Removal efficiency and mechanism of bio-treated coking wastewater by catalytic ozonation using MnO_2 modified with anionic precursors

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ABSTRACT

In this paper, MnO_2 catalyst were firstly prepared and modified by four kinds of anionic precursors (i.e., NO_3^- , AC^- , SO_4^{2-} and Cl^-) through redox precipitation method. After that, bio-treated coking wastewater (BTCW) was prepared and employed as targeted pollutants to investigate the catalytic ozonation performance of prepared- MnO_2 catalyst was investigated and characterized by the removal efficiencies and mechanism of the prepared bio-treated coking wastewater (BTCW), which was employed as the targeted pollutants. Specifically, the effects of specific surface area, crystal structure, valence state of Mn element and lattice oxygen content on catalytic activity of MnO_2 materials were characterized by BET, XRD and XPS, respectively. Results showed that COD of BTCW could be removed 47.39% under $\text{MnO}_2\text{-NO}_3^-$ catalyst with 2 h reaction time, which was much higher than that of $\text{MnO}_2\text{-AC}^-$ (3.94%), $\text{MnO}_2\text{-SO}_4^{2-}$ (12.42%), $\text{MnO}_2\text{-Cl}^-$ (12.94%) and pure O_3 without catalyst (21.51%), respectively. So, $\text{MnO}_2\text{-NO}_3^-$ presented the highest catalytic performance among these catalysts. The reason may be attributed to a series of better physiochemical properties including the smaller average grain, the larger specific surface area and active groups, more crystal defect and oxygen vacancy, higher relative content of Mn^{3+} and adsorbed oxygen (O_{ads}) than that of another three catalysts.

Keywords: Anionic precursors, Bio-treated coking wastewater, MnO_2 catalyst, Ozonation

1. Introduction

Advanced oxidation processes (AOPs) that utilized free-radical reactions are considered as an effective and promising method for the degradation and mineralization refractory organic compounds in wastewater treatment. Many studies have been conducted on the degradation persistent organic compounds by AOPs technologies, such as photocatalysis process [1, 2], Fenton or Fenton-like oxidation [3, 4], ozonation [5, 6] and non-thermal plasma [7]. Among them, heterogeneous catalytic ozonation technology has been widely studied because they can generate more reactive oxygen species (ROS) to ensure highly efficient in degrading the refractory organic contaminants in wastewater. Among them, heterogeneous catalytic ozonation technology has been widely studied because they can generate more reactive oxygen species (ROS) to ensure highly efficient in degrading the refractory organic contaminants in waste-

water [8-10]. Among heterogeneous catalytic ozonation technologies, catalytic ozonation using MnO_2 catalyst has been widely used in wastewater treatment with the characteristics of complex composition, high organic matter concentration and recalcitrance [11-13]. In particular, Manganese dioxide (MnO_2) has its advantages, such as unique $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox cycle involving a single electron transfer, environmental friendliness and diverse crystallographic structure, which may help MnO_2 been extensively developed for applications in heterogeneous catalytic ozonation technologies to produce active radicals [14-16]. Obviously, catalysts play a significant role in catalytic ozonation. Refractory organic pollutants could be efficiently degraded by MnO_2 based catalyst owning the excellent physical and chemical properties. Some studies indicated that different preparation conditions have a certain effect on the catalytic performance of the catalyst, such as acid treatment [17], reactant ratio, reaction time and temperature [18], calcination time

