

Article



Catalytic Ozonation of Ethyl Acetate with Assistance of MMn₂O₄ (M = Cu, Co, Ni and Mg) Catalysts through In Situ DRIFTS Experiments and Density Functional Theory Calculations

Yulin Sun ^{1,2}, Peixi Liu ², Yiwei Zhang ², Yong He ^{1,2}, Yanqun Zhu ^{1,2} and Zhihua Wang ^{1,2,*}

- ¹ Qingshanhu Energy Research Center, Zhejiang University, Hangzhou 311300, China; sunyulin@zju.edu.cn (Y.S.); heyong@zju.edu.cn (Y.H.); yqzhu@zju.edu.cn (Y.Z.)
- ² State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China; liupx@zju.edu.cn (P.L.); yiwei_zhang@zju.edu.cn (Y.Z.)
- * Correspondence: wangzh@zju.edu.cn; Tel.: +86-571-8795-3162

Abstract: Catalytic ozonation, with enhanced efficiency and reduced byproduct formation at lower temperatures, proved to be efficient in ethyl acetate (EA) degradation. In this work, MMn_2O_4 (M = Cu, Co, Ni, Mg) catalysts were prepared via a redox-precipitation method to explore the catalytic ozonation mechanism of EA. Among all the catalysts, CuMn exhibited superior catalytic activity at 120 °C, achieving nearly 100% EA conversion and above 90% CO₂ selectivity with an O₃/EA molar ratio of 10. Many characterizations were conducted, such as SEM, BET and XPS, for revealing the properties of the catalysts. Plentiful active sites, abundant oxygen vacancies, more acid sites and higher reduction ability contributed to the excellent performance of CuMn. Moreover, the addition of NO induced a degree of inhibition to EA conversion due to its competition for ozone. H₂O had little effect on the catalytic ozonation of CuMn, as the conversion of EA could reach a stable platform at ~89% even with 5.0 vol.% of H₂O. The presence of SO₂ usually caused catalyst deactivation. However, the conversion could gradually recover once SO₂ was discontinued due to the reactivation of ozone. A detailed reaction mechanism for catalytic ozonation was proposed via in situ DRIFTS measurements and DFT calculations.

Keywords: ethyl acetate; low temperature; catalytic ozonation; MnO_x; reaction mechanism

1. Introduction

As major contributors to air pollution, volatile organic compounds (VOCs) pose significant threats to both ecological systems and the human body. VOCs are mainly emitted from many industry process, like chemical processes, petroleum refineries, transportation and so on. VOCs are also considered important precursors of ground-level ozone, PM2.5 and photochemical smog [1–3]. Moreover, long-term exposure to VOCs may result in serious diseases like lung cancer, leukemia, memory loss, etc. [4]. On account of rapid urbanization and industrialization, the emissions of VOCs exhibit an upward trend [1]. Presently, many countries have released strict environmental legislations to regulate VOC emissions. Thus, developing an effective method for VOC "green" elimination can have no delay.

Compared to other treatment methods, i.e., physical adsorption [5], biological degradation [6], photocatalytic degradation [7], etc., catalytic oxidation is recognized as one of the most effective techniques for the direct destruction of VOC molecules and less secondary pollution generation [8]. However, its higher reaction temperature and incomplete oxidation result in higher energy consumption and toxic intermediate by-product formation [9]. The catalytic ozonation method proved to be more attractive in VOC degradation, especially at low temperatures. The introduction of ozone to catalytic reactions can achieve



Citation: Sun, Y.; Liu, P.; Zhang, Y.; He, Y.; Zhu, Y.; Wang, Z. Catalytic Ozonation of Ethyl Acetate with Assistance of MMn_2O_4 (M = Cu, Co, Ni and Mg) Catalysts through In Situ DRIFTS Experiments and Density Functional Theory Calculations. *Catalysts* **2023**, *13*, 1491. https:// doi.org/10.3390/catal13121491

Academic Editor: Leonarda Liotta

Received: 16 November 2023 Revised: 1 December 2023 Accepted: 1 December 2023 Published: 2 December 2023



Copyright: © 2023 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/). higher efficiency at lower temperatures and suppress the generation of by-products due to its strong oxidability [10]. Moreover, the participation of catalysts could lower the activation energy and accelerate the reaction rate [11]. In this way, the performance of catalytic ozonation is significantly influenced by the activity of catalysts. Although noble metal catalysts perform well in VOC removal, their high price, catalyst poisoning and sintering effects limit their practical application. By contrast, transition metal catalysts (Mn, Cu, Co, Ni, etc.) with higher electronic mobility, better oxidation capacity and favorable stability have more potential for the catalytic ozonation of VOCs [12].

Among them, MnO_x has been well explored due to its abundant oxygen species, superior redox properties and multiple valence states. Li et al. [13] prepared different crystal phases of MnO_2 (α -, β -, γ - and δ -) and analyzed the relationship between their chemical properties and catalytic activity. This revealed that a larger specific surface area, more oxygen vacancies and better redox ability contributed to the better performance of MnO_2 . Besides morphology regulation, doping active metals is an efficient method to improve the performance of catalysts under different reaction conditions. Xiang et al. [14] doped Cu on hollow urchin-like MnO_2 , and the catalyst attained a steady 100% DCM (dichloromethane) conversion at 120 °C with the promotion of ozone (O_3 /DCM molar ratio of about 10). A higher O_{ads} content and weak acidity, enhanced low temperature reducibility and abundant oxygen vacancies contributed to its excellent performance.

The exhaust gas from industrial kilns usually contains multi-species VOCs, and ethyl acetate (EA) is a typical species which is difficult to oxidize completely. Commonly used in the coating, printing, pharmaceutical and chemical industries, it may lead to pollution of the environment and pose chronic toxicity to human beings [1]. Konsolakis et al. [15] synthesized Ce-Co bimetallic catalysts and applied them to EA catalytic oxidation. The catalysts containing 20 wt.% of Co had the best catalytic activity, achieving nearly a complete conversion of EA at 260 °C. Zhu et al. [16] prepared an effective MnCu catalyst to oxidize EA with O₂. At around 210 °C, the conversion of EA reached nearly 100% for the activation of abundant oxygen vacancies. Moreover, it has been discovered that the synergistic effects of composite oxides contribute to the significant enhancement of catalytic activities, such as Cu–Mn–O [17], Co–Mn–O [18], Ni–Mn–O [19] and Mg–Mn–O [20]. Due to its lower working temperature and higher selectivity to CO₂, catalytic ozonation has become one of the popular methods for VOC degradation in recent years. Unfortunately, the research on EA catalytic ozonation is still very limited.

Herein, a series of MMn_2O_4 (M = Cu, Co, Ni and Mg) catalysts with spinel structures were prepared through the redox-precipitation method to study the catalytic ozonation effect for the degradation of EA. During the activity tests, the EA conversion efficiency and CO_x selectivity of catalysts were evaluated. Furthermore, the physicochemical properties (textual properties, oxygen species, acidity, element valance, etc.) were determined by various characterization methods, such as SEM, XRD, BET, XPS and TPD/TPR. As a typical pollutant, NO_x usually coexists with EA in the surface coating industry, so the effect of NO was also evaluated in this work. The sulfur and water vapor resistance were also tested for the prepared catalyst, as SO_2 and H_2O usually co-exist in flue gas. Additionally, for further research on intermediates' formation and the reaction mechanism during the catalytic ozonation process, an analysis of in situ DRIFTs combined with the DFT calculation was carried out as well.

