Research Progress on Manganese Oxide-Based Materials for Ozone Removal

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Abstract. Ozone brings severe risks to human health and ecosystems. Catalytic ozone decomposition enables efficient ozone removal under ambient conditions. Manganese oxide-based catalysts have garnered great interest because of their low cost, diverse valence states and excellent catalytic activity. Manganese oxide catalysts, renowned for their excellent chemical stability, thermal resistance, and cost-effectiveness, have become a key focus in ozone catalytic decomposition research. This review systematically examines various manganese oxide catalysts for ozone decomposition, with particular emphasis on three critical aspects: supported catalysts, different crystalline forms, and synthesis methodologies. The discussion concludes with an analysis of current challenges and future development directions for manganese oxide catalysts.

Keywords: Oxide catalysts; ozone; manganese.

1. Introduction

Ozone (O_3) is an allotrope of oxygen, with a molecular structure of three oxygen atoms arranged in a V-shape, having a bond angle of 116.8°and a bond length of 0.1278 nm. At room temperature and pressure, ozone is a pale blue gas with a pungent odor, detectable at extremely low concentrations (0.01–0.05 ppm).Ozone is one of the main pollutants in the atmosphere, which is harmful to human health, plant growth and ecosystem stability, and corrodes buildings and materials. According to the statistics of the World Health Organization, ozone is especially harmful to human beings.[1]Ozone Oxidation Hazards to Human and Crop.[2]Ozone can damage the respiratory mucosa, tear film and skin barrier function, and also can destroy the chlorophyll in leaves, which leads to the inhibition of photosynthesis and the decrease of yield.

Under ultraviolet radiation, ozone participates in photochemical reactions and acts as a co-occurring pollutant for volatile organic compounds (VOCs) and nitrogen oxides (NO_x).[3],[4], [5].The WHO Air Quality Guidelines recommend an 8-hour average ozone concentration limit of 0.05 ppm. China's Environmental Air Quality Standards (GB 3095-2012) set the maximum daily 8-hour average ozone concentration at 100 μg/m³ (0.05 ppm) for Grade I and 160 μg/m³ (0.08 ppm) for Grade II. Additionally, the Indoor Air Quality Standard (GB/T 18883-2002) specifies an 1-hour average ozone concentration limit of 160 μg/m³ (0.08 ppm) for indoor environments.In metropolitan areas, ozone concentrations are notably elevated due to the combustion of fossil fuels (e.g., oil and coal), which releases large amounts of NO_x and VOCs. These ozone precursors are key contributors to urban O_3 pollution.

In September 2025, agas with air quality exceeding standards in the Beijing-Tianjin-Hebei region were attributed to ozone (O_3) as the primary pollutant.[6]This shows that gas pollution has changed from the past coal and haze to the present photochemical pollution which is mainly ozone. In addition, ozone has indoor emission sources, such as laser printers and copiers, air purification equipment (fresh air systems and electrostatic, negative ion and plasma air purifiers), ozone disinfection equipment, etc.[7],[8]

Ozone catalytic decomposition is a highly efficient method for ozone degradation at room temperature, producing pure oxygen without secondary pollution. As the most promising ozone removal technology with significant research value and application potential, its effectiveness hinges on high-performance catalytic materials. Current research focuses on three main categories: carbon-based catalysts [9], noble metal catalysts[10] , [11], and transition metal oxide catalysts[12]. Among

these, manganese oxide catalysts have garnered the most extensive research and publications. This paper elucidates the catalytic mechanisms of manganese oxide materials in ozone decomposition, systematically categorizes representative manganese oxide catalysts, and identifies both current challenges and future opportunities in this field.

2. Research Status of Ozone Decomposition Catalysts for Manganese Oxide

The principle and reaction course of ozone decomposition by manganese oxide catalyst were discussed.[13]

Kinetics and mechanism

There has been little work on the kinetics and mechanism of the ozone decomposition reaction. A sequence has been suggested involving first the adsorption of ozone on a site to produce a free oxygen molecule and a surface oxygen atom and then the reaction of the atom with another ozone molecule to produce two more oxygen molecules. No assumptions were made about the nature of the active sites and the state of the adsorbed oxygen.

$$O_3+*\rightarrow O_2+O^* \quad (1)$$

$$O3+O*\rightarrow O2+O2* \quad (2)$$

$$O2*\rightarrow O2+* \quad (3)$$

Manganese oxide catalysts have been extensively studied by researchers for their superior performance and low cost since their application in ozone decomposition. Classified by type and crystal structure, these catalysts mainly include supported MnO_x, pure-phase MnO_x (such as α-MnO2, γ-MnO2, ε-MnO2, δ-MnO2, and amorphous manganese oxides), and element-doped MnOx.