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and temperature, precursor anions, etc. Although the precursor anions did not change the elemental composition of the MnO_2 catalyst, it would largely affect the structural characteristics of the MnO_2 catalyst and then generate different catalytic performance. Jung *et al.* [19] used various Mn^{2+} precursors to prepare MnO_2 by a simple redox method, which were used to investigate the influence of Mn-precursors in the CO oxidation. The catalytic performance was arranged from high to low as: $\text{MnO}_2\text{-SO}_4^{2-}$, $\text{MnO}_2\text{-AC}^-$, $\text{MnO}_2\text{-NO}_3^-$, $\text{MnO}_2\text{-Cl}^-$. Hwang *et al.* [20] used manganese nitrate and manganese acetate to prepare $\text{MnO}_2/\text{TiO}_2$ catalysts through a sol-gel method, concluding that the catalysts synthesized with manganese acetate showed high catalytic performance as a result of abundant MnO_2 species and strong acid sites. Yue Yu, *et al.* [21] used manganese acetate, manganese nitrate, manganese chloride and manganese sulfate to prepare MnO_2 catalysts on the toluene oxidation. The catalytic performance was arranged from high to low as: $\text{MnO}_2\text{-AC}^-$, $\text{MnO}_2\text{-NO}_3^-$, $\text{MnO}_2\text{-Cl}^-$, $\text{MnO}_2\text{-SO}_4^{2-}$, which resulted in $\text{MnO}_2\text{-AC}^-$ owned potential for practical applications. Pena *et al.* [22] observed that catalysts prepared using manganese nitrate yielded MnO_2 and displayed enhanced catalytic performance than the corresponding catalyst prepared with manganese acetate. In fact, there remains on-going debate over how catalytic activity is influenced by the active phase of Mn-based catalysts prepared with different precursors. However, it is still unclear that the Bio-treated coking wastewater (BTCW) are degraded by catalytic ozonation using MnO_2 catalyst modified with anionic precursors. So, it is interesting to know that the reaction mechanism and removal performance of BTCW is catalyzed by different MnO_2 catalyst modified with anionic precursors.

BTCW removal has been widely studied by catalytic ozonation due to the characteristics of strong toxicity, structural stability and low concentration of organic matter [23]. Liu *et al.* [24] synthesized a kind of CuFe_2O_4 nanocomposite as catalyst to investigate and evaluate the feasibility of the catalytic ozonation for the treatment of biologically treated coking wastewater. Their results showed that the total organic carbon removal efficiency in the catalytic ozonation was 2.9 times higher than that in the uncatalyzed ozonation. Zhang *et al.* [25] prepared different kinds of zinc ferrite catalysts for ozonation of BTCW, which showed that the presence of catalysts also generated a high removal efficiency for BTCW compared to non-catalytic ozonation, and the performance of the catalysts was primarily determined by their synthesis method defining the surface properties. However, few researchers studied the catalytic performance and mechanism of ozonation of BTCW with different precursors of manganese dioxide.

In this study, BTCW was selected as the target pollutant in this study, four kinds of MnO_2 catalysts were synthesized from various Mn^{2+} precursors of manganese chloride, manganese nitrate, manganese acetate and manganese sulfate by redox precipitation method. Moreover, based on evaluating the catalytic performance of four MnO_2 catalysts in the process of ozone oxidation for removal of bio-refractory organic pollutants in BTCW, the role mechanisms of different precursors on catalytic activities will be analyzed by XRD, TEM, BET and XPS, respectively.