2. Results and Discussion

2.1. Catalytic Ozonation of EA

The EA conversion and CO_2/CO selectivity are shown in Figure 1 with ozone and CuMn, CoMn, NiMn and MgMn catalysts. The reaction temperature ranged from 40 to 140 °C, and the O_3/EA molar ratio was set to 10 according to the complete oxidation of EA according to Equation (1).



Figure 1. Catalytic ozonation of EA over prepared catalysts (initial concentration of O_3 : 500 ppm; EA: 50 ppm). (a) EA conversion; (b) CO/CO₂ selectivity.

In the whole range of temperatures, CuMn exhibited the best catalytic performance, achieving 99% EA conversion at 120 °C. Above 80 °C, the EA conversion of CuMn was kept over 90%, as shown in Figure 1a. Moreover, it also had the highest CO₂ selectivity and the lowest CO selectivity, demonstrating its better capability for deep oxidation, as shown in Figure 1b. Slightly more than NiMn, the EA conversion of MgMn could reach around 98% at 120 °C. However, the CO₂ selectivity of NiMn was relatively higher, and its CO selectivity was lower than MgMn, indicating the incomplete oxidation of MgMn. However, CoMn shows the lowest catalytic activity, with only 89% EA conversion achieved at 120 °C, generating much more CO and less CO₂ at the same time.

$$C_4H_8O_2 + (10 - x)O_3 \rightarrow xCO + (4 - x)CO_2 + (10 - x)O_2 + 4H_2O$$
 (1)

Overall, T₉₀ (the temperature of 90% EA conversion) increased in the following order: CuMn (70 °C) < MgMn (76 °C) < NiMn (80 °C) < CoMn (135 °C). T₅₀ increased in the following order: CuMn (40 °C) < MgMn (43 °C) < NiMn (45 °C) < CoMn (47 °C). With the temperature increasing, the EA conversion and selectivity of CO₂ were all improved, while the formation of CO was suppressed. However, the conversion of EA exhibited little increase above 120 °C, due to the acceleration of ozone decomposition at higher temperatures [21].

2.2. Catalyst Characterization

2.2.1. Crystalline Structures

The XRD patterns of the CuMn, CoMn, NiMn and MgMn catalysts are depicted in Figure 2, and the catalysts show characteristic diffraction peaks of α -MnO₂ (PDF#44-0141) at 12.8, 28.8°, 37.5° and 39.0°, corresponding to the planes of (1 1 0), (3 1 0), (2 1 1), and (3 3 0), respectively [22]. CuMn demonstrated several well-dispersive diffraction peaks at 18.5°, 35.8° and 37.5°, which could be linked to the (1 1 1), (3 1 1) and (2 2 2) planes of spinel-type-structured CuMn₂O₄ (PDF#76-2296) [23]. The characteristic peaks of CoMn appearing at 18.2° and 36.8° were identified as the (1 0 1) and (2 0 2) lattice planes of a body-centered tetragonal CoMn₂O₄ spinel (PDF#77-0471) [24]. Meanwhile, the peaks at 18.3° and 37.3° were ascribed to the (1 1 1) and (2 2 2) planes of cubic NiMn₂O₄ (PDF#01-1110), while the peaks at 18.2°, 36.3° and 38.8° should be linked to the (1 0 1), (2 1 1) and (0 0 4) planes of MgMn₂O₄ (PDF#72-1336), respectively [25,26]. In contrast, CoMn exhibited a higher intensity of diffraction peaks, indicating the strengthening of crystallinity and an increasing particle size, which were not conducive to the enhancement of catalytic activity.



Figure 2. XRD patterns of prepared catalysts.

To reveal the catalysts' morphologies, SEM images were acquired, and the pictures are shown in Figure 3. Apparently, CuMn, CoMn and MgMn presented similar bulk-like structures, while NiMn consisted of numerous spherical particles. However, the porous structure facilitated the surface defect formation of CuMn, providing a larger contact area for reactants for deep oxidation [27]. An EDS analysis was carried out to prove the elements' distribution (Figure S2). The images revealed that the Mn, Cu, Co, Ni and Mg elements were uniformly dispersed in their corresponding catalysts, which was favorable for active site exposure and defect formation [28].



Figure 3. SEM images of (a1,a2) CuMn, (b1,b2) CoMn, (c1,c2) NiMn and (d1,d2) MgMn.

2.2.2. Textual Properties

The N₂ adsorption–desorption isotherms and the pore size distribution curves are illustrated in Figure S3. Without a saturated adsorption platform, the isotherms of the catalysts showed the characteristics of a typical type IV isotherm with a type H3 hysteresis loop, indicating the irregular pore structures with abundant mesopores of catalysts [29]. And the corresponding specific surface area, pore volume and average pore diameter are calculated and shown in Table 1. According to the literature, a higher specific surface area would facilitate the formation of more defects, which was conductive to the generation of active sites [14]. In the meantime, more active sites applied for adsorption and ozonation ultimately enhance catalytic performance [30]. Clearly, CuMn exhibited the largest surface area (126.6 m²·g⁻¹) and pore volume (0.52 cm³·g⁻¹), while the surface area (59.3 m²·g⁻¹) and pore volume (0.20 cm³·g⁻¹) of CoMn were fairly lower, in accordance with their best and worst catalytic performance.

verage Pore ameter ^b /nm
17.6
15.7
8.2
6.9

Table 1. Textual properties of prepared catalysts.

^a BJH desorption cumulative volume of pores. ^b BJH desorption average pore diameter.

2.2.3. Surface Properties

To characterize the valance states and the distribution of surface elemental species, an XPS analysis was conducted, and the results are shown in Figure 4. The proportion of each species was determined by the deconvolution of XPS curves and tabulated in Table 2. As depicted in Figure 4a, the Mn $2p_{3/2}$ spectrum consisted of two characteristic peaks at ~642.0 eV and 643.7 eV, corresponding to Mn³⁺ and Mn⁴⁺ species, respectively. For all the catalysts, Mn³⁺ was the main Mn species, and the content of Mn³⁺ decreased in the order CuMn (65.8%) > MgMn (65.5%) > NiMn (64.0%) > CoMn (63.1%), consistent with the trends of catalytic activity. It is reported that Mn³⁺ can trigger the Jahn–Teller distortion, and to sustain charge balance, oxygen vacancies are created (Equation (2), V_o refers to oxygen vacancy) [31]. Additionally, oxygen vacancies could promote the decomposition of ozone into more active oxygen species, which is favorable for EA catalytic ozonation [32,33].

$$4 \operatorname{Mn}^{4+} + \operatorname{O}^{2-} \to 4 \operatorname{Mn}^{4+} + \frac{1}{2} \operatorname{O}_2 + \frac{2e}{V_0} \to 2 \operatorname{Mn}^{4+} + 2 \operatorname{Mn}^{3+} + \frac{1}{2} \operatorname{O}_2 + V_0 \quad (2)$$



Figure 4. XPS spectra of (a) Mn 2p, (b) Mn 3s and (c) O 1s for synthesized catalysts.

Table 2. Distribution of Mn ions and O species of prepared catalysts based on XPS results.

