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Recent advances in catalytic decomposition of ozone

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ABSTRACT

Ozone (O_3), as a harmful air pollutant, has been of wide concern. Safe, efficient, and economical O_3 removal methods urgently need to be developed. Catalytic decomposition is the most promising method for O_3 removal, especially at room temperature or even subzero temperatures. Great efforts have been made to develop high-efficiency catalysts for O_3 decomposition that can operate at low temperatures, high space velocity and high humidity. First, this review describes the general reaction mechanism of O_3 decomposition on noble metal and transition metal oxide catalysts. Then, progress on the O_3 decomposition performance of various catalysts in the past 30 years is summarized in detail. The main focus is the O_3 decomposition performance of manganese oxides, which are divided into supported manganese oxides and non-supported manganese oxides. Methods to improve the activity, stability, and humidity resistance of manganese oxide catalysts for O_3 decomposition are also summarized. The deactivation mechanisms of manganese oxides under dry and humid conditions are discussed. The O_3 decomposition performance of monolithic catalysts is also summarized from the perspective of industrial applications. Finally, the future development directions and prospects of O_3 catalytic decomposition technology are put forward.

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hr average O_3 concentration and the prescribed 1 hr average O_3

concentration are both 160 μ g/m³ (~82 ppb). O₃ in the atmosphere

mainly comes from the photochemical reactions of volatile organic

(VOCs) and nitrogen oxides (NO_x). Tropospheric O_3 is a kind of

greenhouse gas that determines the oxidizing capacity of the

atmosphere and the lifetime of other species in the atmosphere by

forming OH radicals. The long-term observational results show that

the O₃ concentration in the atmosphere has increased year by year

(Gao et al., 2017; Tang et al., 2009; Vingarzan, 2004; Wang et al., 2017; Xu et al., 2016; Zhang et al., 2014). From June to August

2016, O₃ replaced PM₁₀ and PM_{2.5} as the primary pollutant in the

Beijing-Tianjin-Hebei region, the Yangtze River delta and the Pearl

River delta (Liu et al., 2018a). Due to air exchange, an increase in

outdoor O₃ concentration will lead to an increase in indoor O₃

Introduction

Ozone (O₃) is a powerful oxidant that can harm crops, ecosystems and human health. High-concentration O₃ can cause cardio-vascular and respiratory dysfunction and increase mortality (Feng et al., 2015; Liu et al., 2018a; Wolkoff, 2013). In the Pearl River Delta region of China, the average O₃ concentration increased by 10 μ g/m³ (~5.1 ppb) every time, the total non-accidental mortality rate, the mortality rate of cardiovascular disease and respiratory disease increased by 0.81%, 1.01%, and 1.33%, respectively (Tao et al., 2012). The World Health Organization (WHO) has established a guideline value of 100 μ g/m³ (~51 ppb) for the 8-hour average O₃ concentration. On October 1, 2015, the American Environmental Protection Agency (EPA) tightened the national ambient air quality standards" (GB3095-2012) and "indoor air quality standards" (GB/T 18883-2002), the level 2 standard of allowable 8

inese "ambient or air quality of allowable 8 vironment Simula-1 Sciences, Chinese d and O_3 converter (Bhangar et al., 2008; Bhangar and Nazaroff, 2013; Weisel et al., 2013). Besides its direct effects on health, O_3

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can react with VOCs to produce more-toxic oxidation products, which means that O_3 concentrations below the regulated levels are also harmful (Wolkoff, 2013). Therefore, removing O_3 is of great significance for environmental protection and human health.

