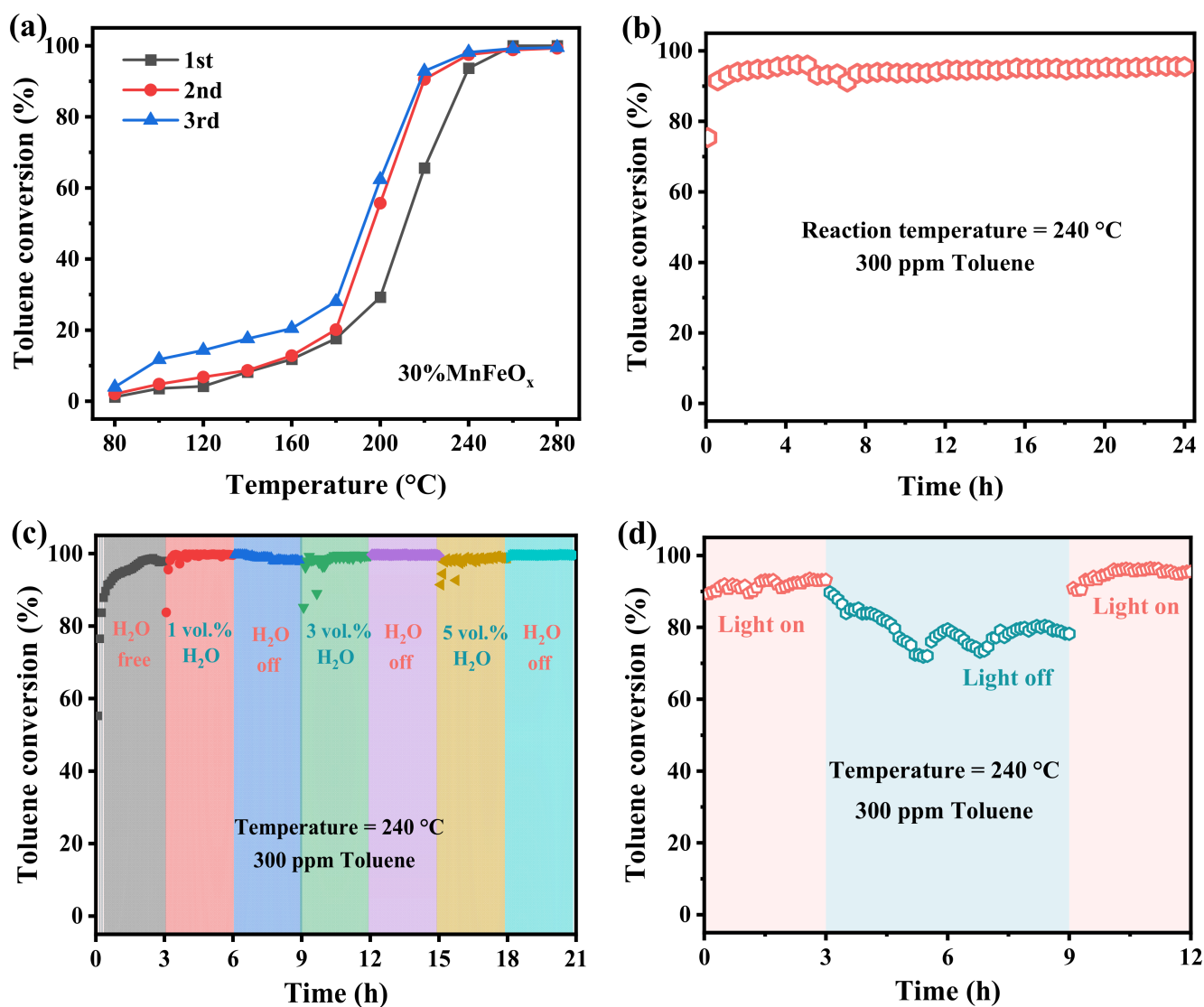


Figure 8. The (a) reusability, (b) long-term stability, (c) water resistance and (d) light–dark cycle stability of toluene photothermal catalysis over $30\%\text{MnFeO}_x$.