Catalysts	Mn 2p _{3/2}		O 1s		1.0.0		
	Mn ⁴⁺ (%)	Mn ³⁺ (%)	O _{la} (%)	O _{ad} (%)	AOS	Mn ³⁺ /Mn ⁴⁺	O_{ad}/O_{la}
CuMn	34.2	65.8	44.6	55.4	3.49	1.92	1.24
CoMn	36.9	63.1	51.4	48.6	3.80	1.72	0.95
NiMn	36.0	64.0	49.4	50.6	3.71	1.78	1.02
MgMn	34.5	65.5	47.7	52.3	3.61	1.90	1.10

Figure 4b presents the XPS spectra and the binding energy of the doublet splitting (Δ Es) of Mn 3s. The average oxidation state (AOS) of Mn species could be calculated through Equation (3) [34], and the AOS value increased in the following sequence: CuMn

(3.49) < MgMn (3.61) < NiMn (3.71) < CoMn (3.80). A lower AOS value demonstrates the generation of more oxygen vacancies, which are advantageous for the activation of ozone and the oxidation of EA [35,36]. Among the catalysts tested, CuMn exhibited the lowest AOS value, corresponding to its highest content of Mn³⁺ and best catalytic performance.

$$AOS = 8.956 - 1.126\Delta Es$$
 (3)

The curves of the O 1s spectra had two distinct peaks upon deconvolution (Figure 4c), and the peak at ~529.8 eV was attributed to lattice oxygen species (O_{la}), while the peak at ~530.9 was related to surface-adsorbed oxygen species (O_{ad}), respectively [37]. As depicted in Table 2, the proportion of O_{ad} decreased as follows: CuMn (55.4%) > MgMn (52.3%) > NiMn (50.6%) > CoMn (48.6%). Abundant surface-adsorbed oxygen species (O_{ad}) accelerate the formation of oxygen vacancies, which could create more active sites for ozone decomposition, reactive oxygen species adsorption, and EA degradation [38,39]. For CoMn, its ratio of O_{ad}/O_{la} was relatively lower, resulting in its poor performance in catalytic activity tests.

Overall, the results of the XPS analysis were consistent with the performance of the catalysts to some extent. Among all the catalysts, CuMn possessed the highest Mn^{3+} and O_{ad} contents and a relatively lower AOS value, which promoted the generation of oxygen vacancies and active sites, consequently accelerating the progress of the catalytic reaction.

2.2.4. Temperature-Programmed Studies

As shown in Figure 5a, the reducibility of the prepared catalysts was evaluated through H₂-TPR profiles. The successive reduction of $Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0$ formed two peaks at 156 and 245 °C for the CuMn catalyst, while the peak at around 416 °C was ascribed to the reduction of Co^{2+} to Co^0 for CoMn [40,41]. As for the NiMn catalyst, the broad peak centered at 383 °C resulted from the reduction of Ni²⁺ to Ni [42]. And the peaks at 270~360 °C were assigned to the successive reduction process of $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$ from Mn^{4+} to Mn^{2+} [43]. Moreover, the reduction temperature of CuMn was relatively lower than that of the other three catalysts, contributing to more active oxygen species and its better performance at low temperatures [31,44]. As tabulated in Table 3, the H₂ uptake amount increased in the following order: MgMn (8.25 mmol·g_{cat}⁻¹) < NiMn (9.29 mmol·g_{cat}⁻¹) < CuMn (9.35 mmol·g_{cat}⁻¹) < CoMn (10.2 mmol·g_{cat}⁻¹). Nevertheless, the order did not accord with the activity tests, suggesting that there is no direct correlation between H₂ uptake amount and catalytic activity.



Figure 5. H₂-TPR, NH₃-TPD and O₂-TPD profiles of synthesized catalysts: (**a**) H₂-TPR; (**b**) NH₃-TPD; (**c**) O₂-TPD.

Catalyst	H ₂ Uptake /(mmol·g _{cat} ⁻¹)	NH ₃ Desorption /(mmol·g _{cat} ⁻¹)	O_2 Desorption /(a.u.· g_{cat}^{-1})
CuMn	9.27	3.86	5.98
CoMn	10.2	3.69	3.94
NiMn	9.29	3.84	4.18
MgMn	8.25	3.81	5.45

Table 3. Amount of O_2 , NH_3 desorption and H_2 uptake over synthesized catalysts.

To investigate the catalysts' surface acidity, NH₃-TPD experiments were conducted, and the profiles are shown in Figure 5b. With different strengths, the acid sites could be divided into weak acidity (100~280 °C), moderate acidity (280~450 °C) and strong acidity (450~600 °C), respectively [45]. Apparently, all the catalysts exhibited both weak and strong active sites, assigned to Lewis and Brönsted acid sites, respectively. In general, Lewis acid sites promote the cleavage of C–C bonds and the deep oxidation of VOCs at low temperatures due to the generation of active oxygen species, while Brönsted acid sites are highly related to VOC adsorption [46,47]. Thus, surface acidity was closely linked to the ozonation process of EA, including EA adsorption, ozone activation and complete degradation. The total acid site amount of CuMn was the highest, ca. 3.86 mmol·g_{cat}⁻¹, fitting with its excellent catalytic activity. With the lowest total acid sites (3.69 mmol·g_{cat}⁻¹), CoMn did not perform well in the EA ozonation. Hence, creating more surface acidity could be a possible way to optimize catalyst design to remove VOCs.

O₂-TPD profiles are researched and shown in Figure 5c to further reveal the properties of oxygen species. Usually, oxygen species are divided into physically adsorbed oxygen (<250 °C), surface lattice oxygen (250~650 °C) and bulk lattice oxygen (>650 °C) [48]. The total O₂ desorption amounts of catalysts are tabulated in Table 3 and decreased in the sequence CuMn (5.98 mmol·g_{cat}⁻¹) > NiMn (5.45 mmol·g_{cat}⁻¹) > MgMn (4.18 mmol·g_{cat}⁻¹) > CoMn (3.94 mmol·g_{cat}⁻¹), consistent with the order of activity tests. With the highest EA conversion, CuMn exhibited better oxygen adsorption ability and higher oxygen species mobility, confirming that more active oxygen species were beneficial for the degradation of EA [49].

2.3. Effect of NO

As a common pollutant which usually co-exists with EA in surface coating industries, NO can also be deeply oxidized by O₃. To evaluate the effect of the presence of NO on EA ozonation, 100 ppm NO was added to the flue gas, and the results are illustrated in Figure 6. According to the stoichiometric reaction (Equation (4)), the theoretical molar ratio of O₃/NO for complete oxidation is 1.5. As presented in Figure 6a, the addition of NO induced a degree of inhibition in EA conversion. In comparison, CuMn still achieved the best catalytic activity, reaching 87% EA conversion at 140 °C. However, compared with the individual ozonation of EA (Figure 1a), the efficiencies of the catalysts were all reduced. The order of T₅₀ was consistent with the individual ozonation and increased as follows: CuMn (43 °C) < MgMn (49 °C) < NiMn (52 °C) < CoMn (56 °C). This showed that T₅₀ shifted to higher temperatures as well. Meanwhile, the selectivity of CO₂ also exhibited a certain decline, while the selectivity of CO increased (Figure 6b), indicating that the addition of NO exacerbated the incomplete oxidation of EA to some extent.

$$2NO + 3O_3 = N_2O_5 + 3O_2 \tag{4}$$

The NO conversion and NO₂ selectivity are shown in Figures 6c and 6d, respectively. All the catalysts achieved their highest NO conversion at 60 °C and decreased in the following sequence: CuMn (94%) > CoMn (93%) > NiMn (92%) > MgMn (85%). Above 60 °C, the NO conversion presented a downward trend, while the EA conversion improved with temperature increasing. Clearly, there was a competitive effect between the NO and EA molecules, and the ozonation of NO was prior to the ozonation of EA at lower

temperatures. With a rise in temperature, the NO conversion decreased to ~70%, and the NO₂ selectivity rose to ~65% at 140 °C as EA may compete with NO for more ozone at higher temperatures. No N₂O was observed during the reaction process; hence, lower NO₂ selectivity demonstrated the formation of more N₂O₅, while higher NO₂ selectivity proved the suppression of deep NO oxidation. Moreover, with a higher NO conversion and lower NO₂ selectivity, CuMn performed well in both NO and EA ozonation, proving its great potential for the simultaneous elimination of EA and NO_x.