According to the sources of O₃ mentioned above, there are two approaches to controlling O₃ pollution: one is to control O₃ precursors, and the other is to eliminate O₃ itself. Since there is an equal-concentration curve (EKMA curve) for O₃ generation (Kelly and Gunst, 1990), it is necessary to draw an EKMA curve based on regional characteristics to reduce O₃ concentrations through collaborative control of VOCs and NO_x (Ou et al., 2016). When the concentration ratio of VOCs and NO_x is high, O₃ generation is controlled by NO_x. The O₃ concentration increases with the increase of NO_x, while changes in VOCs have little influence on O₃. Conversely, when the ratio of VOCs and NO_x is low, O_3 formation is controlled by VOCs. The O3 concentration increases with the increase of VOCs, but an increase in NO_x concentration will reduce the O₃ concentration. Urban areas are generally in the regime of control by VOCs. The sources of VOCs are complex, and effective control technology for non-point source VOCs is lacking. On the other hand, VOCs from natural sources cannot be controlled. The control of NO_x can result in a rebound in the O₃ concentration in the short term. The direct removal of outdoor O₃ provides a new way to reduce O₃ in the atmosphere. In the Pearl River Delta region of China, O₃ precursors are well controlled, but O₃ concentrations can still exceed 100 ppb (Ou et al., 2016; Shen et al., 2015; So and Wang, 2003; Zhang et al., 2008), which also illustrates the necessity of eliminating O₃ itself. Previous studies have shown that coating catalysts onto vehicle radiators can effectively eliminate O₃ in the atmospheric environment (Farrauto and Heck, 2000; Wu and Kelly, 1998), which demonstrates the feasibility of direct removal of O_3 from the atmosphere. On the other hand, O_3 pollution in confined spaces, such as indoors and in aircraft cabins, can only be controlled by eliminating O₃ itself (Weisel et al., 2013). Although the decomposition of O₃ into oxygen is not limited thermodynamically, the half-life of O_3 at 20 $^\circ\mathrm{C}$ is up to 3 days, so measures need to be adopted to remove O_3 (Hao et al., 2001).

At present, the common methods to treat O₃ include activated carbon, thermal decomposition, liquid absorption and catalytic decomposition. Activated carbon itself can absorb and decompose O₃ molecules; its degradation mechanism is mainly adsorbing and concentrating O₃, catalytic decomposition of O₃ into oxygen, and reacting directly with O₃ (Beltran et al., 2002). As a simple and low-cost method, activated carbon is often used for the removal of low-concentration O₃. The process of treating high-concentration O₃ with activated carbon involves great heat dissipation, and it can easily explode if not properly treated. Besides, activated carbon is easily deactivated and needs to be regenerated or replaced frequently, and the removal efficiency is greatly affected by humidity, airflow, pressure, concentration and other factors, which present great limitations (Subrahmanyam et al., 2005). O3 removal by thermal decomposition requires heating the gas to about 400 °C, which has good removal efficiency for high-concentration O₃. However, the method cannot be applied in outdoor and indoor O₃ removal, and is only suitable for the treatment of high-concentration industrial exhaust (Hellen et al., 2012). The reagents used in liquid absorption are mainly sodium thiosulfate or sodium sulfite, but the biggest problem with this method is that the waste liquid is difficult to deal with (Williams and Grosjean, 1990). The catalytic decomposition of O_3 has become a research focus because of its advantages such as mild reaction conditions, high treatment efficiency, environmental friendliness, safety, economy and stability. However, some challenges remain for catalytic decomposition of O_3 . The catalysts for O_3 decomposition need to decompose O_3 efficiently at room or even low temperature, under high humidity and high space velocity. The presence of water vapor tends to

occupy the active sites, thus reducing the O_3 decomposition activity of catalysts (Liu and Zhang, 2017b; Wu and Kelly, 1998). The conditions of low temperature and high space velocity also impose very strict requirements for catalysts. Therefore, it is important to develop catalysts with high activity and high humidity resistance at room temperature, and even at sub-zero temperatures.