Figure 8d shows the catalytic performance of toluene photothermal oxidation over $30\%\text{MnFeO}_x$ under conditions of the presence and absence of light at 240 °C. During the initial illumination stage, the toluene conversion rate remained at approximately 90–94%. After the light source was turned off, the conversion rate gradually decreased and stabilized at approximately 72–80%, indicating that $30\%\text{MnFeO}_x$ still has a strong intrinsic thermal catalytic oxidation ability in the dark state, but its activity significantly decreased without the promotion of light. When the light source was turned on again, the toluene conversion rate rapidly recovered to approximately 90%, and then further increased to approximately

95%, and the recovered activity was basically consistent with that in the initial illumination stage. This reversible response rules out the possibility of permanent structural changes caused by short-term light exposure, indicating that light energy has an immediate and recoverable promoting effect on the catalytic reaction. This further confirmed the light–heat synergy effect for toluene degradation over 30%MnFeO_x.

To explore the reasons for the performance improvement after the cycle, XRD, physical adsorption, and XPS were conducted on 30%MnFeO_x after the reaction. Figure 9 displays the XRD patterns of 30%MnFeO_x before and after toluene photothermal oxidation. As shown in Figure 9, the diffraction peaks of 30%MnFeO_x-After are similar with those of 30%MnFeO_x, suggesting that the photothermal oxidation of toluene did not change the crystal structure of 30%MnFeO_x. The results of N₂ adsorption–desorption curves (Figure 10a), pore size distribution (Figure 10b), and corresponding physical parameters (Table 4) suggested that toluene photothermal oxidation did not cause changes in N₂ adsorption–desorption curves and the pore structure, which also confirmed the good stability of 30%MnFeO_x. Notably, after the reaction, the surface area and pore volume were increased from 40.2 m²/g and 0.361 cm³/g to 53.1 m²/g and 0.372 cm³/g. This increase may be related to the surface reconfiguration induced by the reaction; that is, removing weakly bound surface species or rearranging particle aggregates leads to the opening of the inter-particle pores that were previously difficult to access. Meanwhile, the larger accessible surface area can expose more metal–oxygen centers, oxygen vacancies, and adsorbed oxygen species for the adsorption of toluene and O₂, while the slightly increased pore volume may facilitate the diffusion of reactants and oxygen-containing intermediates. This could promote the adsorption of toluene molecules, enhancing toluene degradation [35].

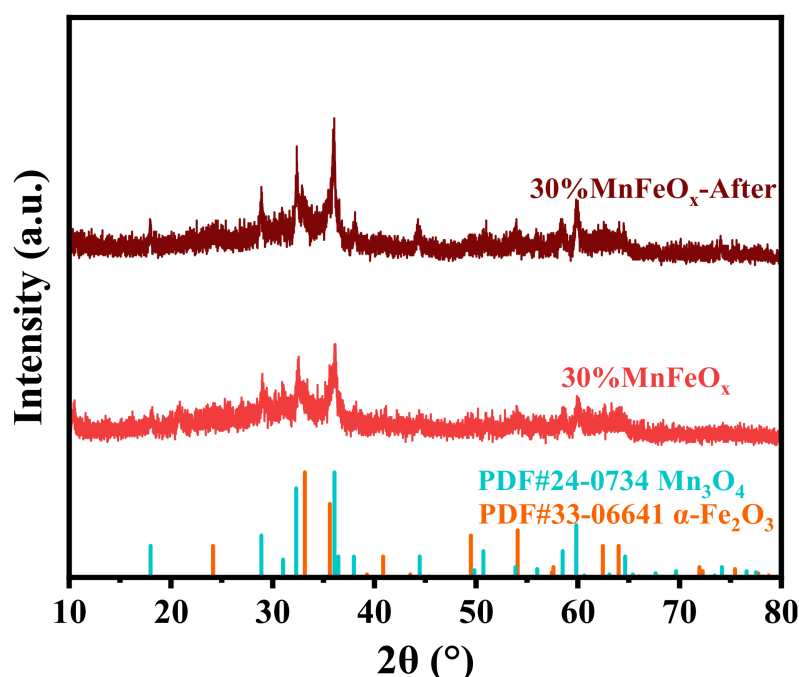


Figure 9. XRD patterns of 30%MnFeO_x before and after photothermal catalysis of toluene.

Table 4. Physical parameters of MIL-100(Fe)-derived FeO_x and corresponding 30%MnFeO_x catalysts.