2. Experimental

2.1. Synthesis of Catalyst

The reagents and chemicals were of analytical grade and purchased from national drug chemical reagents Co. Ltd (China). The redox-precipitation method is a typical catalyst preparation method by liquid phase preparation process for manganese-based catalyst, which has the advantages of simple preparation procedure and mild reaction conditions and thus has been becoming the research hotspot in recent years [21]. So, the redox-precipitation method is employed and selected as the synthetic method for MnO_2 based catalysts in this study. Furthermore, the structure defects and the crystallinity of the catalyst can be controlled and improved its performance by changing the preparation conditions such as choice of reactant precursor, reactant ratio, pH, reaction time, temperature and calcination time, respectively [21, 26, 27]. Therefore, the above preparation conditions need to be comprehensively considered to manipulate the synthetic process of catalysts. The preparation process of four MnO_2 catalysts are showed as follows. Firstly, 100 mL (0.45 mol/L) of solution A (manganese nitrate solution, manganese acetate solution, manganese sulfate solution or manganese chloride solution) was added dropwise into 75 mL (0.2 mol/L) of solution B (potassium permanganate solution, KMnO_4), which was stirred magnetically for 15 min. After that, ammonia was used to adjust the pH of the mixture to 1.5. After crystallizing for 11 h, the product was collected by filtration and fully rinsed several times with deionized water to remove the remaining KMnO_4 . Finally, the collecting production were dried for 13 h at 105°C in the oven and calcined at 400°C for 4.5 h in the tubular furnace, and the catalysts denoted as $\text{MnO}_2\text{-SO}_4^{2-}$, $\text{MnO}_2\text{-AC}^-$, $\text{MnO}_2\text{-Cl}^-$ and $\text{MnO}_2\text{-NO}_3^-$ were obtained, which were used to carry the oxidizing experiments and characteristic analysis, respectively.

2.2. Characterization of Catalysts

The atomic arrangement inside the crystal was determined by X-ray powder diffraction (model: D8 ADVANCE, Bruker, Germany). The XRD had monochromatic radiation Cu-K α as the source of X-rays and operates at 40 kV, 30 mA. The surface compositions of the catalysts were determined by x-ray photoelectron spectroscopy (XPS), which was performed with ESCALAB250Xi system equipped with an Al-K α excitation source and operated at 15 kW and 1486.6 eV. The spectra were fitted with Casa XPS software. Charging effects were corrected by adjusting the binding energy of C 1 s to 284.8 eV.

2.3. Catalyst Activity Test

The catalytic ozonation treatment of simulated BTCW was performed in a semi-batch reactor showed in Fig. S1. The fixed reactor adopted a double-layer design and the inner layer was the catalytic ozonation reaction layer fed with 1 L aqueous solution. The constant temperature of water bath pot was used to keep the stable temperature of the inner layer reaction. Ozone was generated by ozone generator (COM-AD-01, Germany) from oxygen with high purity. During the reaction, the gaseous ozone was fed through a porous diffuser at the bottom of the reactor with a flow rate of 2.0 L/min and the concentration of 2.6 mg/L. The tail gas produced in the experiment was absorbed by potassium iodide solution. In the

typical catalytic ozonation procedure, 2 g catalyst was mixed with 1 L simulated BTCW (cyclohexanone: aniline = 20:1, pH = 7.2, 323 ± 1 K; the initial COD was 470 mg/L) in the reaction system. During the reaction process, the samples were taken to analyze at certain intervals.

3. Results and Discussion

3.1. Catalytic Ozonation Performances

The degradation performance of BTCW by ozonation and catalytic ozonation is showed in Fig. 1. Compared with the alone ozonation process, it can be observed that the degradation rates of BTCW are greatly improved with the addition of the prepared-catalysts. The degradation rates are accordingly increased about 8.57%, 9.09%, 17.57% and 21.51%, respectively when $\text{MnO}_2\text{-Cl}^-$, $\text{MnO}_2\text{-SO}_4^{2-}$, $\text{MnO}_2\text{-AC}^-$ and $\text{MnO}_2\text{-NO}_3^-$ are employed as the catalysts to enhance the ozonation efficiency on BTCW. The difference may be due to the different morphology and distribution of active components formed on the catalyst surface after calcination of different precursors. The catalytic reaction mechanism will be further discussed in part 3.2 through part 3.5. Reaction kinetics of four prepared-catalysts were further investigated to the catalytic ozonation performance. The mathematic equation of pseudo first-order and second-order kinetic model could be expressed as Eq. (1) and Eq. (2), respectively.

$$-\ln(C_t/C_0) = K_1 t \quad (1)$$

$$C_0/C_t = K_2 C_0 t + 1 \quad (2)$$

Where K_1 is the pseudo first-order rate constant (min^{-1}); K_2 is the pseudo second-order rate constant ($(\text{mg/L})^{-1}\text{min}^{-1}$); t represents the reaction time; C_0 and C_t stand for the COD concentration at 0 min and t min, respectively.

