Reviewing MnO$_x$-based catalysts for decomposition of indoor ozone

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Abstract. Ozone is a highly reactive gas and one of important air pollutants for both indoor and outdoor environments. The Occupational Safety and Health Administration (OSHA) guideline for the ozone level limit at workplaces is 100 ppb for 8-hour exposure and the Health Canada guideline for the residential buildings is 20 ppb for 8 hour exposure. Therefore, applying an ozone removal technology in indoor environments is crucial when outdoor ozone concentration is high and/or where strong ozone emission sources exist. Activated carbon-based filters, thermal oxidation, catalytic oxidation, and photocatalytic oxidation are air treatment technologies that have been applied for ozone removal. Among these technologies, the catalytic oxidation approach showed better results, particularly manganese oxide (MnO$_x$) based catalysts, which can decompose ozone to oxygen at room temperature. The low cost as well as high catalytic activity are among the advantages of MnO$_x$-based catalysts. High specific surface area, high density of oxygen vacancy, high reducibility, low average oxidation state, and low relative humidity are beneficial for ozone decomposition over the catalyst. This review presents the importance of ozone removal from the indoor environments, its exposure issues, and the recent studies on MnO$_x$-based catalyst for ozone decomposition.

1. Introduction

Ozone has high reactivity so it can react with all of the elements in the periodic table except noble metals, inert gases, and fluorine [1]. Ozone takes part in the reactions with organic compounds containing unsaturated carbon-carbon bonds [2, 3]. These reactions are of high concern in the indoor environment, where there are many materials and substances containing unsaturated organic compounds [3]. Ozone is passively removed from the indoor environment by taking part in these reactions; however, secondary pollutants are generated [4, 3]. Some of these compounds are more harmful than the ozone itself. For instance, formaldehyde, acetaldehyde and hydroxyl radical are known as carcinogens [5]. Ozone sources are in both indoor and outdoor environments. In the indoor, devices such as photocopiers, laser printers, and fax machines can generate ozone. In addition, some of air purifiers like ozone generators, ion generators, and electrostatic precipitators (ESP) increase the amount of indoor ozone [2]. In the industrial environment, ozone generators that work continuously are the main sources of ozone [6]. Ozone leakage can occur since ozone can destruct ozone generator components and relevant vessels such as tank, piping, gaskets, joint sealers, and valves [7]. A large number of workers and occupants that deal with ozone generators and other instruments that produce it are at risk of exposure to high levels of ozone. For instance, during arc-welding ozone could be generated up to 10 ppm in the breathing zone of the welder [6]. Hence, applying an ozone removal technology especially in industrial environments that use ozone is highly essential for workers’ and occupants’ health. Another source of indoor ozone is outdoor. The outdoor ozone introduces to the indoor through natural or mechanical
ventilation. Various parameters affect the concentration level of ambient ozone. For instance, at a certain meteorological conditions, i.e. high temperature, intense solar radiation, high humidity, low wind speed in addition to appropriate levels of VOC and NOx, the concentration of ambient ozone will increase [8]. Besides, wildfire and biomass burning emit a considerable amount of NOx, VOCs, and CO that lead to ozone production up to 45 ppb.h⁻¹ in some places [9]. Therefore, the ambient ozone concentration will increase in the regions near a wildfire, which leads to the increment of indoor ozone concentration level. Furthermore, ozone concentration is higher at over 12 km altitude where aircraft flying paths are located. Therefore, aircrew and passengers are at risk of exposure to high levels of ozone up to 250 ppb, which is hazardous in long-term flights [10].

The other parameter that affects the indoor ozone level is its reaction with chemicals in the building, in the air (homogeneous reactions) or on the surface of the materials (heterogeneous reactions). These reactions act as ozone scavengers, i.e. ozone sinks, and therefore reduce the indoor ozone concentration [11].

Generally, in non-industrial environments the indoor ozone level is 20% to 70-80% of the outdoor level in the absence of indoor ozone sources, and in the majority of the buildings, the ozone concentration is lower than the exposure limits. However, this does not mean that the indoor ozone has no harmful effects on human health. Because, usually ozone-initiated products, even at low levels, have more harmful effects and are responsible for observed health effects [2, 3]. Furthermore, researchers estimated that the daily inhalation of indoor ozone is about 25% to 60% of the daily ozone intake, while the inhalation of its reaction products in mass can be up to two times the indoor ozone intake [5]. Therefore, ozone removal from the indoor environments is crucial, not only because of the adverse effects of ozone but also due to the wide range of hazardous chemical compounds that form through various reactions involving ozone. Different health organizations such as world health organization (WHO) determine guidelines for the ozone concentration limit in the indoor environment. These guidelines are presented in table 1.