Samples	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Pore Diameter (nm)
30%MnFeO _x	40.2	0.361	3.0–4.9
30%MnFeO _x -After	53.1	0.372	3.0–4.2

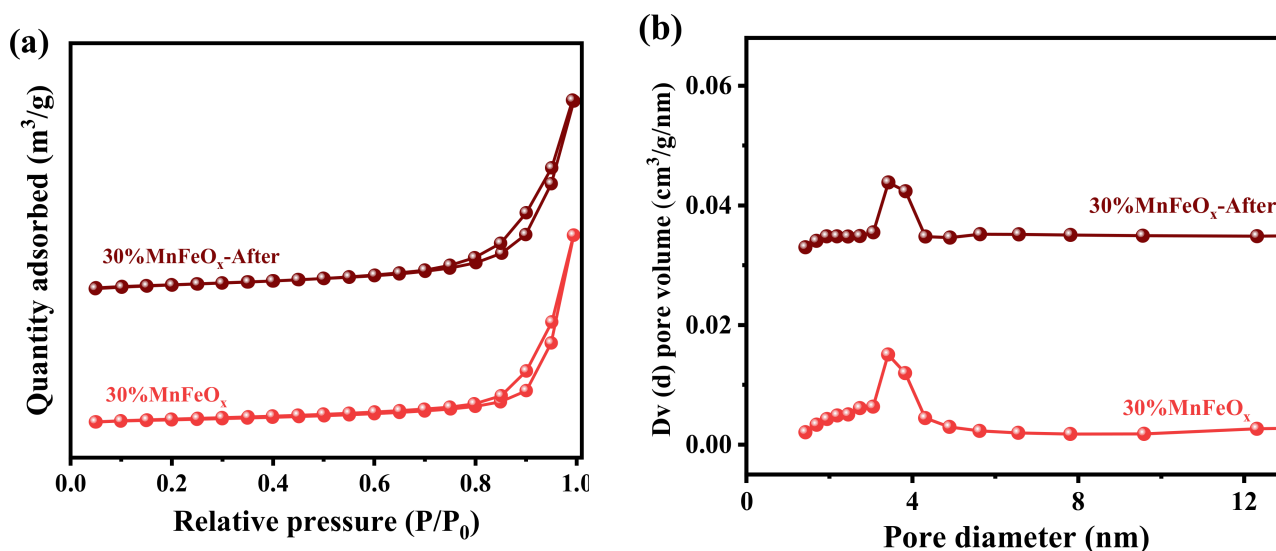


Figure 10. (a) N₂ adsorption–desorption isotherms and (b) pore size distributions of 30%MnFeO_x before and after photothermal catalysis of toluene.

Figure 11 shows the XPS spectra of Fe 2p, Mn 2p, O 1s, and Cl 2p orbits for 30%MnFeO_x before and after the reaction. Compared with the fresh 30%MnFeO_x (Fe²⁺/Fe³⁺ = 1.49, Mn³⁺: 35.8%, O_{ads}/O_{lat} = 0.54), the content of surface Fe²⁺/Fe³⁺, Mn³⁺, and O_{ads}/O_{lat} in 30%MnFeO_x-After is increased to 1.78, 40.8%, and 0.63, respectively. The increase in Fe²⁺ and Mn³⁺ species could improve the reversible electron transfer between Fe²⁺/Fe³⁺ and Mn²⁺/Mn³⁺, enhancing the redox cycle. Additionally, the improved surface O_{ads}/O_{lat} value suggests that more low-coordinated oxygen environments and defect sites capable of adsorbing gaseous O₂ may have been formed during the reaction, which could boost the adsorption and activation of gaseous oxygen species and the surface oxygen migration capabilities, promoting toluene oxidation. Therefore, based on the above analysis, the enhanced catalytic performance of 30%MnFeO_x after the reaction for toluene degradation might be ascribed to the increase in surface area and surface Fe²⁺, Mn³⁺, and O_{ads} species.