Fig. 1. BTCW degradation performance by four prepared-catalysts and without catalyst.

Fig. 2. The fitting curves of pseudo first-order (a) and pseudo second-order (b) reaction kinetics for different ozonation.

The fitting curves and kinetic parameters of pseudo first-order and pseudo second-order reaction kinetics for different ozonation are showed in Fig. 2(a), (b) and Table S1. As showed in Table S1, the linear correlation coefficient R^2 of the second-order reaction kinetics was significantly higher than that of the first-order reaction kinetics. Therefore, under the condition of ozonation and catalytic ozonation, the degradation process of BTCW was more in line with the pseudo second-order reaction kinetics. Fig. 2(b) and Table S1 show that the rate constants (K_2) of catalytic ozonation of $\text{MnO}_2\text{-Cl}^-$, $\text{MnO}_2\text{-SO}_4^{2-}$, $\text{MnO}_2\text{-AC}^-$ and $\text{MnO}_2\text{-NO}_3^-$ were calculated to be 0.00297, 0.00367, 0.00377, 0.00544 and 0.00625 $(\text{mg/L})^{-1}\text{min}^{-1}$, respectively. The kinetic rate of $\text{MnO}_2\text{-NO}_3^-$ catalyst are almost two times of ozonation without catalyst. To sum up, four kinds of prepared-catalysts have different catalytic ozonation performance and nitrate modified MnO_2 (i.e., $\text{MnO}_2\text{-NO}_3^-$) has the highest catalytic ozonation activity on BTCW.

3.2. Specific Surface and Pore size Distribution

The results of BET surface area for different catalysts are showed in Table 1. Compared with the other three catalysts, $\text{MnO}_2\text{-NO}_3^-$ catalyst has the highest specific surface area, which is about 9 times of $\text{MnO}_2\text{-Cl}^-$ catalyst and thus $\text{MnO}_2\text{-NO}_3^-$ catalyst has the best catalytic activities. Moreover, the total pore volume of $\text{MnO}_2\text{-NO}_3^-$ is also the highest among the four different MnO_2 catalysts, which is beneficial to the adsorption and then increases the mass transfer rate between catalyst and BTCW [28]. So, the highest kinetic and removal rate through $\text{MnO}_2\text{-NO}_3^-$ catalyst are observed in Fig. 1 and Fig. 2, respectively.

Table 1. Specific Surface Area and Pore Volume of Four Prepared- MnO_2 Catalysts

Catalyst	Specific surface area (m^2/g)	Pore volume (cm^3/g)
$\text{MnO}_2\text{-SO}_4^{2-}$	39.570	0.0035
$\text{MnO}_2\text{-AC}^-$	115.428	0.0097
$\text{MnO}_2\text{-Cl}^-$	14.683	0.0013
$\text{MnO}_2\text{-NO}_3^-$	132.303	0.0105

3.3. Crystal Phase

In order to analyze the crystalline structure of the different MnO_2 catalysts, the XRD studies were carried out in this section. The XRD patterns of MnO_2 prepared by different precursor anions (NO_3^- , AC^- , SO_4^{2-} , Cl^-) are presented in Fig. 3. The $\text{MnO}_2\text{-SO}_4^{2-}$ and $\text{MnO}_2\text{-Cl}^-$ catalyst have the characteristic diffraction peaks at around $2\theta = 28.2^\circ$, 37.5° , 42.9° and 56.7° , and these diffraction peaks are assigned to the (110), (101) and (211) reflections of $\beta\text{-MnO}_2$ (JCPDS No.24-0735 or JCPDS No.81-2261). The $\text{MnO}_2\text{-NO}_3^-$ catalyst has the diffraction peaks at around $2\theta = 37.7^\circ$, 42.8° and 56.9° , and these diffraction peaks are assigned to the (101), (111) and (211) reflections of $\beta\text{-MnO}_2$ (JCPDS No.24-0735 or JCPDS No.81-2261). The $\text{MnO}_2\text{-AC}^-$ catalyst has characteristic diffraction peaks at around $2\theta = 12.9^\circ$, 18.2° , 28.6° , 37.4° and these diffraction peaks are assigned to the (110), (200), (310), (121) and (301) reflections of $\alpha\text{-MnO}_2$ (JCPDS No.44-0141 or JCPDS No.72-1982). From the above XRD results, it can be seen that the different anions affect the crystallization and phase transition of catalysts to some extent [21].