| Organization        | Guideline                                           |
|---------------------|-----------------------------------------------------|
| WHO [12] Ambient air| 0.05 ppm (100 µg/m³) 8 h exposure                   |
| Health Canada [13] Residential buildings | 0.02 ppm (40 µg/m³) 8 h exposure                   |
| CAAQS[14] Ambient air | 0.063 ppm (126 µg/m³) 8 h exposure (effective in 2015) |
| CAAQS [14] Ambient air | 0.062 ppm (124 µg/m³) 8 h exposure (effective in 2020) |
| OSHA [15] Workplace  | Permissible exposure limit: 0.1 ppm (200 µg/m³) workers not be exposed to an average concentration of more than 0.1 ppm for 8 h per day and 5 days per week |
| NIOSH [16] Workplace | Recommended exposure limit: ≤0.1 ppm (200 µg/m³)/ no to be exceeded at any time |

1. Canadian ambient air quality standard
2. Occupational safety and health administration
3. National institute for occupational safety and health

2. Ozone removal technologies

Air treatment technologies are include mechanical filtration, adsorption, photocatalytic oxidation, electronic filtration, UV photolysis, non-thermal plasma, membrane separation, biofiltration, and botanical purification [17]. Among these technologies, adsorption, liquid absorption, thermal decomposition, catalytic and photocatalytic decomposition are the technologies that have been reported for removing ozone [18]. Decomposing ozone into harmless products using catalytic and photocatalytic oxidation methods can be promising ozone removal technologies due to the moderate reaction conditions, high efficiency, and low cost [18]. According to the following reaction (equation 1), the process of decomposing ozone is thermodynamically favoured [1].

\[ 	ext{O}_3 \rightarrow \frac{3}{2} \text{O}_2 \quad \Delta G^\circ_{298} = -163 \text{ KJ/mol}^{-1} \] (1)

Ozone is thermodynamically unstable; on the other hand, it is thermally stable up to 523 K. Therefore, ozone will stay in the environment unless being treated or decomposed through an oxidation reaction [19]. There are various catalytic materials for decomposition of ozone at room temperature such as metals including platinum (Pt), palladium (Pd), rhodium (Rh), silver (Ag), and copper (Cu); metal oxides include
manganese (Mn), cobalt (Co), copper (Cu), iron (Fe), nickel (Ni), gold (Au), silver (Ag), and aluminium (Al); zeolite and perlite. In addition, the use of transition metal oxides supported on Al2O3, SiO2, TiO2, Activated Carbon (AC), and zeolite were reported for ozone catalytic decomposition [20]. Among them, MnOx gained more interest due to its highest catalytic activity; therefore, literature review on catalytic decomposition via MnOx-based catalysts are presented in the following.

3. MnOx-based catalysts for ozone decomposition

High catalytic activity of MnOx-based catalysts that is attributed to its ability to form oxides with different oxidation states, as well as low price (compare with noble metals), and good stability are responsible for its wide application in ozone decomposition process [18, 20-23]. The density of oxygen vacancies on the surface of the MnO2 catalyst in addition to its reducibility is responsible for the ozone decomposition efficiency of the catalyst. The mechanism of ozone decomposition is presented in two forms (equations 2 and 3), which determine the importance of oxygen vacancies and reducibility. A catalyst with higher surface area has higher density of oxygen vacancies, i.e. higher density of active sites. Therefore, the morphology and the structure of the catalyst are of high concern [20-23]. The effect of different crystal structures of MnO2 catalyst on its ozone decomposition efficiency was investigated [20-23].

\[
\begin{align*}
O_3 + V_0 & \rightarrow O_2 + O^{2-} \\
O_3 + O^{2-} & \rightarrow O_2 + O^{2-} \\
O_2^{2-} & \rightarrow O_2 + V_0
\end{align*}
\]

(2)

\[
\begin{align*}
O_3 + [\text{Mn}^{n+}] & \rightarrow O_2 + O^-[\text{Mn}^{n+1}] \\
O_3 + O^-[\text{Mn}^{n+1}] & \rightarrow 2O_2 + [\text{Mn}^{n+}]
\end{align*}
\]

(3)