2.1. Catalyst for Ozone Decomposition of Manganese Oxide Supported on Carbon

The catalyst of manganese oxide for ozone decomposition is usually used with other carriers of large specific surface area in practical application, because the specific surface area of manganese oxide is relatively small. The carrier can not only disperse the catalyst effectively and give it a stable structure strength but also promote the catalytic decomposition reaction of ozone synergistically, providing a double guarantee for the catalytic process.

2.1.1. MnO@C catalyst

Yang et al. developed a high-humidity-resistant ozone decomposition catalyst, with the core being the use of hydrophobic carbon materials loaded with manganese oxide active components. The design of this mesoporous MnO@C catalyst incorporates three key technical strategies: First, the formation of manganese vacancies to create Lewis acid-base active centers, which can simultaneously act as electron donors and acceptors, thereby enhancing electron transfer efficiency in the reaction system; Second, the utilization of mesoporous structures to maximize the material's specific surface area, exposing more active sites; Third, the application of hydrophobic carbon coatings to block water molecule adsorption at active sites, thereby improving the catalyst's moisture resistance. According to the experimental data from Yang et al., the Meso-MnO@C-2G catalyst achieved 100% ozone conversion rate within 2 hours under 65% humidity conditions, and even after continuous reactions for 100 hours, the conversion rate remained at 99.5%.[14]This catalyst not only achieves stable and efficient ozone decomposition across a wide humidity range, but also simultaneously removes volatile organic compounds. It demonstrates significant application potential in practical air purification fields.[14]

2.1.2. Supported manganese oxide catalysts using manganese(II) acetate as precursor

Radhakrishnan et al. prepared supported manganese oxide catalysts using manganese acetate as a precursor through isovolumetric impregnation on four different supports: Al_2O_3, ZrO_2, TiO_2, and SiO_2. XRF analysis revealed that the supported catalysts on Al_2O_3 exhibited mononuclear manganese active

sites without observable Mn-Mn interactions. In contrast, Mn-Mn interactions with bond lengths of approximately 0.350 nm were detected on ZrO_2, TiO_2, and SiO_2 supports, forming polynuclear active sites. NEXAFS spectroscopy further demonstrated a stable decreasing trend in manganese oxidation states across the four supports, with the order being Al_2O_3 <ZrO_2 <TiO_2 <SiO_2. [15]

Radhakrishnan et al. demonstrated that the structural properties of supported manganese oxide catalysts and their ozone decomposition performance are primarily governed by the characteristics of the support materials. Al_2O_3, ZrO_2, TiO_2, and SiO_2 significantly influence the kinetics and reaction mechanisms of ozone decomposition by modulating the dispersion, aggregation state, oxidation state, and electronic properties of the active manganese oxide sites. Notably, all manganese oxide active sites exhibit pentacoordination structures. Catalysts supported on Al_2O_3 demonstrate mononuclear site characteristics, whereas those supported on the other three supports exhibit multinuclear site characteristics. The ozone decomposition reaction follows heterogeneous surface kinetics, with desorption becoming the rate-limiting step.[15]

2.1.3. Supported MnO_x catalysts

Through crystal structure studies, Jia et al. evaluated the ozone decomposition efficiency of three MnO_2 forms: α-MnO_2, γ-MnO_2, and β-MnO_2, ranking them as α-MnO_2> γ-MnO_2> β-MnO_2. Morphological analysis confirmed that α-MnO_2 exhibited the highest specific surface area among the three forms (nanofibers: 80.7 $m^2 g^{-1}$; nanorods: 33.8 $m^2 g^{-1}$; nanotubes: 39.2 $m^2 g^{-1}$). This superior performance of α-MnO_2 stems from its higher oxygen vacancy density and lower average Mn oxidation state, which significantly enhances its decomposition efficiency compared to the other two forms.[16]