According to the principle of Voigt single line method [29], the average size and lattice distortion of MnO_2 grain could be calculated from the diffraction peak parameters of the crystal plane. The calculation results are showed in Table 2. The average grain size of MnO_2 material was arranged from high to low as: $\text{MnO}_2\text{-Cl}^-$, $\text{MnO}_2\text{-SO}_4^{2-}$, $\text{MnO}_2\text{-AC}^-$, $\text{MnO}_2\text{-NO}_3^-$, and the micro strain capacity was arranged from high to low as: $\text{MnO}_2\text{-NO}_3^-$, $\text{MnO}_2\text{-AC}^-$, $\text{MnO}_2\text{-SO}_4^{2-}$, $\text{MnO}_2\text{-Cl}^-$. Some studies indicated that the crystal defect was the main cause of lattice distortion, which might promote the migration of adsorbed oxygen, and the migration of adsorbed oxygen played an important role in the decomposition and transformation of organic matter, and finally affected the catalytic performance of the catalyst [30, 31]. Therefore, although all the four MnO_2 materials have some crystal defects, the $\text{MnO}_2\text{-NO}_3^-$ catalyst has the smallest grain size and the largest lattice distortion, which

might be also a reason that this catalyst has the best catalytic activities in the process of ozonation for removing organic pollutants.

Fig. 3. XRD patterns of different MnO_2 catalysts prepared by different precursor anions.

Table 2. Grain size and lattice distortion of different MnO_2 catalysts

Catalyst	Grain size (nm)	Lattice distortion
$\text{MnO}_2\text{-SO}_4^{2-}$	14.5	7.567×10^{-3}
$\text{MnO}_2\text{-AC}^-$	12.6	8.6526×10^{-3}
$\text{MnO}_2\text{-Cl}^-$	15.2	7.190×10^{-3}
$\text{MnO}_2\text{-NO}_3^-$	11.9	9.151×10^{-3}

3.4. Surface Chemical Compositions

Oxygen vacancy is one of the most common crystal defects, which has significant influence on the catalytic ozonation performance of MnO_2 materials. The presence of Mn^{3+} on the surface of MnO_2 material is an important reason for the occurrence of oxygen vacancy, and its reaction mechanism is showed as follows [32]:

Where Δ represents oxygen vacancy, so a higher Mn^{3+} relative content indicates that there are more oxygen vacancies in MnO_2 material.

In order to analyze the influence of four precursor anions on the valence state of Mn on the surface of MnO_2 , Peak-splitting fitting was performed on energy spectrum (narrow sweep) of four MnO_2 materials through XPS PEAK41. Fig. 4(a) illustrated Mn 2p XPS spectra of MnO_2 prepared by different precursor anions. Due to existing a fixed energy interval and peak area ratio between $\text{Mn}2\text{p}_{1/2}$ and $\text{Mn}2\text{p}_{3/2}$ in MnO_2 , in this article, only $\text{Mn}2\text{p}_{3/2}$ was analyzed in detail. It could be seen from Fig. 4(a) that MnO_2 materials prepared by four anions could be divided into two characteristic

Fig. 4. (a) The Mn 2P and (b) O 1s XPS spectra of MnO₂ prepared by different precursor anions.