In 1997, Dhandapani and Oyama (1997) summarized the catalysts for O_3 decomposition reported in the previous literatures, including the components, preparation methods, and activity of catalysts. In addition, kinetics and characterization experiments were carried out to explain the previously reported results, and p-type oxides were found to be best as active components. Among them, MnO_2 had the best activity for O_3 decomposition, and their kinetic experimental results accorded with the existence of intermediate peroxy and superoxy species. Subsequently, catalysts for O_3 decomposition with excellent activity and moisture resistance were further developed.

In this review, we mainly focus on recent advances in the catalytic decomposition of O₃ over the past three decades. This review is organized from the following four aspects. Firstly, we present an overview of the general reaction mechanism of O₃ decomposition on noble metal catalysts and transition metal oxide catalysts. The second section summarizes the O₃ decomposition performance of noble metal catalysts, the relationship between support structure and noble metal loading content and O₃ decomposition performance, and the detailed reaction process of O_3 on the surface of noble metals. In the third section, the O3 decomposition performance of transition metal oxides and their structure-activity relationships are summarized. The main focus of this section is the O3 decomposition performance of manganese oxides, including the supported manganese oxides and non-supported manganese oxides. Then, the methods used to improve the performance of manganese oxides are summarized from the following three aspects: increasing the content of oxygen vacancies; enhancing the moisture resistance of manganese oxides; and improving the stability of oxygen vacancies on manganese oxides. In addition, the deactivation mechanisms of the non-supported manganese oxides under dry and humid conditions are discussed. In the fourth section, the O₃ decomposition performance of various monolithic catalysts is also reviewed from the perspective of industrial application. Finally, we present the remaining challenges facing the catalytic decomposition of O3 and provide some viewpoints on future research directions.

1. General reaction mechanism

On noble metal and transition metal oxide catalysts, the reaction process of O3 decomposition is mainly divided into the following steps (Fig. 1): Firstly, an O_3 molecule adsorbs on the surface of catalyst, and then dissociates into an oxygen molecule and an atomic oxygen species. The remaining atomic oxygen species will react with another O₃ molecule to form an adsorbed peroxide species (0_2^{2-}) or superoxide (0_2^{-}) and an oxygen molecule (Chang and Lin, 2005; Gong et al., 2017, 2019; Kameya and Urano, 2002; Konova et al., 2018; Li et al., 1998; Li and Oyama, 1998; Stoyanova et al., 2006). Finally, the adsorbed O_2^{2-} or O_2^{-} decompose into oxygen molecules and desorb from the active site of catalysts. The first two steps of the reaction mechanism are mainly the process of oxidation of active sites, and the last step is the reduction of active sites, restoring the original state and participating in the next reaction cycle. The final reduction process is generally considered to be the rate-controlling step in the O₃ decomposition reaction, but there is still a lack of clear evidence for this on many catalysts. Besides, the valence states and properties of intermediate oxygen species involved in this reaction mechanism are also unclear. The intermediate oxygen species on the MnO₂ catalyst can be



Fig. 1. General reaction mechanism of O_3 decomposition on transition metal oxide and noble metal catalysts.

essentially identified as O₂²⁻, but the intermediate oxygen species on other catalysts have not been observed or identified. O_2^- was demonstrated to be the intermediate oxygen species generated on Ag₂O catalysts during the O₃ decomposition reaction by CO reactivity testing, ESR and ESCA experiments (Imamura et al., 1991). Imamura et al. (1991) and Chang and Lin (2005) applied molecular CO as a probe to investigate the properties of intermediate oxygen species forming on the surface of various transition metal oxides, Pt/Rh, and Pd/Rh catalysts during O₃ decomposition, and found that the intermediate oxygen species on different catalysts have different CO reactivities. This proves that the intermediate oxygen species formed on the surface of different catalysts have different chemical properties. Therefore, the O₃ reaction mechanism on different catalysts may be different and needs to be studied in detail. Then, more efficient catalysts for O₃ decomposition can be designed according to the reaction mechanism.