To enhance the performance of MnOx-based catalysts, Jia et al. developed various modification strategies, including altering Mn^{2+} precursors, regulating calcination temperature, metal doping, proton exchange, and support loading. These methods improve catalytic activity by optimizing reaction conditions.[16]

The above catalysts are supported MnO_x catalysts.Each of these modifications have several effects include enhancement of specific surface area, improvement of oxygen vacancies dispersion, increasing the oxygen vacancy density, increasing the ratio of Mn3+/Mn4+, increment of catalyst reducibility, enhancing the diffusion of ozone into the catalyst structure, and also decreasing the average oxidation state of Mn which are improved catalytic activity toward ozone decomposition. By changing the synthesizing procedure (e.g. changing the calcination temperature), using different Mn2+ precursors, acid treatment, and synthesizing the catalyst on a support, the crystal structure and the morphology of the catalyst are changed that result in changing the specific surface area. Higher specific surface area means higher density of oxygen vacancies that are the active sites for ozone decomposition. Moreover, doping the catalyst with other transition metal oxides will increase the formation of surface defects, which are the oxygen vacancies.

2.2. Research Progress on Different Manganese Oxide Crystals

While supported Mn catalysts demonstrate significant advantages in practical applications, current academic research on ozone catalytic decomposition primarily focuses on the crystalline structure of manganese oxide. Manganese oxide (MnO_x) catalysts exhibit diverse crystal structures, with Mn^{3+}/Mn^{4+} oxide crystals being the most extensively studied for ozone decomposition. Most studies indicate that the active sites in manganese oxides are structure-dependent, while element doping to generate secondary cations remains a common strategy for performance optimization.

2.2.1. α-MnO_2catalytic material

Zhu's team successfully synthesized an oxygen-enriched α-MnO_2 crystal material that significantly enhanced its ozone catalytic decomposition performance. Experimental results showed the ozone removal rate increased from 32.6% to 95% within 20 hours. Subsequent experiments revealed competitive adsorption of water vapor and ozone on the catalyst surface. This caused a temporary decline in ozone removal efficiency, but the deactivation was reversible. When humidity decreased,

the catalyst activity recovered rapidly. Based on these experimental observations, Zhu's team hypothesized a new pathway for ozone decomposition in humid airflows and proposed a novel reaction mechanism.[17]The high activity of the catalyst is mainly due to the oxygen vacancy mechanism.[18-20]The academic community generally agrees that Zhu et al. successfully introduced high-concentration oxygen vacancies on the surface of α-MnO_2 nanofibers. These oxygen vacancies serve as the core active sites for ozone adsorption and decomposition, significantly enhancing the efficiency of ozone adsorption and decomposition.[17]

Furthermore, Zhu et al. reported a KOH-modified α-MnO_2 catalyst that exhibited enhanced ozone decomposition performance. Their research demonstrated that when α-MnO_2 was hydrothermally treated with 1M potassium hydroxide solution for 4 hours, its service life to maintain 100% ozone removal efficiency was extended from 3 hours to 15 hours. Subsequent experiments revealed that K^+ introduction induced the generation of abundant oxygen vacancies, but the accumulation of intermediate oxygen species led to catalyst deactivation. Regeneration of the catalyst was achieved through calcination in an argon atmosphere.[21]The catalytic mechanism can be summarized as follows: The increase in K+ content reduces the formation energy of oxygen vacancies, thereby increasing their quantity. The presence of active oxygen vacancies accelerates the decomposition reaction of ozone.

Ma et al. synthesized a Ce-doped α-MnO_2 catalyst that demonstrated outstanding performance in high-speed ozone decomposition reactions. Their research revealed that Ce doping effectively extends the O-O bond length after ozone adsorption, thereby reducing the energy barrier for ozone decomposition and enhancing its dissociation efficiency. Subsequent experiments showed the catalyst exhibited optimal catalytic performance at 600°C. The $CeMn_{10}O_x$ catalyst demonstrated 2.5 times higher decomposition activity than α-Mn_2O_3 for 40 ppm O_3 under conditions of 65% relative humidity and 840 L g^{-1} h^{-1} space velocity.[22]Secondly, the introduction of Ce also induces significant surface restructuring in α-Mn_2O_3, resulting in a more textured surface structure. This modification facilitates molecular adsorption, thereby enhancing the ozonolysis activity of Mn_2O_3.[22]