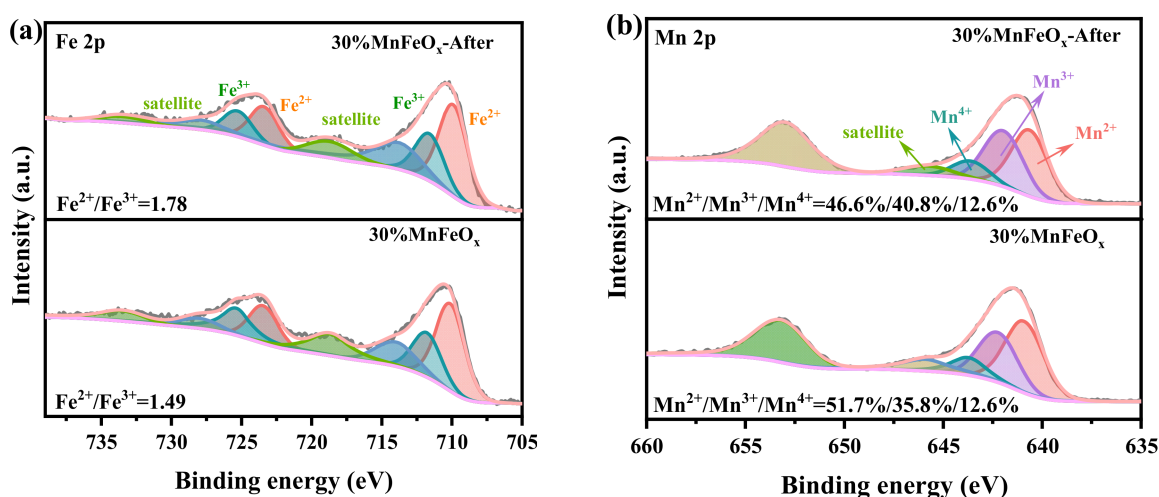


Figure 11. Cont.

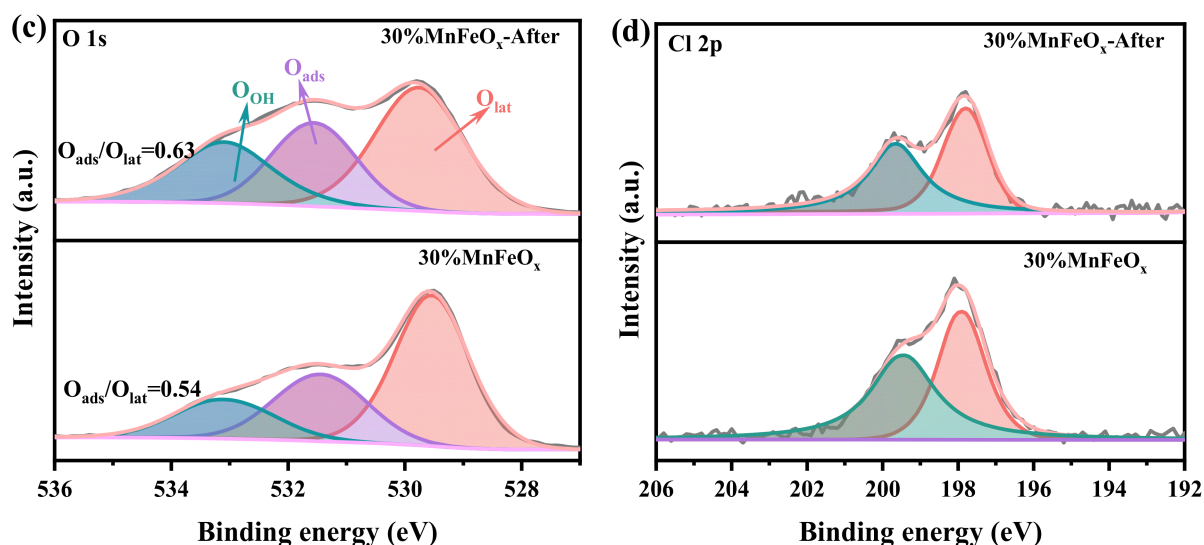


Figure 11. XPS spectra of 30%MnFeO_x before and after photothermal catalysis of toluene: (a) Fe 2p; (b) Mn 2p; (c) O 1s; and (d) Cl 2p.