2. Noble metal catalysts

Noble metal catalysts have excellent activity for O_3 decomposition, as well as excellent moisture resistance, and have attracted the attention of many researchers. The properties of silver (Ag), gold (Au), platinum (Pt), palladium (Pd) and rhodium (Rh) catalysts, which are generally supported on molecular sieves, activated carbon, transition metal oxides, SiO₂, Al₂O₃, or perlite, have been reported in previous studies. The O₃ decomposition performance of noble metal catalysts is related to the chemical state of the noble metal, which depends on the support, preparation method, loading amount of noble metal, *etc.*

The O_3 decomposition activity data for noble metal catalysts reported in the literature are summarized in Table 1. Details on the catalysts will be discussed in the following section.

2.1. Ag-based catalysts

Ag-based catalysts have been extensively studied due to their excellent O_3 decomposition activity and water resistance. Imamura et al. (1991) found that the O_3 decomposition activity of Ag₂O is higher than that of other transition metal oxides, and the introduction of 4.2% water vapor (the saturated concentration of water at 30 °C) had no effect on the O_3 removal efficiency of Ag₂O.

The chemical state of Ag, interactions between the metal and support, and O₃ decomposition performance were all found to be affected by the support properties, Ag loading content, and preparation method. Kumar et al. (2004, 2007) and Konova et al. (2018) used Ag-modified H-MCM-41, H-Beta, and SiO₂ catalysts to study the influence of the acidity, structure, and Si/Al ratio of the support and the Ag loading content on O3 decomposition performance. They found that the adsorption of O₃ molecules was stronger at weakly acidic sites, and supports with high specific surface area and uniform pore structure were more conducive to O₃ decomposition. Besides, the Ag content and specific surface area of the support affected the chemical state of Ag and the O₃ decomposition performance, and the O₃ decomposition activity of Ag clusters with smaller size was higher than that of isolated silver ions. As shown in Table 1, a 5 wt% Ag-H-MCM-41-50 catalyst with low acidity, high Si/Al ratio, high specific surface area, and uniform pore structure had the highest O₃ decomposition activity.

The initial chemical state of Ag was different on different supports. The chemical state of Ag species changed during the course of the O₃ decomposition reaction, and the activity of the catalyst also changed. Imamura et al. (1991) found that the O₃ decomposition activity of AgZ molecular sieve (NaY zeolite ion-exchanged with Ag) increased with the reaction, which may be because of the high reactive activity of the oxygen species on Ag₂O and the generation of more oxidized states (AgO) during O₃ decomposition. Ag/SiO₂ and Ag/clinoptilolite catalysts were synthesized by incipient wet impregnation and ion-exchange methods, respectively. Ag atoms existed as Ag⁰ on the Ag/SiO₂ catalyst, which had better O3 decomposition performance, but were easily oxidized to AgO and Ag₂O₃, and then deactivated. For the Ag/clinoptilolite catalyst, silver entered into the zeolite channels in the form of Ag⁺ ions, and their activity was lower than that of metallic Ag⁰ on the surface of SiO₂, but the chemical state of Ag and the activity of Ag/clinoptilolite catalysts was stable (Nikolov et al., 2010). The activity of Ag/Al₂O₃ was better than that of Ag/CL, Ag/Perlite, and Ag/ZSM-5 catalysts, and the XPS and Ag M₄VV Auger spectra demonstrated that the metallic Ag on the Al₂O₃-SiO₂ support was oxidized to Ag₂O after O₃ treatment, which resulted in deactivation of the catalysts (Batakliev et al., 2015). Naydenov et al. (2008) also used XRD and AES to study the changes in the Ag chemical state on a Ag/SiO₂ catalyst before and after O₃ treatment, and after oxygen desorption in an argon flow heated to 380 °C (after O₃ treatment). Ag atoms on the fresh catalyst existed in the form of metallic silver, and most of the Ag supported on the SiO₂ was oxidized to AgO and Ag₂O₃ after O₃ treatment. Then when the catalyst was heated to 380 °C in an argon flow, the oxidized silver on the surface returned to the metallic state. The above study revealed that the chemical state of Ag had a great influence on the O₃ decomposition performance of catalysts, and provided guidance for subsequent development of Ag-based catalysts with high O3 decomposition performance.