Figure 6. Effect of NO on EA catalytic ozonation over synthesized catalysts. (**a**) EA conversion, (**b**) CO_2/CO selectivity, (**c**) NO conversion and (**d**) NO₂ selectivity. (Initial concentration of O₃ was 500 ppm, NO was 100 ppm and EA was 50 ppm).

2.4. Effect of SO_2 and H_2O

To evaluate the interference of H₂O and SO₂, long-time resistance tests were conducted on CuMn due to its excellent catalytic performance at 120 °C. As shown in Figure S4a, the simulated flue gas was successively introduced with 2.5 and 5.0 vol.% of H₂O. The catalytic efficiency dropped slightly, reaching a stable platform at ~97% in 2.5 vol.% of H₂O and ~89% in 5.0 vol.% of H₂O, respectively. However, with the removal of H₂O, the EA conversion efficiency gradually recovered, indicating that the deactivation caused by H₂O was reversible. Furthermore, the presence of H₂O facilitated the creation of OH-active radicals, which were conducive to the further oxidation of CO and other intermediates to CO₂ [50].

As shown in Figure S4b, under 50 ppm of SO₂, the catalytic efficiency slightly declined to ~97%. While under 100 ppm of SO₂, the EA conversion reduced rapidly to 79%. Apparently, the introduction of SO₂ caused sulphur poisoning and incomplete oxidation as it occupied the active sites of the catalyst. However, different from catalytic oxidation, where the poisoning of SO₂ was irreversible, the EA conversion in catalytic ozonation could gradually recover once SO₂ was stopped due to the activation of ozone [51]. The formation of intermediate species during catalytic ozonation was investigated through an in situ DRIFTS analysis over the CuMn catalyst. Firstly, 50 ppm of EA with N₂ as a background gas was introduced to evaluate the EA adsorption process (Figure S5). The bands centered at 1710, 1562, 1433, 1385, 1280 and 1053 cm⁻¹ could be attributed to the stretching vibrations of C=O, the asymmetric stretching of COO⁻, CH₃ bending vibrations, CH₃ bending, the stretching of C–O and the C–O–C stretching vibrations of EA, respectively [52,53]. Moreover, the bands exhibited an increase in intensity over time, proving the gradual accumulation of EA on the catalyst.

After the saturation of EA adsorption, O_3 was added to the flue gas (Figure 7a). Obviously, the bands of EA declined, indicating its fast reaction with the ozone. The peak observed at ~1760 cm⁻¹ could be attributed to the C=O stretching vibrations of aldehyde or carboxylic acid species, while the bands at ~1555 and 1440 cm⁻¹ corresponded to the COO⁻ antisymmetric and symmetric stretching vibrations of acetic acid, respectively [53–55]. Moreover, the peaks at ~1250 and 1053 cm⁻¹ were related to the stretching vibrations of C–OH, suggesting the formation of ethanol and an ethoxy group during the ozonation process [56].



Figure 7. In situ DRIFTS measurement under various conditions: (**a**) 50 ppm EA and 500 ppm O₃; (**b**) 50 ppm EA, 100 ppm NO and 500 ppm O₃.

Then, NO was introduced to the EA ozonation process, and the images are depicted in Figure 7b. The bands newly appearing at 1602 and 1296 cm⁻¹ were ascribed to nitrates (NO₃⁻) and nitrites (NO₂⁻), respectively [57]. In addition, the band intensity of EA ozonation decreased slightly, demonstrating a certain inhibiting effect of NO, which was consistent with the activity tests (Figure 6a). In addition, the peak at 1680 cm⁻¹ revealed the generation of more carboxylic acid or aldehyde species, indicating that more intermediate products were created and absorbed on the catalyst surface [54]. Thus, the introduction of NO could cause an incomplete oxidation during the reaction, which was in accordance with the previous statement (Figure 6b).

2.6. Theoretical Calculation and Reaction Mechanism

DFT calculations were carried out on the CuMn catalyst to further investigate the

reaction mechanism. CuMn₂O₄, with an Fd3m space group, was a spinel cubic crystal. The optimized bulk lattice parameters (a = b = c = 8.315 Å) closely matched experimental values (a = b = c = 8.327 Å), confirming the reliability of the calculation methods in this work [58]. The CuMn₂O₄ (1 0 0) surface was easily exposed and catalytically active. Consequently,

it was used to research the adsorption process on the CuMn catalyst, as presented in Figure 8 [59].



Figure 8. Schematic structure model of (a) Mn-terminated surface and (b) Cu-terminated surface of $CuMn_2O_4$ (1 0 0).

As adsorption was an important step of the heterogeneous catalytic reaction, the bond lengths and adsorption energies of the reactants were calculated [60]. As depicted in Figure 9, the adsorption energy of O₃ on the Mn-terminated surface ($E_{ads} = -0.4542 \text{ eV}$) was lower than that on the Cu-terminated surface ($E_{ads} = -0.4345 \text{ eV}$). On the Cu-terminated surface, the adsorption energy of EA ($E_{ads} = -1.2101 \text{ eV}$) was lower than that on the Mn-terminated surface ($E_{ads} = -1.1748 \text{ eV}$). Research indicates that a smaller adsorption energy and bond length signify a stronger interaction between the catalyst and adsorbate, suggesting a preference for O₃ to adsorb on the Mn-terminated surface, whereas the Cu-terminated surface was more suitable for EA adsorption [61].



Figure 9. The most stable configurations, bond lengths and adsorption energies of O_3 , EA and NO over the (**a**) Mn-terminated surface and (**b**) Cu-terminated surface of CuMn₂O₄ (1 0 0).

To study the effect of NO, the adsorption energies of NO on the Mn-terminated ($E_{ads} = -0.9613 \text{ eV}$) and Cu-terminated ($E_{ads} = -0.6018 \text{ eV}$) surfaces were calculated. Obviously, NO tended to adsorb on the Mn-terminated surface, which was also active for O₃ adsorption. As O₃ and NO simultaneously adsorbed on the Mn-terminated surface, it could be easier for them to react with each other, which may be the reason why O₃ reacted preferentially with NO rather than EA. Thus, insufficient O₃ may cause the incomplete

oxidation of EA and lead to lower EA conversion, corresponding with the experimental results (Figure 6).

Based on the in situ DRIFTS measurements and DFT calculation, the proposed reaction mechanism is presented in Figure 10. Firstly, EA adsorbed on the Cu-terminated surface, while O_3 occupied the Mn-terminated surface. Next, O_3 was activated and decomposed into O_2 and active oxygen radicals (O*). With the assistance of O* radicals, the C–O bond of EA was first cleaved for its lowest bond energy and then formed alkoxides and acetates. For deep oxidation, the alkoxides were rapidly converted into aldehydes and then oxidized into acetates. At last, the acetates could be easily resolved into CO_2 and H_2O , generating harmless inorganic products. As NO and O_3 could simultaneously adsorb on the Mn-terminated surface, O_3 would preferentially react with NO first for their full contact. Primarily, NO was transformed into NO_2 and then deeply oxidized into N_2O_5 , which was more easily absorbed. However, the introduction of NO inhibited the conversion of EA and suppressed EA deep oxidation, resulting in the generation of more carboxylic acid or aldehyde species.