2.5. Toluene Degradation Pathway

To clarify the surface reaction pathways of toluene oxidation on the 30%MnFeO_x catalyst, in situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) tests were conducted at different temperatures under both thermal catalytic and photothermal catalytic conditions. Figure 12a shows the in situ DRIFTS of toluene oxidation under thermal conditions, and the corresponding assignment of the intermediates is summarized in Table 5. As shown in Figure 12a, under thermal catalytic conditions, the absorption peak at $\sim 3070\text{ cm}^{-1}$ corresponds to the C–H stretching vibration of the aromatic ring [60,61]. The double peaks at 2384 and 2320 cm^{-1} correspond to the ν_3 asymmetric stretching vibration of gaseous or weakly adsorbed CO₂ [62,63]. Their intensities gradually increase with the rise in temperature, indicating that toluene and its oxygen-containing intermediates undergo continuous deep oxidation and mineralization [64]. Meanwhile, some new absorption peaks appeared as the temperature increased. The peaks at 1868 and 1300 cm^{-1} are assigned to the symmetric and asymmetric $\nu(\text{C}=\text{O})$ stretching of cyclic anhydride, suggesting the formation of maleic anhydride during toluene oxidation [65]. The absorption peaks at 1601 , 1552 , 1501 and 1428 cm^{-1} are attributed to the COO[−] asymmetry and symmetry vibration of benzoate [66]. The other absorption bands at 1233 , 1196 , 1148 and 1098 cm^{-1} are ascribed to the $\nu(\text{C}-\text{O})$ stretching vibration of alkoxide species [67]. The appearance of these intermediates indicates that toluene was oxidized.

Table 5. Assignment of the species generated in the in situ DRIFTS spectra for toluene photothermal and thermal oxidation.

Position (cm ^{−1})	Assignment	Characteristic of	Refs.
~ 3070	$\nu(\text{C}-\text{H})$ stretching vibration of aromatic ring	Aromatic ring	[60,61]
~ 2384 , ~ 2320	ν_3 asymmetric stretching vibration of CO ₂	Gaseous CO ₂	[62,63]
~ 1868 , ~ 1300	symmetric and asymmetric $\nu(\text{C}=\text{O})$ stretching of cyclic anhydride	Maleic anhydride	[65]
~ 1601 , ~ 1552 , ~ 1501 , ~ 1428	The COO [−] asymmetry and symmetry vibration of benzoate	benzoate	[66]
~ 1233 , ~ 1196 , ~ 1148 , ~ 1098 , ~ 1041	$\nu(\text{C}-\text{O})$ stretching vibration of alkoxide species	Benzyl alcohol	[67]