Based on the chemical state of Ag on the catalyst after O_3 treatment, the following mechanism for the O_3 decomposition reaction was deduced (Blaskov et al., 2015; Konova et al., 2018):

$$O_3 + nAg^0 \to O^-Ag_n^+ + O_2$$
 (1)

$$0^{-}Ag_{n}^{+} \to Ag_{2}O \tag{2}$$

$$O_3 + Ag_2 O \rightarrow 2AgO + O_2 \tag{3}$$

$$2AgO + O_3 \rightarrow Ag_2O + 2O_2 \tag{4}$$

$$2\text{AgO} + \text{O}_3 \rightarrow \text{Ag}_2\text{O}(\text{O}_x) + \text{O}_2 \tag{5}$$

Table 1 O_3 catalytic decomposition activity over noble metals^a.

Catalyst	Preparation method	O ₃ concentration (ppm)	Temperature (°C)	GHSV (hr ⁻¹)	RH (%)	Reaction time (hr)	O ₃ conversion (%)	Reaction rate (×10 ^{−6} mol/ (g·min))	Reference
5Ag-H-MCM-41-50	IMP	4390	23	133,000	Dry	6	94	_	Konova et al. (2018)
Ag/perlite	SP	21,000	-	12,000	Dry	3	75	68.61	Blaskov et al. (2015)
Ag/Al ₂ O ₃	IMP	20,000	-	$(6 L g^{-1} h r^{-1})$	Dry	3	95	89.29	Batakliev et al. (2015)
Ag/CL	IE	20,000	-	$(6 L g^{-1} h r^{-1})$	Dry	3	85	78.95	Batakliev et al. (2015)
Ag/perlite	IMP	24,000	25	$(6 L g^{-1} h r^{-1})$	Dry	2	20	21.43	Genov et al. (2011)
Ag/SiO ₂	IMP	4390	23	133,333	Dry	120	90	_	Nikolov et al. (2010)
5%Ag-H-Beta-11	IMP	4390	23	133,333	Dry	0.25	45	-	Kumar et al. (2004,
									2007)
Ag ₂ O	precipitation	3000	0	9000	Dry	-	79.5	-	Imamura et al. (1991)
1%Au/Fe ₂ O ₃	CP	3000	0	10,000	-	-	98	-	Hao et al. (2001)
5%Au/AC	SI	23.33	-	120,000	45	41.7	91	3.22	Zhang et al. (2009)
Pt/Rh	Commercial	588	25	15,000	-	0.83	15	-	Chang and Lin (2005)
Pd/Rh	Commercial	588	25	15,000	-	0.83	98	-	Chang and Lin (2005)
Pd/Al ₂ O ₃	IMP	0.2-0.25	30	176,000	Dry	-	80	6.04	Wu and Kelly (1998)
Pd/Al ₂ O ₃	IMP	0.2-0.25	30	176,000	50	-	78	5.89	Wu and Kelly (1998)
0.1Pd-Co-MnO _x -Al	IMP	1500	25	$(48 \ L \cdot g^{-1} \cdot hr^{-1})$	70	4	100	53.57	Tao et al. (2019a)
Pd-MnO _x /SiO ₂ -Al ₂ O ₃ - 350 °C	IMP	0.6	40	635,000	55-65	80	90	_	Yu et al. (2009a)
Pd-MnO _x /SiO ₂ -Al ₂ O ₃ with 80% MnO _x	IMP	0.58	45	510,000	55-65	95	>90	-	Yu et al. (2009b)
Pd-MnOx/La-Al2O3	IMP	0.6	14	380,000	85-90	_	82	-	Ren et al. (2014)
Pd-MnO _x /SiO ₂	IMP	0.6	14	380,000	85-90	_	82	-	Ren et al. (2014)
$Pd-MnO_x/\gamma -Al_2O_3$	IMP	0.6	14	380,000	85-90	_	77	_	Ren et al. (2014)
Pd/MnO ₂	IMP	510	26	15,000	90	120	89	_	Kameya and Urano
									(2002)