Figure 10. Proposed reaction mechanism for catalytic ozonation of NO and EA over CuMn₂O₄ catalyst.

3. Materials and Methods

3.1. Catalyst Preparation

The MMn₂O₄ (M = Cu, Co, Ni, Mg) catalysts were all prepared by the redox-precipitation method. Initially, 0.04 mol of KMnO₄ (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and 0.02 mol of $M(NO_3)_2 \cdot xH_2O$ (M = Cu, Co, Ni and Mg) (Sinopharm, China) were dissolved into 400 mL of deionized water under vigorous stirring, and the molar ratio of M:Mn was 1:2. Subsequently, 0.1 mol/L of a H₂C₂O₄ (Sinopharm, China) solution was instilled into the mixed solution dropwise to reach complete precipitation. The suspensions were magnetically stirred for 3 h to be fully equilibrated at room temperature. After centrifugal separation, thorough washing with deionized water and further drying at 100 °C for 12 h, the obtained powder was calcined at 400 °C for 3 h with a ramp rate of 5 °C·min⁻¹ in air. The catalysts were denoted as CuMn, CoMn, NiMn and MgMn, respectively. The reagents used were all of analytical grade, and the as-prepared samples were ground to 40~60 mesh prior to the activity tests.

3.2. Catalytic Activity

The catalytic activity of the prepared catalysts was evaluated on the self-designed catalytic platform (WFS-2017, Tianjin Xianquan Co., Ltd., Tianjin, China), as shown in Figure S1. Ozone generation was achieved through a dielectric barrier discharge (DBD)

reactor (VMUS-1S, AZCO Industries., Ltd., Vancouver, BC, Canada), with one O_3/O_2 mixture stream directed towards an ozone analyzer (BMT-964BT, OSTI, Inc., Monterey, CA, USA) to monitor the concentration of ozone and the other O_3/O_2 stream flowing to the reactor. The simulated flue gas was provided by standard cylinder gases (Jingong Gas Co., Ltd., Hangzhou, China), including C₄H₈O₂ (EA, 500 ppm/N₂), NO (2000 ppm/N₂), SO₂ (1000 ppm/N₂), N₂ (99.99%) and O₂ (99.99%), and controlled by mass flow controllers (MFC S500, HIRIBA METRON Co., Ltd., Irvine, CA, USA). During the catalytic activity tests, 0.15 g of catalyst was mixed with a certain amount of SiO₂ (Sinopharm, 40~60 mesh) and placed in a quartz tube in an electrically heated furnace. The gas hour space velocity (GHSV) was maintained at 30,000 h⁻¹.

The initial concentration of EA was set to 50 ppm, and the total flow rate was controlled at 200 mL/min with 10 vol% of O_2 in the stream. To investigate the effect of H_2O , water vapor was introduced into the simulated flue gas by bubbling, and the moisture content was measured with a humidity analyzer. After the reaction, the exhaust gas was analyzed using a gas chromatograph (GC9790II, Zhejiang Fuli Co., Ltd., Taizhou, China), which was equipped with one flame ionization detector (FID) for measuring the concentration of EA and another for analyzing CO and CO₂ generation. An FTIR gas analyzer (Gasmet FTIR DX4000, Finland) was used to detect the concentration of NO and NO₂ continuously, and the residual O_3 in the exhaust gas was monitored with an ozone analyzer of low concentration (BMT-932-1, OSTI Inc., Monterey, CA, USA).

The catalytic activity was assessed based on EA, NO and O_3 conversion and the selectivity of CO, CO_2 and NO_2 , which were determined by the following equations:

$$[EA]_{conv.} = \frac{[EA]_{initial} - [EA]_{outlet}}{[EA]_{initial}} \times 100\%$$
(5)

$$NO]_{conv.} = \frac{[NO]_{initial} - [NO]_{outlet}}{[NO]_{initial}} \times 100\%$$
(6)

$$[O_3]_{\text{conv.}} = \frac{[O_3]_{\text{initial}} - [O_3]_{\text{outlet}}}{[O_3]_{\text{initial}}} \times 100\%$$
(7)

$$[CO]_{selec.} = \frac{[CO]_{outlet}}{([EA]_{initial} - [EA]_{outlet}) \times 4} \times 100\%$$
(8)

$$[CO_2]_{selec.} = \frac{[CO_2]_{outlet}}{([EA]_{initial} - [EA]_{outlet}) \times 4} \times 100\%$$
(9)

$$[NO_2]_{selec.} = \frac{[NO_2]_{outlet}}{[NO]_{initial}} \times 100\%$$
(10)

where [EA]_{initial}, [NO]_{initial} and [O₃]_{initial} are the initial concentrations of EA, NO and O₃, and [EA]_{outlet}, [NO]_{outlet}, [O₃]_{outlet}, [CO]_{outlet}, [CO₂]_{outlet} and [NO₂]_{outlet} are the outlet concentrations of EA, NO, O₃, CO, CO₂ and NO₂, in unit ppm, respectively.

3.3. Catalyst Characterization

The X-ray diffraction (XRD) patterns were evaluated to reveal the crystal structure of the catalysts using a Rigaku D/max 2550PC diffractometer (PANalytical B.V., Almelo, The Netherlands) with a Cu K α radiation source ($\lambda = 0.15406$ nm; 10 °C·min⁻¹; diffraction angle: 10~80°) at 40 kV and 40 mA. The specific surface area and pore structure were measured through N₂ adsorption–desorption isotherms by the BET and BJH methods, using an automatic gas adsorption analyzer (Micromeritics ASAP 2460, Norcross, GA, USA) at 77 K. The morphology and microstructure were analyzed with a field emission scanning electron microscope (FE-SEM, Zeiss Sigma 300, Jena, Germany). The chemical states of the elements were analyzed with an X-ray photoelectron spectrometer (XPS, Thermo Scientific K-Alpha, Mass. Waltham, MA, USA) with a standard Al K α source

(1486.6 eV), with binding energies referring to the C 1s peak (284.8 eV). The H₂-TPR, NH₃-TPD and O₂-TPD measurements were performed on a chemical temperature- programmed chemisorption analyzer (AutoChem II 2920, Micromeritics, Norcross, GA, USA). The spectra of the adsorption and ozonation processes were collected on an in situ diffuse reflectance infrared Fourier transform spectrometer (in situ DRIFTS, Thermo Scientific Nicolet iS50, Waltham, MA, USA), equipped with an MCT/A detector and a high-temperature reaction chamber (Harrick, ZnSe windows). All the spectra were recorded in the range of 600 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹. Prior to the measurements, the catalysts were pretreated at 120 °C with N₂ (200 mL/min) for 30 min to remove surface impurities.

3.4. DFT Calculation

The catalytic mechanism was investigated through the density functional theory (DFT) method and implemented in CASTEP code [62]. The PBE (Perdew–Burke–Ernzerhof) exchange–correlation potential with a GGA (generalized gradient approximation) function was employed. And the cutoff energy of 450 eV was set on a plane-wave basis. In addition, the geometry optimization was completed until the absolute energy, the force and the maximum displacement were below 1.0×10^{-5} eV/atom, 0.03 eV/Å and 1.0×10^{-3} Hartree, respectively. For the self-consistent field (SCF), the convergence criterion was set as 1.0×10^{-6} eV/atom. The Brillouin zone of the unit cell was set as $4 \times 4 \times 4$, while for the surface, it was set as $3 \times 3 \times 1$ Monkhorst Pack k-point grids.