Table 3. XPS Energy Spectra Analysis of MnO₂ Prepared by Different Precursor Anions

	MnO ₂ -SO ₄ ²⁻	MnO ₂ -AC ⁻	MnO ₂ -Cl ⁻	MnO ₂ -NO ₃ ⁻
Mn ³⁺ (%)	36.11	39.26	34.94	44.27
Mn ⁴⁺ (%)	63.89	60.74	65.06	55.73
Mn ³⁺ / Mn ⁴⁺	0.57	0.65	0.54	0.79
O _{ads} (%)	24.65	20.99	24.76	29.24
O _{lat} (%)	75.35	79.01	75.24	70.76
O _{ads} / O _{lat}	0.32	0.27	0.33	0.41

peaks in Mn2p_{3/2}, and the binder energy of the peak at 641.8ev and 643.3ev was attributed to Mn³⁺ and Mn⁴⁺, respectively. As was showed in Table 3, the Mn³⁺ relative content of MnO₂-NO₃⁻ was the highest at 44.27%, the Mn³⁺ relative content of MnO₂-Cl⁻, nO₂-SO₄²⁻ and MnO₂-AC⁻ was 34.94%, 36.11% and 39.26%, respectively. Moreover, the MnO₂-NO₃⁻ catalyst had the highest molar ratio of Mn³⁺/Mn⁴⁺ on the surface. Therefore, MnO₂-NO₃⁻ had the most oxygen vacancy, which would promote the conversion of ozone to reactive oxygen species (ROS) and beneficial to the activation and migration of oxygen in the gas phase [33].

Furthermore, two types of surface oxygen species were identified according to the O 1s spectra in Fig. 4(b). The peaks were located at 529.6-529.8ev and 531.4-531.5ev corresponding to lattice oxygen (O_{lat}) and adsorbed oxygen (O_{ads}), respectively [34]. O_{lat} was the oxygen in the crystal structure, and the different relative contents of Mn³⁺ and Mn⁴⁺ of the four catalysts led to the difference in the binding energy of lattice oxygen. The O_{ads} was the oxygen on the crystal surface, mainly including •OH, •O, •O₂⁻ and other active groups, which had an important impact on the catalytic performance of MnO₂ [35]. The adsorbed oxygen had higher mobility than that of surface lattice oxygen, so adsorbed oxygen played more important role in oxidation reactions than lattice oxygen [24, 36]. In this work, the MnO₂-NO₃⁻ catalyst contained the highest surface adsorbed oxygen ratio O_{ads}/O_{lat} at 0.41, which was corresponding to its highest content of active groups on its surface, and had the highest catalytic activities among four MnO₂ catalysts.

3.5. Morphology Formation of Catalyst

The XPS energy spectra (wide sweep) of MnO₂ prepared by different precursor anions (NO₃⁻, AC⁻, SO₄²⁻, Cl⁻) were presented in Fig. 5. In terms of the MnO₂-SO₄²⁻ and MnO₂-Cl⁻ and MnO₂-NO₃⁻ catalyst, they all contain the elements of Mn, O and C, but the MnO₂-AC⁻ catalyst contains the elements of K, Mn, O and C, and the difference is mainly related to the crystal type of the catalyst. From the above XRD results, it can be seen that the MnO₂-SO₄²⁻ and MnO₂-Cl⁻ and MnO₂-NO₃⁻ are all β-MnO₂ crystals, while the catalyst MnO₂-AC⁻ is α-MnO₂.