^a GHSV: gas hourly space velocity, RH: relative humidity, IMP: impregnation, SP: spray pyrolysis, CL: clinoptilolite, IE: ion exchange, CP: co-precipitation, AC: activated carbon, SI: sol immobilization.

$$Ag_2O(O_x) + O_3 \rightarrow 2AgO + (1 + x/2)O_2$$
 (6)

The balance between the different silver oxides during O_3 decomposition depends on the temperature and O_3 concentration in the reaction gas, and each reaction from Reactions (3) to (6) will have a different relative share when reacting in different temperatures and concentrations of O_3 (Konova et al., 2018). Imamura et al. (1991) have applied molecular CO as a probe in combination with the CO oxidation reaction to verify that the intermediate oxygen species on Ag₂O were different from those on other transition metal oxides during O_3 decomposition, and found that the O_3 decomposition activity of Ag₂O is higher than that of other transition metal oxides. The above studies revealed the O_3 decomposition mechanism for Ag-based catalysts and the reason for their excellent activity.

2.2. Au-based catalysts

Initially, the catalytic activity of gold catalysts was considered to be poor due to the chemical inertness and poor dispersive ability of Au. However, Haruta (1997) and Haruta and Date (2001) found that Au-based catalysts showed unexpectedly high activity and selectivity in many heterogeneous reactions. Subsequently, the Au-based catalysts were regarded as a new class of catalytic materials with excellent catalytic performance and were widely studied. Hao et al. (2001) found that supported gold catalysts had better O₃ decomposition performance than Ag and Ni catalysts. The chemical state of Au atoms on the Fe₂O₃ support is highly dispersed nano-structured Au^{δ +}, and the O₃ decomposition process of the 1%Au/Fe₂O₃ catalyst involves superoxide (O₂⁻) species. Then, Au/AC catalysts were prepared by a sol immobilization method, and the influence of the heating method and the pH value of the gold sol precursor on the size and dispersion of gold nanoparticles was studied. When the pH of the gold precursor solution was 8 and the catalyst was prepared by the microwave heating method, the gold nanoparticles were much smaller and

more evenly dispersed on the activated carbon support, so the resulting catalyst had better O_3 decomposition activity than catalysts prepared by the traditional conduction heating method and using gold precursor solutions at other pH values (Zhang et al., 2009).

2.3. Pd-based catalysts

Compared with other noble metal catalysts, Pd-based catalysts had superior O_3 decomposition activity and water resistance, and so have been widely studied. Pt/Rh and Pd/Rh monolith honeycomb catalysts were purchased from K.J. Environmental Technology Co. Ltd. to compare their O_3 decomposition performance, and the O_3 decomposition activity of Pd/Rh catalysts was significantly higher than that of Pt/Rh catalysts at room temperature (Chang and Lin, 2005). The O_3 decomposition performance of PdO-CeO₂/ZSM-5 catalysts at room and higher temperatures was also studied, and the catalyst exhibited about 92% O_3 conversion during the initial stage of the O_3 decomposition reaction. Then the O_3 conversion of the catalyst slightly decreased to 69% after 3 hr, but its O_3 decomposition performance was found to almost fully recover after a 24 hr break for every new catalytic reaction cycle (Nikolov et al., 2009).