To avoid the next periodic slab effects, a vacuum layer (16 Å) was constructed in the z direction. The adsorption energy (E_{ads}) of the adsorbates on the surface of the catalyst was calculated with the following equation:

$$E_{ads} = E_{(adsorbate-catalyst)} - (E_{catalyst} + E_{adsorbate})$$
(11)

where $E_{(adsorbate-catalyst)}$ is the total energy of the catalyst–adsorbate system, $E_{catalyst}$ is the total energy of the catalyst, and $E_{adsorbate}$ is the total energy of the gas-phase molecule.

4. Conclusions

This study focused on the investigation of the catalytic ozonation of EA over MMn_2O_4 (M = Cu, Co, Ni and Mg) catalysts at relatively low temperatures. With the best performance, CuMn maintained above a 90% EA conversion in the range of 80 to 140 °C, achieving nearly 100% EA conversion and above 90% CO₂ selectivity at 120 °C. The abundant surface defects of CuMn contributed to its large surface area and pore volume, which facilitated the generation of active sites for deep oxidation. Moreover, its higher Mn^{3+} content and lower AOS value were conductive to the formation of oxygen vacancies, while more O_{ad} promoted the adsorption of reactive oxygen species, and a higher O_2 desorption amount accelerated the mobility of oxygen species. Together with plentiful acid sites and lower reduction temperatures, the adsorption, activation and oxidation of EA at lower temperatures were enhanced, corresponding to the excellent performance of CuMn.

Moreover, the addition of NO proved to inhibit the degradation of EA to some extent, as NO would compete with EA for ozone. In comparison, CuMn performed well in both the NO and EA ozonations, exhibiting great potential for simultaneous elimination. With the treatment of H₂O, the conversion of EA dropped slightly, reaching a stable platform at ~89% in 5.0 vol.% of H₂O. On the other hand, after the addition of SO₂, the EA conversion decreased rapidly to 79% and was gradually recovered for the activation of ozone. Additionally, the presence of H₂O contributed to higher CO₂ selectivity because of the formation of OH active radicals. With the combination of in situ DRIFTS measurements and the DFT calculation, a reaction mechanism for catalytic ozonation was proposed: adsorption (O₃ and NO on the Mn-terminated surface and EA on the Cu-terminated surface), O₃ activation, the formation of intermediates (alkoxides \rightarrow aldehydes \rightarrow acetates) and deep oxidation (acetates \rightarrow CO₂ and H₂O, NO \rightarrow NO₂ \rightarrow N₂O₅).

Supplementary Materials: The following supporting information can be downloaded at https: //www.mdpi.com/article/10.3390/catal13121491/s1: Figure S1: Schematic of experimental set-up; Figure S2: SEM images of (a1, a2): CuMn, (b1, b2): CoMn, (c1, c2): NiMn and (d1, d2): MgMn; Figure S3: N₂ adsorption–desorption isotherms and pore size distribution curves of synthesized catalysts; Figure S4: Effect of (a) H₂O and (b) SO₂ on EA conversion efficiency and outlet CO_x concentration over CuMn catalyst; Figure S5: In situ DRIFTS measurement over CuMn catalyst at 120 °C with 50 ppm EA.

Author Contributions: Y.S.: investigation, conceptualization, methodology, validation, writing original draft. P.L.: investigation, data curation, visualization. Y.Z. (Yiwei Zhang): writing—review and editing, conceptualization, visualization. Y.H.: project administration, resources, methodology. Y.Z. (Yanqun Zhu): conceptualization, supervision, project administration. Z.W.: writing—review and editing, methodology, supervision, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the "Pioneer" and "Leading Goose" R&D Program of Zhejiang (2023C03126), the National Natural Science Foundation of China (52125605) and the Fundamental Research Funds for the Central Universities (2022ZFJH04) and the the Zhejiang Provincial Natural Science Foundation (LZ21E06003).

Data Availability Statement: Data will be made available on request.

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

References

- 1. 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]
- Xu, Y.; Liu, X.; Wang, H.; Zeng, X.; Zhang, Y.; Han, J.; Xu, M.; Pan, S. Influences of in-furnace kaolin addition on the formation and emission characteristics of PM2.5 in a 1000 MW coal-fired power station. *Environ. Sci. Technol.* 2018, 52, 8718–8724. [CrossRef] [PubMed]
- Kamal, M.S.; Razzak, S.A.; Hossain, M.M. Catalytic oxidation of volatile organic compounds (VOCs)—A review. *Atmos. Environ.* 2016, 140, 117–134. [CrossRef]
- 4. Jiang, F.; Zhou, Z.; Zhang, C.; Feng, C.; Xiong, G.; Wang, Y.; Fei, Z.; Liu, Y.; Pan, Y. Structural regulation of single-atom catalysts for enhanced catalytic oxidation performance of volatile organic compounds. *Nano Res.* **2022**, *16*, 1967–1983. [CrossRef]
- Li, M.; Wu, S.C.; Shih, Y. Characterization of volatile organic compound adsorption on multiwall carbon nanotubes under different levels of relative humidity using linear solvation energy relationship. *J. Hazard.* 2016, 315, 35–41. [CrossRef] [PubMed]
- Malhautier, L.; Quijano, G.; Avezac, M.; Rocher, J.; Fanlo, J.L. Kinetic characterization of toluene biodegradation by Rhodococcus erythropolis: Towards a rationale for microflora enhancement in bioreactors devoted to air treatment. *Chem. Eng. J.* 2014, 247, 199–204. [CrossRef]
- Hernández-Alonso, M.D.; Tejedor-Tejedor, I.; Coronado, J.M.; Anderson, M.A. Operando FTIR study of the photocatalytic oxidation of methylcyclohexane 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]
- 8. Lin, F.; Xiang, L.; Zhang, Z.; Li, N.; Yan, B.; He, C.; Hao, Z.; Chen, G. Comprehensive review on catalytic degradation of Cl-VOCs under the practical application conditions. *Crit. Rev. Environ. Sci. Technol.* **2022**, *52*, 311–355. [CrossRef]
- Huang, Y.; Tian, M.; Jiang, Z.; Ma, M.; Chen, C.; Xu, H.; Zhang, J.; Albilali, R.; He, C. Inserting Cr₂O₃ dramatically promotes RuO₂/TiO₂ catalyst for low-temperature 1, 2-dichloroethane deep destruction: Catalytic performance and synergy mechanism. *Appl. Catal. B Environ.* 2022, 304, 121002. [CrossRef]
- 10. Lin, F.; Wang, Z.; Zhang, Z.; He, Y.; Zhu, Y.; Shao, J.; Yuan, D.; Chen, G.; Cen, K. Flue gas treatment with ozone oxidation: An overview on NO_x, organic pollutants, and mercury. *Chem. Eng. J.* **2020**, *382*, 123030. [CrossRef]
- 11. Ge, Y.; Fu, K.; Zhao, Q.; Ji, N.; Song, C.; Ma, D.; Liu, Q. Performance study of modified Pt catalysts for the complete oxidation of acetone. *Chem. Eng. Sci.* 2019, 206, 499–506. [CrossRef]
- 12. Guo, Y.; Wen, M.; Li, G.; An, T. Recent advances in VOC elimination by catalytic oxidation technology onto various nanoparticles catalysts: A critical review. *Appl. Catal. B Environ.* **2021**, *281*, 119447. [CrossRef]
- Li, L.; Chu, W.; Liu, Y. Insights into key parameters of MnO₂ catalyst toward high catalytic combustion performance. *J. Mater. Sci.* 2021, 56, 6361–6373. [CrossRef]
- Xiang, L.; Lin, F.; Cai, B.; Li, G.; Zhang, L.; Wang, Z.; Yan, B.; Wang, Y.; Chen, G. Catalytic ozonation of CH₂Cl₂ over hollow urchin-like MnO₂ with regulation of active oxygen by catalyst modification and ozone promotion. *J. Hazard. Mater.* 2022, 436, 129217. [CrossRef] [PubMed]