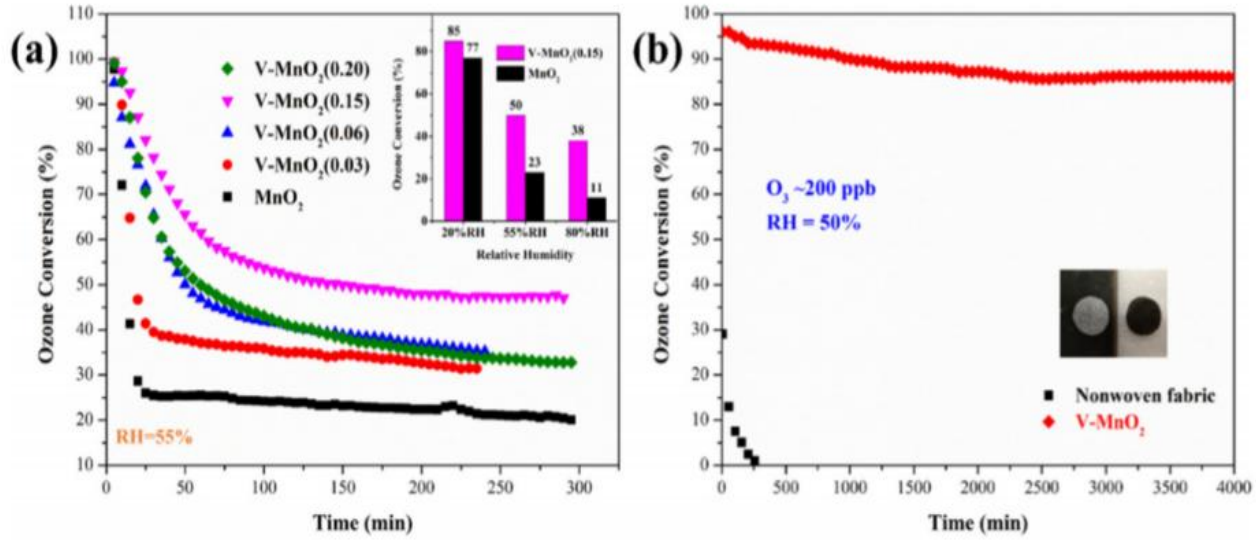

Figure 1. (a) Performance of MnO_2 and V-doped MnO_2 for ozone removal in humid atmosphere (RH=55%) at room temperature (25°C), the inset shows the ozone conversion of V-MnO_2 (0.15) and MnO_2 at 20%, 55% or 80% relative humidity after running 150 min, inlet ozone = 110 ppm, GHSV = 600L/g_{cat}·h. (b) Performance of V-MnO_2 (0.15) loaded on the nonwoven fabric for ozone removal in humid condition (RH=50%) at room temperature (25°C), inlet ozon = 200 ppb, face velocity was 5.1cm/s [23].

Yang et al. synthesized vanadium-doped MnO_2 catalysts. Experimental results demonstrated that vanadium doping significantly enhances the ozone catalytic decomposition performance of MnO_2 in three key aspects: First, it reduces the average oxidation state of Mn in MnO_2, enabling the generation

of more oxygen vacancies. Second, it substantially increases the number of acidic sites on the catalyst surface. Third, it improves the mobility of adsorbed oxygen species. These effects correspond to three distinct mechanisms: (1) Decreasing crystallinity and increasing specific surface area, thereby promoting reactant adsorption and active site exposure; (2) Introducing stress and structural distortions to increase oxygen vacancy numbers, facilitating oxygen adsorption and activation to generate active species such as peroxides; (3) Enhancing surface acidity to improve the catalyst's resistance to environmental disturbances in humid conditions, thereby promoting O_3 decomposition reactions, as shown in Figure 1.

2.2.2. γ-MnO_2catalytic material

Li et al. synthesized a series of Ce-modified γ-MnO_2 materials through pH control, exhibiting distinct properties. Their comprehensive experiments revealed that under humid conditions, the pH=7 catalyst demonstrated optimal hydrophobicity, maintaining 98% high conversion rate even at 65% humidity. Under dry and high-speed conditions, SO_4^{2-} adsorption was found to reduce the adsorption capacity of ozone molecules on pH=2 and pH=4 catalysts. Subsequent kinetic experiments showed that activation energy higher than that of the pH=7 catalyst hindered ozone molecule activation. At 2,000,000 hr^{-1}, the conversion rate dropped to only 70%, significantly lower than the 99% achieved by the pH=7 catalyst, as shown in Figure 2.