The results of recent studies on MnOx-based catalytic oxidation process for ozone decomposition including the efficiency of different types of MnOx-based catalyst at different test conditions (i.e. initial ozone concentration, temperature, and relative humidity) in addition to the effect of the modification procedures on the specific surface area and the ozone decomposition efficiency are summarized in table 2. Jia et al. [20] investigated ozone conversion by three tunnel-structure polymorphs of MnO2: α, β and γ-MnO2. These manganese oxides are mesoporous with non-uniform pores. In the experiments, initial ozone concentration was 14 ppm. The ozone decomposition performances of catalysts were tested at different temperatures 5-100 °C. The conversion efficiencies of three MnO2 polymorphs followed the order of α-MnO2 > γ-MnO2 > β-MnO2 and increased by increasing the temperature. The highest efficiency of α-MnO2 is attributed to its largest surface oxygen vacancy density, due to its highest specific surface area along with its lowest activation energy. The removal efficiency of α-MnO2 remained 100% at all temperatures after 2 h (even at 5°C), but the efficiency was decreased to 80% after 99 h reaction time at room temperature. In another study [22] the effect of three different morphologies of α-MnO2 including nanofibers, nanotubes, and nanorods, on its ozone conversion efficiency was investigated. The inlet ozone concentration and the temperature were kept at 23 ppm and 25°C, respectively. The α-MnO2 nanofibers has the largest specific surface area and crystal facet, which result in higher amount of oxygen vacancies, in addition to the lowest average Mn oxidation state. Therefore, it has the highest catalytic activity toward the ozone decomposition. The ozone conversion of all three α-MnO2 catalysts were decreased over time, but the rate of reduction for nanofibers was lower than the others were. After 90 min of reaction, the ozone conversion was maintained above 80% for nanofibers, but reduced to less than 60% and 50% for nanorods and nanotubes, respectively.

Todorokite-type MnO2 (T-MnO2) is another kind of MnO2 catalyst with a 3*3 tunnel structure. Its initial ozone conversion efficiency was reported to be 50% and dropped rapidly to less than 30 % (the inlet ozone concentration was 50-60 ppm), which is not acceptable. This catalyst was modified by cerium doping (Ce-MnO2) which leads to a significant improvement in catalytic activity as well as stability. Cerium modification caused the enhancement of specific surface area, formation of more oxygen vacancies, and easier recovery of oxygen vacancies. The highest conversion was obtained at Ce/Mn ratio of 0.28, was greater than 80% after 3 h reaction time [21]. Two other types of MnOx catalyst that were studied for ozone decomposition are δ-MnO2, and cryptomelane MnOx (OMS-2), which have
K⁺ ions in their tunnels [23-25]. In OMS-2 type, Mn is present with various valences that improve its catalytic activity [24, 25].

Table 2. Summary of literature on ozone decomposition by MnOₓ-based catalysts

| Ref | Material | Modification procedure | Sᵃ (m².g⁻¹) | [O₃]ᵇ (ppm) | Tᶜ (°C) | RHᵈ (%) | O₃ decomposition efficiency |
|-----|----------|------------------------|-------------|-------------|---------|---------|---------------------------|
| 20  | α-MnO₂   | Different crystal structures of MnO₂ catalyst | 80.7        | 74.6        | 14      | 25      | 100% after 2 h            |
| 21  | γ-MnO₂   | Different morphologies of α-MnO₂ catalyst | 33.8        | 23          | 25      | 45      | <60% after 2 h            |
| 22  | β-MnO₂   | Bimessite-type MnO₂ (δ-MnO₂) treated by acid nitric | 228        | 145         | 25      | 50      | 50% after 24 h            |
| 23  | H-δ-MnO₂ | Proton containing δ-MnO₂ catalyst | 206        | 2000        | 30      | Dry air | 100% after 8 h            |
| 24  | H-β-MnO₂ | Using Fe(NO₃)₃ precursor for synthesizing the catalyst | 262        | 10000       | 25      | 90      | >90% after 8 h            |
| 25  | Fe-MnO₃ | Fe doped MnO₃ catalyst | 190        | 100         | 25      | 60      | 73% after 6 h             |
| 26  | α-MnO₂   | Pristine α-MnO₂ | 92.9        | 100         | 25      | 60      | 50% after 1 h             |
| 27  | W-δ-MnO₂ | Tungsten doped α-MnO₂ catalyst | 297        | 120         | 25      | 65      | >50% after 4 h            |
| 28  | α-MnO₂   | Pristine α-MnO₂ | 91.3        | 120         | 25      | 65      | 20% after 4 h             |
| 29  | Ce-MnO₂  | Cerium (Ce) doped T-MnO₂ catalyst | 108        | 50-60       | 25      | Dry air | >75% after 3 h            |
| 30  | OMS-2-Ac | Cryptomelane type MnO₂ (OMS-2) catalyst synthesized with different Mn²⁺ precursors (MnAc₂, Mn(NO₃)₂, MnCl₂) | 137        | 40±2        | 30      | 90      | 75% after 6 h             |
| 31  | OMS-2-NO₃ | | | 83 | | | >60% after 6 h |
| 32  | OMS-2-Cl | | | 78 | | | >60% after 6 h |
| 33  | MnOₓ-350 | MnOₓ and CoOₓ catalysts calcined at different temperatures, the best results obtained at 350 °C | 116.159    | 1000        | 25      | -       | 98.5% after 4 h           |
| 34  | MnOₓ/AC  | MnOₓ catalyst supported on AC (1.1 % Mn loading) | -           | 21.5-24     | 25      | 60      | >80% after 24 h           |
| 35  | Mn/Al₂O₃ | Alumina supported oxides of manganese and mixed manganese-copper | 239        | 27          | 23      | -       | 35% after 3 h             |
| 36  | Mn-Cu/Al₂O₃ | Submicron, spherical MnCO₃ powder catalyst | 40.5       | 14          | 25      | 1       | >85% after 24 h           |