- Konsolakis, M.; Carabineiro, S.A.C.; Marnellos, G.E.; Asad, M.F.; Soares, O.S.G.P.; Pereira, M.F.R.; Órfão, J.J.M.; Figueiredo, J.L. Effect of cobalt loading on the solid state properties and ethyl acetate oxidation performance of cobalt-cerium mixed oxides. J. Colloid Interface Sci. 2017, 496, 141–149. [CrossRef] [PubMed]
- 16. Zhu, J.; Cheng, Y.; Wang, Z.; Zhang, J.; Yue, Y.; Qian, G. Low-energy production of a monolithic catalyst with MnCu-synergetic enhancement for catalytic oxidation of volatile organic compounds. *J. Environ. Manag.* **2023**, *336*, 117688. [CrossRef]
- 17. Tang, W.; Wu, X.; Li, S.; Shan, X.; Liu, G.; Chen, Y. Co-nanocasting synthesis of mesoporous Cu-Mn composite oxides and their promoted catalytic activities for gaseous benzene removal. *Appl. Catal. B Environ.* **2015**, *162*, 110–121. [CrossRef]
- 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]
- 19. Tang, W.; Deng, Y.; Li, W.; Li, J.; Liu, G.; Li, S.; Wu, X.; Chen, Y. Importance of porous structure and synergistic effect on the catalytic oxidation activities over hierarchical Mn–Ni composite oxides. *Catal. Sci. Technol.* **2016**, *6*, 1710–1718. [CrossRef]
- El Khawaja, R.; Rochard, G.; Genty, E.; Poupin, C.; Siffert, S.; Cousin, R. Optimization of Mn-Mg-Al Mixed Oxides Composition on their Activity towards the Total Oxidation of Aromatic and Oxygenated VOCs. *Eur. J. Inorg. Chem.* 2023, 26, e202300213. [CrossRef]
- Rezaei, E.; Soltan, J.; Chen, N. Catalytic oxidation of toluene by ozone over alumina supported manganese oxides: Effect of catalyst loading. *Appl. Catal. B Environ.* 2013, 136, 239–247. [CrossRef]
- Chen, G.; Wang, Z.; Lin, F.; Zhang, Z.; Yu, H.; Yan, B.; Wang, Z. Comparative investigation on catalytic ozonation of VOCs in different types over supported MnO_x catalysts. *J. Hazard. Mater.* 2020, 391, 122218. [CrossRef] [PubMed]
- 23. Ye, Z.; Giraudon, J.M.; Nuns, N.; Simon, P.; De Geyter, N.; Morent, R.; Lamonier, J.F. Influence of the preparation method on the activity of copper-manganese oxides for toluene total oxidation. *Appl. Catal. B Environ.* **2018**, 223, 154–166. [CrossRef]
- 24. Zhao, H.; Qu, Z.; Sun, H. Rational design of spinel CoMn₂O₄ with Co-enriched surface as high-activity catalysts for NH₃-SCO reaction. *Appl. Surf. Sci.* **2020**, *529*, 147044. [CrossRef]
- Zhang, M.; Guo, S.; Zheng, L.; Zhang, G.; Hao, Z.; Kang, L.; Liu, Z.H. Preparation of NiMn₂O₄ with large specific surface area from an epoxide-driven sol-gel process and its capacitance. *Electrochim. Acta* 2013, *87*, 546–553. [CrossRef]
- Yu, J.; Qiu, W.; Lin, X.; Wang, Y.; Lu, X.; Yu, Y.; Gu, H.; Heng, S.; Zhang, H.; Ma, J. Periodate activation with stable MgMn₂O₄ spinel for bisphenol A removal: Radical and non-radical pathways. *Chem. Eng. J.* 2023, 459, 141574. [CrossRef]
- 27. 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. [CrossRef]
- Chen, J.; Chen, X.; Xu, W.; Xu, Z.; Jia, H.; Chen, J. Homogeneous introduction of CeO_y into MnO_x-based catalyst for oxidation of aromatic VOCs. *Appl. Catal. B Environ.* 2018, 224, 825–835. [CrossRef]
- Esmaeilirad, M.; Zabihi, M.; Shayegan, J.; Khorasheh, F. Oxidation of toluene in humid air by metal oxides supported on γ-alumina. J. Hazard. Mater. 2017, 333, 293–307. [CrossRef]
- Du, C.; Lu, S.; Wang, Q.; Buekens, A.G.; Ni, M.; Debecker, D.P. A review on catalytic oxidation of chloroaromatics from flue gas. Chem. Eng. J. 2018, 334, 519–544. [CrossRef]
- He, C.; Wang, Y.; Li, Z.; Huang, Y.; Liao, Y.; Xia, D.; Lee, S. Facet engineered α-MnO₂ for efficient catalytic ozonation of odor CH₃SH: Oxygen vacancy-induced active centers and catalytic mechanism. *Environ. Sci. Technol.* 2020, 54, 12771–12783. [CrossRef] [PubMed]
- 32. Jia, J.; Zhang, P.; Chen, L. Catalytic decomposition of gaseous ozone over manganese dioxides with different crystal structures. *Appl. Catal. B Environ.* **2016**, *189*, 210–218. [CrossRef]
- 33. Yang, L.; Ma, J.; Li, X.; Zhang, C.; He, H. Enhancing oxygen vacancies of Ce-OMS-2 via optimized hydrothermal conditions to improve catalytic ozone decomposition. *Ind. Eng. Chem. Res.* **2019**, *59*, 118–128. [CrossRef]
- Hou, J.; Li, Y.; Mao, M.; Ren, L.; Zhao, X. Tremendous effect of the morphology of birnessite-type manganese oxide nanostructures on catalytic activity. ACS Appl. Mater. Interfaces 2014, 6, 14981–14987. [CrossRef] [PubMed]
- 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] [PubMed]
- Xu, P.L.; Wei, T.; Yue, H.Y.; Wen, Y.C.; Wei, Y.; Guo, T.J.; Li, S.J.; Li, W.; Wang, X.Q. Effect of different nitric acid concentrations on manganese/activated carbon-modified catalysts for the catalytic ozonation of toluene. *Catal. Sci. Technol.* 2020, 10, 6729–6737. [CrossRef]
- Dong, C.; Qu, Z.; Qin, Y.; Fu, Q.; Sun, H.; Duan, X. Revealing the highly catalytic performance of spinel CoMn₂O₄ for toluene oxidation: Involvement and replenishment of oxygen species using in situ designed-TP techniques. *Acs Catal.* 2019, *9*, 6698–6710. [CrossRef]
- Costa, E.P.; Roccamante, M.; Amorim, C.C.; Oller, I.; Pérez, J.A.S.; Malato, S. New trend on open solar photoreactors to treat micropollutants by photo-Fenton at circumneutral pH: Increasing optical pathway. *Chem. Eng. J.* 2020, 385, 123982. [CrossRef]
- Nawaz, F.; Cao, H.; Xie, Y.; Xiao, J.; Chen, Y.; Ghazi, Z.A. Selection of active phase of MnO₂ for catalytic ozonation of 4-nitrophenol. *Chemosphere* 2017, 168, 1457–1466. [CrossRef]
- 40. Yang, Y.; Huang, J.; Zhang, S.; Wang, S.; Deng, S.; Wang, B.; Yu, G. Catalytic removal of gaseous HCBz on Cu doped OMS: Effect of Cu location on catalytic performance. *Appl. Catal. B Environ.* **2014**, *150*, 167–178. [CrossRef]
- Xiao, K.; Qi, X.; Bao, Z.; Wang, X.; Zhong, L.; Fang, K.; Lin, M.; Sun, Y. CuFe, CuCo and CuNi nanoparticles as catalysts for higher alcohol synthesis from syngas: A comparative study. *Catal. Sci. Technol.* 2013, 3, 1591–1602. [CrossRef]