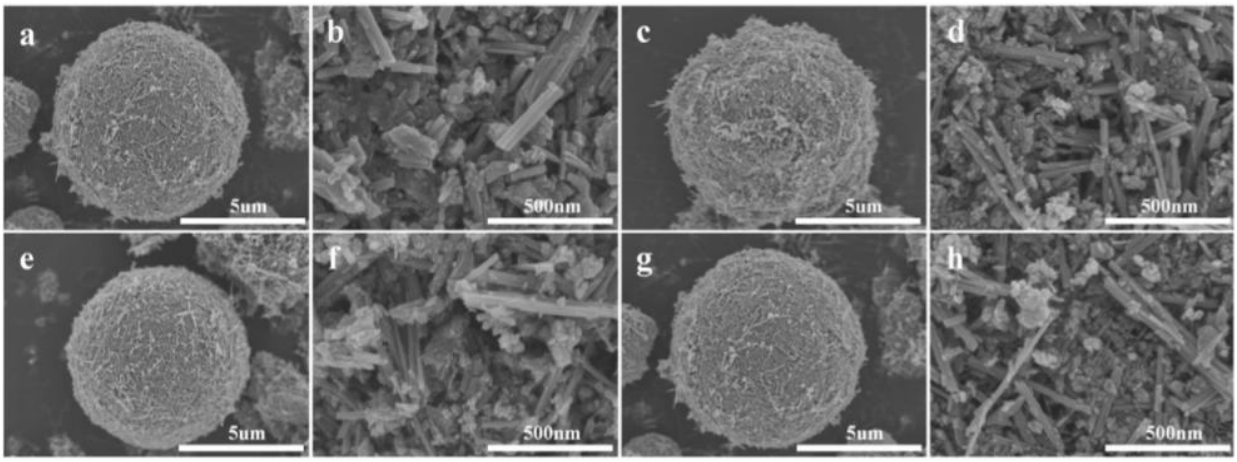

Figure 2. Scanning electron microscopy (SEM) images of (a, b) pH=1, (c, d) pH=2, (e, f) pH=4 and (g, h) pH=7 catalysts [24].

Li et al. further synthesized various catalysts using silver doping. The γ-MnO_2 support exhibits more abundant defect sites compared to the α-MnO_2 support, forming AgO_x at low silver loading rates (whereas the α-MnO_2 support consistently formed AgO_x across different silver loading rates). When the loading rate increased to 4%, Ag_{n0} was formed. Under experimental conditions of 30°C, 65% relative humidity, and a space velocity of 2800 Lg^{-1} h^{-1}, Li et al. found that the 4% Ag/γ-MnO_2 catalyst achieved an ozone conversion rate of 91% after 6 hours, significantly higher than the 22% conversion rate of the 4% Ag/α-MnO_2 catalyst. Subsequent experiments demonstrated that the 4% Ag/γ-MnO_2 catalyst maintained an ozone conversion rate of 70% even after continuous operation for 144 hours at a space velocity of 1680 Lg^{-1} h^{-1}. Additionally, turnover frequency (TOF) data indicated that the catalytic efficiency of Ag_{n0} was markedly superior to that of AgO_x.[25]Li et al. found that the key factors for the excellent O_3 decomposition performance of 4%Ag/γ-MnO_2 catalyst in humid gas were: (1) O_3 molecules could be rapidly activated; (2) weak competitive adsorption of water and O_3 molecules; (3) O_2^{2-}could be easily desorbed from Agn_0, as shown in Figure 3.