α-MnO₂ is the most common crystalline form of manganese oxide, and the internal channel structure of α-MnO₂ is of [2×2] type and the basic structural unit is [MnO₆], which stacks in the form of hexagonal density. In the process of α-MnO₂ crystal formation, cations often enter into the pores due to its large channel radius, and the ion radius of K⁺ is similar to the channel size of α-MnO₂ crystal, so K⁺ can play the role of template in the synthesis of α-MnO₂ [37, 38]. Additionally, Studies had showed that appropriate K⁺ concentration could stabilize the [2×2] tunnel structure of α-MnO₂, and is a key factor in the formation of α-MnO₂ [39]. Therefore, the MnO₂-AC containing K⁺ is considered to be α-MnO₂. However, H⁺ and K⁺ have a competitive relationship for occupying the [2×2] tunnel site because of the proton exchange under the conditions of high acidity in this study [40]. The addition of weakly alkaline ion would lead to the decrease of H⁺ concentration and K⁺ dominates competition between K⁺ and H⁺ in the tunnel structure. The high concentration of H⁺ will greatly reduce the chance of K⁺

Fig. 5. XPS energy spectra (wide sweep) of MnO_2 prepared by different precursor anions.

occupying the active site of $[2 \times 2]$ tunnel, therefore, the highly acidic conditions are conducive to the generation of $[1 \times 1]$ tunnel structure of MnO_2 , which might be the reason that the $\text{MnO}_2\text{-SO}_4^{2-}$, $\text{MnO}_2\text{-Cl}^-$ and $\text{MnO}_2\text{-NO}_3^-$ are β crystal forms and the constituent elements do not contain K ions.

3.5.1. $\text{MnO}_2\text{-AC}^-$

According to the characterization analysis of XRD and XPS, $\text{MnO}_2\text{-AC}^-$ is $\alpha\text{-MnO}_2$ crystals. In addition, Fig. 3 shows that the intensity of XRD diffraction peak of $\text{MnO}_2\text{-AC}^-$ is weaker than that of $\text{MnO}_2\text{-SO}_4^{2-}$ and $\text{MnO}_2\text{-Cl}^-$. Studies have showed that the smaller the intensity of the diffraction peak, the weaker the crystallinity and the smaller the grain size, which is more conducive to the selective adsorption of some organic molecules [41]. This is why the catalytic activities of $\text{MnO}_2\text{-AC}^-$ catalyst is stronger than that of $\text{MnO}_2\text{-SO}_4^{2-}$ and $\text{MnO}_2\text{-Cl}^-$ catalyst. However, the catalytic activities of $\text{MnO}_2\text{-AC}^-$ catalyst is weaker than that of $\text{MnO}_2\text{-NO}_3^-$ catalyst. The reason for this phenomenon may be that AC^- , which has the largest ionic radius among the four anions, limits the diffusion rate of the precursors Mn^{2+} and Mn^{7+} , and then results in a reduction in the redox reaction rate.

3.5.2. $\text{MnO}_2\text{-Cl}^-$

$\text{MnO}_2\text{-Cl}^-$ has the largest grain size among the three β crystal catalysts. This might be because the Stokes radius of Cl^- was the smallest among the four precursor anions, and it could be uniformly adsorbed on the (110), (101), (111) and (211) crystal plane [42]. The presence of Cl^- reduced the surface energy of the crystal plane, resulting in a low growth rate of the crystal plane, which ultimately led to a large exposed area of the crystal plane and a strong diffraction peak intensity. Therefore, $\text{MnO}_2\text{-Cl}^-$ has the largest grain size, the best crystallinity and the fewest crystal defects. In addition, the $\text{MnO}_2\text{-Cl}^-$ has the smallest specific surface area ($14.683 \text{ m}^2/\text{g}$), the smallest pore volume ($0.0013 \text{ cm}^3/\text{g}$) and a lowest ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ (0.54). The above reasons result in poor catalytic performance of $\text{MnO}_2\text{-Cl}^-$.