- Wang, X.; Wen, W.; Mi, J.; Li, X.; Wang, R. The ordered mesoporous transition metal oxides for selective catalytic reduction of NO_x at low temperature. *Appl. Catal. B Environ.* 2015, 176, 454–463. [CrossRef]
- 43. Shao, J.; Lin, F.; Huang, Y.; Wang, Z.; Li, Y.; Chen, G.; Cen, K. MnO_x fabrication with rational design of morphology for enhanced activity in NO oxidation and SO₂ resistance. *Appl. Surf. Sci.* **2020**, *503*, 144064. [CrossRef]
- Yang, J.; Huang, Y.; Chen, Y.W.; Xia, D.; Mou, C.Y.; Hu, L.; Zeng, J.; He, C.; Wong, P.K.; Zhu, H.Y. Active site-directed tandem catalysis on CuO/V_O-MnO₂ for efficient and stable catalytic ozonation of S-VOCs under mild condition. *Nano Today* 2020, 35, 100944. [CrossRef]
- Shao, J.; Lin, F.; Wang, Z.; Liu, P.; Tang, H.; He, Y.; Cen, K. Low temperature catalytic ozonation of toluene in flue gas over Mn-based catalysts: Effect of support property and SO₂/water vapor addition. *Appl. Catal. B Environ.* 2020, 266, 118662. [CrossRef]
- Weng, X.; Sun, P.; Long, Y.; Meng, Q.; Wu, Z. Catalytic oxidation of chlorobenzene over Mn_xCe_{1-x}O₂/HZSM-5 catalysts: A study with practical implications. *Environ. Sci. Technol.* 2017, *51*, 8057–8066. [CrossRef]
- Tian, M.; Guo, X.; Dong, R.; Guo, Z.; Shi, J.; Yu, Y.; Cheng, M.; Albilali, R.; He, C. Insight into the boosted catalytic performance and chlorine resistance of nanosphere-like meso-macroporous CrO_x /MnCo₃O_x for 1, 2-dichloroethane destruction. *Appl. Catal. B Environ.* 2019, 259, 118018. [CrossRef]
- Dong, L.; Tang, Y.; Li, B.; Zhou, L.; Gong, F.; He, H.; Sun, B.; Tang, C.; Gao, F.; Dong, L. Influence of molar ratio and calcination temperature on the properties of Ti_xSn_{1-x}O₂ supporting copper oxide for CO oxidation. *Appl. Catal. B Environ.* 2016, 180, 451–462. [CrossRef]
- 49. Fernandes, A.; Gagol, M.; Makoś, P.; Khan, J.A.; Boczkaj, G. Integrated photocatalytic advanced oxidation system (TiO₂/UV/O₃/H₂O₂) for degradation of volatile organic compounds. *Sep. Purif. Technol.* **2019**, 224, 1–14. [CrossRef]
- 50. Tang, H.; Wang, Z.; Shao, J.; Lin, F.; Liu, P.; He, Y.; Zhu, Y. Catalytic decomposition of residual ozone over cactus-like MnO₂ nanosphere: Synergistic mechanism and SO₂/H₂O interference. *ACS Omega* **2022**, *7*, 9818–9833. [CrossRef]
- 51. Lin, F.; Wang, Z.; Ma, Q.; Yang, Y.; Whiddon, R.; Zhu, Y.; Cen, K. Catalytic deep oxidation of NO by ozone over MnO_x loaded spherical alumina catalyst. *Appl. Catal. B Environ.* **2016**, *198*, 100–111. [CrossRef]
- 52. Wang, H.; Chen, S.; Wang, Z.; Zhou, Y.; Wu, Z. A novel hybrid Bi₂MoO₆-MnO₂ catalysts with the superior plasma induced pseudo photocatalytic-catalytic performance for ethyl acetate degradation. *Appl. Catal. B Environ.* **2019**, 254, 339–350. [CrossRef]
- 53. Wang, X.; Wu, L.; Wang, Z.; Feng, Y.; Liu, Y.; Dai, H.; Wang, Z.; Deng, J. Photothermal synergistic catalytic oxidation of ethyl acetate over MOFs-derived mesoporous N-TiO₂ supported Pd catalysts. *Appl. Catal. B Environ.* **2023**, 322, 122075. [CrossRef]
- 54. Liu, X.; Han, Q.; Shi, W.; Zhang, C.; Li, E.; Zhu, T. Catalytic oxidation of ethyl acetate over Ru–Cu bimetallic catalysts: Further insights into reaction mechanism via in situ FTIR and DFT studies. *J. Catal.* **2019**, *369*, 482–492. [CrossRef]
- Zeng, J.; Liu, X.; Wang, J.; Lv, H.; Zhu, T. Catalytic oxidation of benzene over MnO_x/TiO₂ catalysts and the mechanism study. J. Mol. Catal. A Chem. 2015, 408, 221–227. [CrossRef]
- Lichtenberger, J.; Amiridis, M.D. Catalytic oxidation of chlorinated benzenes over V₂O₅/TiO₂ catalysts. J. Catal. 2004, 223, 296–308. [CrossRef]
- 57. Qi, G.; Yang, R.T.; Chang, R. MnO_x-CeO₂ mixed oxides prepared by co-precipitation for selective catalytic reduction of NO with NH₃ at low temperatures. *Appl. Catal. B Environ.* **2004**, *51*, 93–106. [CrossRef]
- Waskowska, A.; Gerward, L.; Olsen, J.S.; Steenstrup, S.; Talik, E. CuMn₂O₄: Properties and the high-pressure induced Jahn-Teller phase transition. J. Phys. Condens. Matter 2001, 13, 2549. [CrossRef]
- Yang, Y.; Liu, J.; Liu, F.; Wang, Z.; Ding, J.; Huang, H. Reaction mechanism for NH₃-SCR of NO_x over CuMn₂O₄ catalyst. *Chem. Eng. J.* 2019, *361*, 578–587. [CrossRef]
- 60. Collins, S.S.; Cittadini, M.; Pecharromán, C.; Martucci, A.; Mulvaney, P. Hydrogen spillover between single gold nanorods and metal oxide supports: A surface plasmon spectroscopy study. *Acs Nano* **2015**, *9*, 7846–7856. [CrossRef]
- Zhao, L.; Yang, Y.; Liu, J.; Ding, J. Mechanistic insights into benzene oxidation over CuMn₂O₄ catalyst. J. Hazard. Mater. 2022, 431, 128640. [CrossRef] [PubMed]
- 62. Segall, M.D.; Lindan, P.J.; Probert, M.A.; Pickard, C.J.; Hasnip, P.J.; Clark, S.J.; Payne, M.C. First-principles simulation: Ideas, illustrations and the CASTEP code. *J. Phys. Condens. Matter* **2002**, *14*, 2717. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.