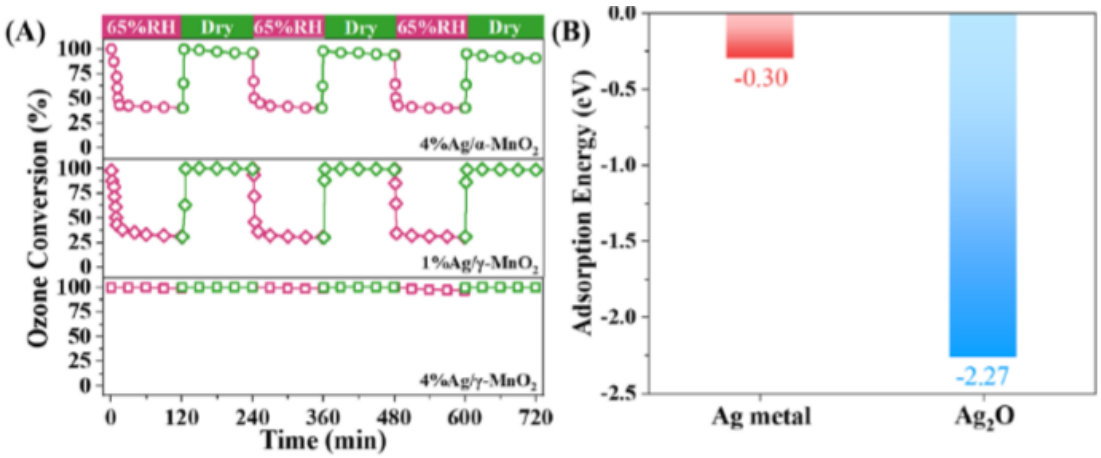

Figure 3. (A) O_3 conversion on the 4% Ag/α-MnO_2, 1% Ag/γ-MnO_2, and 4% Ag/γ-MnO_2 catalysts in alternating humidity conditions; conditions: O_3 inlet concentration 40 ppm, temperature 30°C, and weight space velocity 1680 $L \cdot g^{-1} \cdot h^{-1}$. (B) Adsorption energy of H_2O molecule on Ag metal and Ag_2O surface. [25]

2.2.3. δ-MnO2catalytic material.

Wang et al. synthesized δ-MnO_2 with different exposed crystal planes using g-C_3N_4 as the precursor via hydrothermal method, labeled as Mn-x (where x represents the addition amount of g-C_3N_4), and controlled the K^+ concentration through ion exchange to eliminate interference. The experiment results showed that compared with the δ-MnO2 exposed to the (001) facet, the δ-MnO2 exposed to the (-111) facet has less Vo content. However, the strong oxygen mobilityof δ-MnO2 with the exposed (-111) facet resulted insignificantly enhanced desorption of *O2 on the surface, which led to the stability of its excellent performance.[26] Among them, Wang et al. foundMn-0.2 maintained 95% O3 conversion after 24 h of reaction under harsh conditions (Effect of Facet on Oxygen Vacancy Properties in δ-MnO2 for Stable and Efficient Catalytic Ozone Decomposition.)

Wu et al. also synthesized δ-MnO_2 catalysts that maintained 97% ozone conversion efficiency under high humidity conditions, as shown in Figure 4.