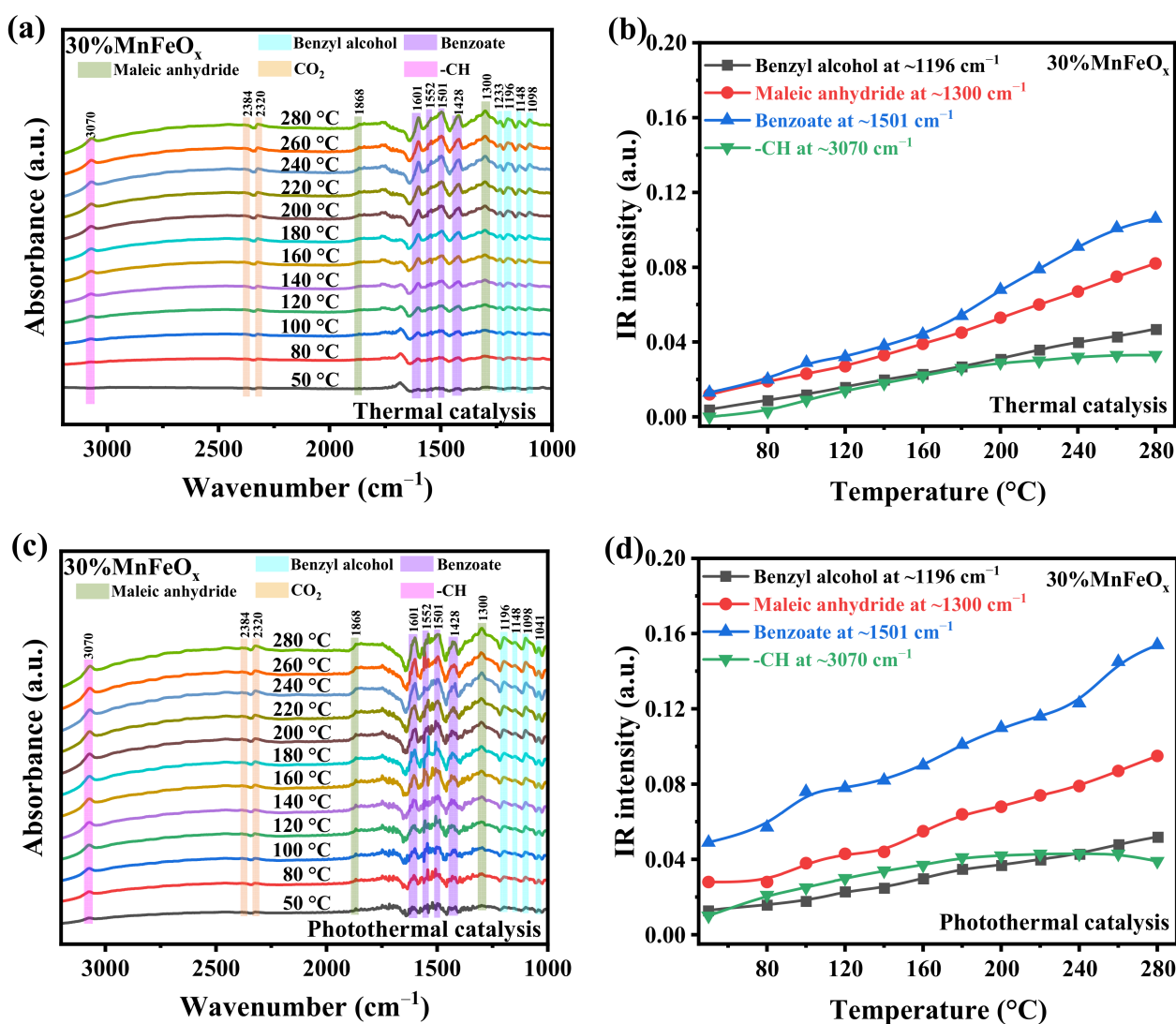


Figure 12. In situ DRIFTS spectra and the plots of IR signal intensities of the surface-adsorbed intermediates of 30%MnFeO_x under toluene (a,b) thermal and (c,d) photothermal catalytic degradation.

To better present the changes of the intermediates, the changes in these peaks' intensity are illustrated in Figure 12b. As the reaction temperature increased from 50 °C to 280 °C, the peak intensities at 1196, 1300 and 1501 cm⁻¹, corresponding to benzyl alcohol, maleic anhydride and benzoate, all continued to increase, among which the signal related to benzoate was always the strongest at 1501 cm⁻¹. This indicates that benzoate is the main intermediate with a relatively high and stable surface coverage of 30%MnFeO_x. The large accumulation of benzoate also means that its subsequent decarboxylation or aromatic ring cracking may be an important kinetic step in the complete oxidation of toluene. At the same time, the peak related to anhydride/maleate at 1300 cm⁻¹ strengthened with the increase in temperature, indicating that the temperature rise promoted the further oxidation and aromatic ring cracking of benzoate.

The DRIFTS spectra obtained under photothermal catalysis conditions are shown in Figure 12c. The main peak positions are basically consistent with those under thermal catalysis conditions, indicating that light irradiation did not fundamentally change the main reaction pathway of toluene oxidation. However, at the same temperature, the signals of benzyl alcohol, benzoate, maleic anhydride-related species, and CO₂ in the photothermal catalysis process were overall stronger than those in the separate thermal catalysis. As can be seen from Figure 12b,d, at 280 °C, the benzoate signal at 1501 cm⁻¹ under photothermal

conditions was approximately 0.155, while it was approximately 0.106 under thermal catalysis. The corresponding 1300 cm^{-1} signals were approximately 0.095 and 0.082, respectively. This indicates that light irradiation promoted the activation of the methyl C–H bond of toluene and the generation and subsequent transformation of oxygen-containing intermediates. Similar phenomena have been observed in manganese oxide photothermal catalytic systems, where light irradiation can enhance the lattice oxygen activity and oxygen migration ability, thereby promoting the formation of benzoate, aromatic ring cracking, and final mineralization [13,68]. Notably, under photothermal catalytic conditions, the aromatic C–H signal at 3070 cm^{-1} tends to stabilize in the medium-high temperature range and slightly decreases at high temperatures. Meanwhile, the signals of benzoate, maleic anhydride-related species, and CO_2 continue to increase. This indicates that the adsorbed toluene is not simply accumulated but is continuously consumed and transformed into oxygen-containing intermediates under the combined effect of light and heat. Combined with the results of catalytic activity and the CO_2 production rate, it can be concluded that light, on one hand, increases the local temperature of the catalyst through photothermal conversion, and on the other hand, may promote the Mn/Fe redox cycle, lattice oxygen migration, and activation of adsorbed oxygen, thereby accelerating the stepwise oxidation and deep mineralization of toluene [58]. Based on the above results, the degradation pathway of toluene over $30\%\text{MnFeO}_x$ is toluene $\rightarrow$ benzyl alcohol $\rightarrow$ benzoate $\rightarrow$ maleic anhydride $\rightarrow$ CO_2 and H_2O .