3.5.3. $\text{MnO}_2\text{-SO}_4^{2-}$

Among three β crystal catalysts, the (110) crystal plane diffraction peak of $\text{MnO}_2\text{-SO}_4^{2-}$ is widened. This phenomenon might be attributed to the fact that the SO_4^{2-} ion has a large radius and can only preferentially adsorb on the (111) crystal plane with the lowest Mn^{4+} density, and then the steric hindrance effect is formed [29]. Therefore, the growth of the crystal along the crystal plane is restricted, and the (110) crystal plane with higher Mn^{4+} density becomes the preferential growth plane, which eventually leads to the phenomenon of broadening the diffraction peak of the (110) crystal plane. In addition, the diffraction peak intensity of $\text{MnO}_2\text{-SO}_4^{2-}$ is weaker than $\text{MnO}_2\text{-Cl}^-$ but stronger than $\text{MnO}_2\text{-NO}_3^-$. Therefore, $\text{MnO}_2\text{-SO}_4^{2-}$ has low crystallinity and some crystal defects, which in turn show good catalytic activity. However, SO_4^{2-} interacts with Mn^{2+} in the system, and its larger ionic radius reduces the diffusion rate of the reactants, thereby reducing the rate of product formation, so the product obtained is also less than that obtained under other conditions [43].

3.5.4. $\text{MnO}_2\text{-NO}_3^-$

The diffraction peak intensity of $\text{MnO}_2\text{-NO}_3^-$ was the weakest and the (110) crystal plane disappears. The above phenomenon indicates that $\text{MnO}_2\text{-NO}_3^-$ has low crystallinity, imperfect crystal growth, and many crystal defects. Complementing this, the XPS characterization results indicate that the $\text{MnO}_2\text{-NO}_3^-$ has the highest ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ (0.79) and the most oxygen vacancies. At the same time, XRD characterization shows that the average grain size of $\text{MnO}_2\text{-NO}_3^-$ is the smallest (11.9 nm), which leads to the smallest crystal plane spacing and grain gap. This will inevitably result in the largest specific surface area of the $\text{MnO}_2\text{-NO}_3^-$ ($132.303 \text{ m}^2/\text{g}$), which is consistent with the BET characterization results. Also, XPS characterization shows that the surface of $\text{MnO}_2\text{-NO}_3^-$ has more adsorbed oxygen (such as surface hydroxyl groups), and crystal defects can further promote the migration of adsorbed oxygen with a higher content of the catalyst surface, while the migration of adsorbed oxygen plays an important role in the decomposition and conversion of ozone, which ultimately affects the catalytic performance of the catalyst. So, $\text{MnO}_2\text{-NO}_3^-$ exhibits the best catalytic activity.

4. Conclusion

Four MnO_2 samples were prepared by the redox precipitation method using KMnO_4 and various Mn^{2+} precursors for catalytic ozonation. The different anionic precursors forming structure form of MnO_2 and its catalytic ozonation performance on simulated BTCW were studied. The results showed that anion precursors played a great role in controlling the morphology of the product MnO_2 , but it did not work in the catalytic performance. The surface chemical composition, content, specific surface area and crystal structure of four MnO_2 materials prepared by different precursor anions (NO_3^- , AC^- , SO_4^{2-} , Cl^-) were significantly different. Among them, $\text{MnO}_2\text{-NO}_3^-$ had the smallest average grain size, the largest crystal defect, the highest relative content of Mn^{3+} , the most oxygen vacancy, the highest relative content of adsorbed oxygen (O_{ads}), the most surface active groups and the largest specific surface

area. The combined action of these factors finally improved the catalytic ozonation performance of $\text{MnO}_2\text{-NO}_3^-$. After 2 h catalytic ozonation, the COD removal rates by $\text{MnO}_2\text{-NO}_3^-$ reached 47.39%, which was 3.94%, 12.42%, 12.94% and 21.51% higher than that of $\text{MnO}_2\text{-AC}^-$, $\text{MnO}_2\text{-SO}_4^{2-}$, $\text{MnO}_2\text{-Cl}^-$ and pure O_3 systems, respectively.

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Author Contributions

D.B. (M.D. student) and D.D. (M.D. student) conducted all the experiments and wrote the manuscript. Z.J. (Associate Professor) and G.S.J. (Associate Professor) wrote and revised the manuscript. H.S.L. (Associate Professor) revised the manuscript.

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