ᵃ Specific surface area
ᵇ Initial ozone concentration
ᶜ Temperature
ᵈ Relative humidity
3.1. MnOx-based catalyst modification

To improve the catalytic performance of MnOx catalyst, there are several modification procedures that are dealing with the synthesis method of MnOx catalyst such as, changing the Mn²⁺ precursors [28], variation of calcination temperature [33], mixing Mn with other transition metal oxides [18, 21, 27, 25, 31], proton exchange [23], and synthesizing the catalyst on AC support [30]. 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. The results of some of these modification procedures are presented in table 2. 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.

All the procedures that are mentioned in table 2 are dealing with changing the specific surface area and increasing the density of oxygen vacancies. However, specific surface area is not the only factor that affects the density of oxygen vacancy. Another factor is the length of Mn-O bond. Long length of the bond leads to easier formation of oxygen vacancies, which means that the catalyst has high reducibility. In addition, high ratio of Mn³⁺/Mn⁴⁺, long length of Mn-O bond, high reducibility, low average oxidation state, and high density of oxygen vacancy are in parallel with each other. While high content of oxygen vacancy is beneficial for ozone decomposition, the formation of bulk oxygen vacancy would cause changing the distribution of surface charge, which has an adverse effect on the catalyst performance.

Another factor that affects the efficiency of the MnOx catalysts is relative humidity. At high RH a film of liquid is formed on the surface of the catalyst and occupy the active sites. Therefore, ozone cannot reach the oxygen vacancies and thus the catalyst activity toward ozone is decreased [18]. For instance, the ozone decomposition of α-MnO₂ is 100% at 1% RH [20] and is decreased to 80% at 45% RH [22]. By increasing the RH to 60%, the efficiency of α-MnO₂ is decreased significantly to 50% [26].

To improve the indoor air quality, MnOx-based filters can be applied in air handling systems for the environments that are at risk of high levels of ozone such as: aircraft cabins, buildings near high traffics, buildings near industries that using ozone generators, commercial buildings using devices that generates ozone, and hospitals that using ozone generators as disinfectant. According to the literature, MnOx-based filters would have high performance and stability at indoor environment conditions.

4. Conclusion

Ozone is one of the most important gaseous pollutants due to its wide application in the industry. Many occupants are at risk of exposure to ozone as well as many workers in the industrial environments. In case of ozone leakage in the industrial environments, immediate evacuation is mandatory. Therefore, ozone removal in industrial environments is a critical issue. Different technologies including AC-based filters, catalytic oxidation and photocatalytic oxidation have been investigated for ozone removal. Among these methods, MnOx-based catalytic processes have the best performances. The density of the oxygen vacancy on the surface of the catalyst is the most important factor that influences its catalytic activity toward ozone. Increasing the specific surface area, increasing the ratio of Mn³⁺/Mn⁴⁺, enhancing the length of Mn-O bond, improving the reducibility, and decreasing the average oxidation state are led to increment of the density of surface oxygen vacancy. Instability is the main drawback of MnOx-based catalysts particularly under high relative humidity. Therefore, improving the MnOx-based filters may be necessary for indoor air applications.

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