3. Materials and Methods

3.1. Chemicals and Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$) and 1,3,5-benzenetricarboxylic acid (H_3BTC , $\geq 98\%$) were obtained from Aladdin Co., Ltd. (Shanghai, China). Manganese acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\geq 99\%$) and toluene (C_7H_8 , 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

3.2. Catalyst Preparation

3.2.1. Preparation of MIL-100(Fe) Precursor

MIL-100(Fe) was prepared by a conventional solvothermal method. Generally, 6 mmol of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and 4 mmol of 1,3,5-benzenetricarboxylic acid (H_3BTC) were dissolved in 30 mL of H_2O and stirred for 1 h to obtain the clarified solution. Then, the above solution was transferred to a Teflon-lined stainless-steel autoclave and reacted at $160\text{ }^\circ\text{C}$ for 15 h. After cooling to room temperature, the powder of MIL-100(Fe) could be acquired via centrifugation, after washing three times with anhydrous ethanol and drying at $60\text{ }^\circ\text{C}$ for 12 h.

3.2.2. Preparation of FeO_x and the Different Contents of Mn-Modified MnFeO_x

FeO_x was synthesized by the sacrificial template method, using MIL-100(Fe) as the precursor. A certain amount of the as-prepared MIL-100(Fe) was placed in a crucible and calcined in a muffle furnace at $350\text{ }^\circ\text{C}$ for 2 h with a heating rate of $1\text{ }^\circ\text{C}/\text{min}$.

For the synthesis of different contents of Mn-modified MnFeO_x , the wet impregnation–calcination method was employed. Firstly, a certain amount of manganese acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) was dissolved in 40 mL of H_2O . Then, 1.0 g of the as-prepared MIL-100(Fe) was dispersed in the above solution and stirred at $80\text{ }^\circ\text{C}$ for 6 h. After that, the mixed solution was placed in an oven and dried at $60\text{ }^\circ\text{C}$ for 12 h. Finally, the dried powder was calcinated in a muffle furnace at $350\text{ }^\circ\text{C}$ for 2 h with a heating rate of $1\text{ }^\circ\text{C}/\text{min}$ to obtain the MnFeO_x sample. The MnFeO_x catalysts with the mass percentages of Mn and

MIL-100(Fe) of 5%, 10%, 30% and 50% were named 5%MnFeO_x, 10%MnFeO_x, 30%MnFeO_x, and 50%MnFeO_x, respectively.

3.3. Catalyst Characterization

The physical and chemical structures of the as-prepared catalysts were characterized by XRD, FT-IR, Raman, N₂ adsorption–desorption, SEM, TEM, XPS, and UV-vis DRS. The detailed information is listed as follows.

XRD patterns of the as-prepared catalysts were obtained from a Bruker D8 Advances X-ray diffractometer (Billerica, MA, USA), equipped with Cu-K α radiation and monochromatic detector in a 2 θ range of 5–80°. The emission current and accelerating voltage were 40 mA and 40 kV, respectively. FT-IR and Raman spectra were acquired from a Thermo Fisher Nicolet iS50 infrared spectrometer (Waltham, MA, USA) and a Horiba LabRAM HR Evolution Raman spectrograph (Paris, France), respectively. The resolution ratio and scan times for FT-IR were 4 and 64, respectively. The excitation wavelength for Raman spectra was 532 nm. The N₂ adsorption–desorption curves were obtained from a Quantachrome Autosorb iQ2 physical adsorption instrument (Boca Raton, FL, USA). Before the test, the samples were pretreated under vacuum conditions at 300 °C for 6 h. The N₂ adsorption–desorption was performed at −196 °C. A Shimadzu UV2600 UV-vis DRS spectrometer (Kyoto, Japan) was employed to obtain the UV-vis DRS spectra. Before the test, the spectrometer was zeroed and calibrated using a BaSO₄ mirror.