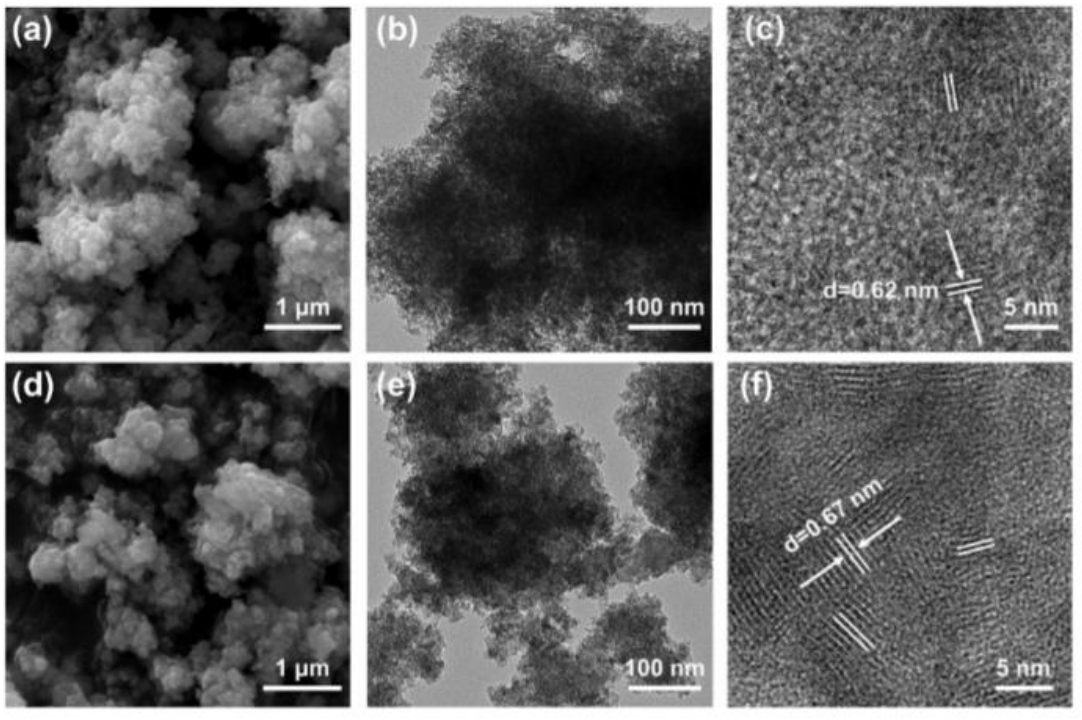

Figure 4. SEM, TEM, and HRTEM images of δ-MnO_2-1 (a-c) and δ-MnO_2-3 (d-f) [27].

Among them, δ-MnO_2-1 demonstrated the best performance, maintaining an ozone conversion rate of 99% after 12 hours of reaction at 35% RH, and achieving 87% conversion rate after 48 hours at 75% RH. Under conditions of 5°C and 25% RH, the conversion rate reached 83% after 12 hours. The catalyst exhibited rapid activity recovery in alternating dry-wet environments, outperforming most previously reported catalysts.[27]δ-MnO_2-1 exhibits a large specific surface area and pore volume. The weak Mn-O bonds enhance the surface lattice oxygen activity, while its excellent redox performance and oxygen mobility accelerate ozone decomposition. Notably, it demonstrates the weakest adsorption capacity for physically adsorbed water. Moreover, the associated adsorbed water can react with O_3 to be consumed ($O_3 + OH \rightarrow H_2O + O_2$), thereby exhibiting outstanding water resistance.[27]

In summary, various products prepared using supported Mn catalysts have been proposed in the market, such as the core-shell structured multifunctional nanofiber membranes obtained by Zhang et al. using MnO_2 nanosheets.[28]Zhao et al. investigated the self-decomposition and catalytic decomposition of ozone in RPB using Fe-MnO X/AC catalyst as the filler.[29]Sun et al. achieved the most acidic Mn-300 catalyst with the highest total number of tetrahedral sites and oxygen vacancies, as well as the best durability, by controlling the reduction temperature to regulate their content.[30] However, the supported Mn catalysts still face many challenges, such as long-term environmental impact, extending the catalyst's service life under extreme conditions, and potential by-products generated during ozone decomposition, which remain important areas for future research.

3. Main synthetic methods

We summarize the main preparation methods adopted in current research to provide references and guidance for future studies:

1. Liquid-phase synthesis: High-valent manganese salts (e.g., potassium permanganate) are combined with low-valent manganese salts (e.g., manganese sulfate) to obtain Mn^{4+}/Mn^{3+} defective crystals.

2. Hydrothermal/solvothermal synthesis. Zhang et al. prepared Mn3O4 nanoparticles and MnOOH nanorods by mixing potassium permanganate with anhydrous ethanol and distilled water to form an ethanol aqueous solution.[31]

3. Sol-gel method. Ravinder N. Reddy et al. utilized sodium fumarate to reduce permanganate into Mn^{3+} and Mn^{2+}, followed by the disproportionation of Mn^{3+} to Mn^{4+} via sulfuric acid (H_2SO_4). Subsequently, the corresponding specialized MnO_2 was prepared using dry gel and disproportionation gel.[32]

4. Homogeneous precipitation method

The primary objective of these methods is to fabricate materials with specific crystal structures and doped elements (e.g., Ce, V). Certain approaches can generate a high density of defects, which serve as crucial active sites for catalytic reactions.

4. Conclusion and Perspectives

Manganese oxide (MnOx) materials play an indispensable role in the field of catalytic ozone decomposition. Their core advantages stem from manganese’s multivalent state characteristics, abundant surface defects, and excellent redox properties, along with great application potential demonstrated in scenarios such as air purification and industrial waste gas treatment.Although the above preparation methods confer excellent properties to MnOx materials, further research is still required to enhance their moisture resistance, durability, and suitability for industrial-scale production.

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