The SEM and TEM images were obtained from a JEOL JSM-7800F scanning electron microscope (Tokyo, Japan) and FEI Talos F200S transmission electron microscope (Portland, OR, USA), respectively. A Thermo ESCALAB 250Xi X-ray photoelectron spectroscopy microprobe (Waltham, MA, USA) was employed to investigate the surface chemistry of the as-prepared catalysts. C 1s (284.8 eV) was used for the energy calibration.

3.4. Photothermal Catalytic Performance Test

The photothermal catalytic reaction was performed on a fixed-bed reactor, equipped with a xenon lamp (300 W, 330 mW/cm², full-spectrum irradiation), using toluene as the model molecule. Generally, 100 mg of the catalyst particle with a size of 20–40 mesh was placed in a quartz reactor. The reaction gas contained 300 ppm toluene, and 20 vol.% O₂ balanced with Ar was introduced to the reaction system in a total flow rate of 50 mL/min. The concentrations of toluene and CO₂ in the inlet and outlet were determined by an online gas chromatography system (GC2026, Ruimin, Shanghai, China) equipped with two flame ionization detectors (FIDs). FID1, equipped with a Ni-based catalyst in the reformer, was used to detect CO₂. FID2 was applied to detect VOC molecules. The toluene conversion (X_t) and corresponding CO₂ yield (Y_C) were calculated according to the following Equations (1) and (2):

$$X_t = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

$$Y_C = C_C/7C_0 \times 100\% \quad (2)$$

where C_t , C_0 , and C_C are the outlet and inlet toluene concentration, and the outlet CO₂ concentration, respectively. At each temperature, the toluene and CO₂ concentrations were detected three times. The toluene conversion and CO₂ yield were calculated based on the average values of the three detected results. The water resistance test was also performed on the fixed-bed reactor. During the water resistance test, 1–5 vol.% water vapor was introduced by a bubbling method. The thermal catalysis was also performed on this reactor without turning on the xenon lamp.

3.5. Intermediates Detection

The toluene degradation intermediates under the thermal and photothermal conditions were determined by in situ DRIFTS spectra, carried out on a Thermo Fisher, Nicolet/iS50 infrared spectrometer (Waltham, MA, USA) equipped with an in situ reaction cell. Typically, 50 mg of the catalyst powder was pretreated at 300 °C for 60 min. After cooling to 30 °C, the gas was switched to 20 vol.% O₂ balanced with Ar. Meanwhile, the background was taken. Then, 300 ppm toluene + 20 vol.% O₂ balanced with Ar was introduced into the reaction system and pre-adsorbed for 60 min. After that, the temperature was heated to the target temperature and the spectra were collected. During the collection of the spectra, the resolution and scanning times were set at 4 and 32, respectively.

4. Conclusions

In summary, MIL-100(Fe) was used as the sacrificial template, and different Mn contents of MnFeO_x catalysts were successfully prepared by the impregnation–calcination method. The Mn content significantly affected the toluene photothermal oxidation performance of the catalysts by regulating the crystal phase structure, pore properties, surface redox state, and optical response. The results of photothermal catalytic performance suggested that the Mn content had a non-monotonic effect on the photothermal catalytic oxidation of toluene. Appropriate addition of Mn can enhance the catalytic performance, while excessive Mn will instead lead to a decrease in activity. Among the various MnFeO_x catalysts, the 30%MnFeO_x catalyst presents the optimal catalytic performance with the T₉₀ value of 237 °C. Meanwhile, the 30%MnFeO_x catalyst possesses good stability and water resistance. Characterization results suggest that the introduction of Mn enhanced the adsorption of light, surface Fe²⁺ and O_{ads} species, promoting toluene photothermal catalytic oxidation. Additionally, in situ DRIFTS results indicate that toluene mainly undergoes a stepwise oxidation process on the 30%MnFeO_x surface, namely toluene → benzyl alcohol → benzoate → maleic anhydride → CO₂ and H₂O. Among them, benzoate is the main intermediate with a relatively high surface coverage, and its subsequent dehydrogenation and aromatic ring cleavage may be important steps affecting the deep oxidation. Light irradiation does not fundamentally change the main reaction pathway of toluene, but can promote the generation of oxygen-containing intermediates and further conversion, accelerating the aromatic ring cleavage and ultimately mineralization. This study provides a feasible strategy for constructing Mn-Fe-based photothermal catalysts for VOC oxidation using non-precious-metal components, thereby avoiding reliance on noble-metal active components.

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Data Availability Statement: The authors declare that all data supporting the findings of this study are available within the article.

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