Next, Pd was combined with manganese oxides to improve the water resistance and the stability of low-valent-Mn species (oxygen vacancies) on manganese oxides (Ren et al., 2014; Tao et al., 2019a; Yu et al., 2009a, 2009b). A series of Pd-MnO_x/SiO₂-Al₂O₃ catalysts were prepared by the incipient wetness impregnation method, and the influence of calcination temperature and MnO_x content on O₃ decomposition performance was studied (Yu et al., 2009a, 2009b). The Pd-MnO_x/SiO₂-Al₂O₃ catalysts calcined at 300–400 °C and with 80%–90% MnO_x content showed the best performance for O₃ decomposition. Then, the effects of different supports and the impregnation order of Pd and MnO_x on catalytic activity, reducibility, texture properties and surface electronic properties of the catalysts were also studied, and the Pd-MnO_x/La-Al₂O₃ and Pd-MnO_x/SiO₂ catalysts had the best catalytic activity (Ren et al., 2014). After Pd was doped in the Co-MnO_x-Al catalyst system, the

Table 2						
O3 catalytic	c decomposition	activity	over	transition	metal	oxides ^a .

Catalyst	Preparation method	O ₃ concentration (ppm)	Temperature (°C)	GHSV (hr ⁻¹)	RH (%)	Reaction time (hr)	O ₃ conversion (%)	Reaction rate (×10 ⁻⁶ mol/ (g·min))	Reference
NiO _x /Al ₂ O ₃	DOP	6067	0	22,000	_	4	100	101.40	Stoyanova et al. (2006)
20Ni5CuO75Al ₂ O ₃	precipitation	10,000	RT	$(60 \ L \cdot g^{-1} \cdot hr^{-1})$	_	3	90	_	Batakliev et al. (2017)
Ni/NiO pH-1	citric sol-gel	1000	25	$(240 \ L \cdot g^{-1} \cdot hr^{-1})$	90	8	98	17.59	Gong et al. (2020b)
α -Fe ₂ O ₃	decomposition	2520	45	13,300	85	2	60	_	Mehandjiev and Naidenov (1992)
M2LFh	template	600	RT	$(1500 \ L \cdot g^{-1} \cdot hr^{-1})$	Dry	_	95	636.16	Mathew et al. (2011)
Cu ₂ O cube-40 nm	RSC	200	25	$(60 \ L \cdot g^{-1} \cdot hr^{-1})$	80	8	100	8.93	Gong et al. (2017)
Cu ₂ O/rGO	ISR	20	25	$(60 \ L \cdot g^{-1} \cdot hr^{-1})$	90	10	98	0.88	Gong et al. (2018a)
Cu ₂ O-CuO-Cu(OH) ₂	SR	20	25	$(240 \ L \cdot g^{-1} \cdot hr^{-1})$	90	16	82	1.46	Gong et al. (2018b)
ultra-fine Cu ₂ O	LPR	3000	25	$(240 \ L \cdot g^{-1} \cdot hr^{-1})$	90	8	95	508.93	Gong et al. (2020a)
CoO _x -350	precipitation	1000	25	$(120 \ L \cdot g^{-1} \cdot hr^{-1})$	-	48	60	53.57	Tang et al. (2014)

^a DOP: deposition oxidation-precipitation, RT: room temperature, M2LFh: mesoporous two-line ferrihydrite, RSC: reductive solution chemistry, ISR: in-situ reduction, SR: solution reduction, LPR: liquid-phase reduction.

activity, stability and water resistance were also significantly improved, which is mainly due to the enhanced stability of oxygen vacancies and weakened adsorption of water molecules on the catalyst surface (Tao et al., 2019a). The activity of a Pd-supported MnO₂ catalyst was also superior to conventional catalysts and activated carbon, especially under wet conditions (Kameya and Urano, 2002).

3. Transition metal oxide catalysts

Noble metal catalysts have excellent catalytic activity for the decomposition of O₃, but their industrial applications are limited by their high cost. Transition metal elements are abundant and inexpensive, and synthetic methods for their oxides have made great progress in recent years. Transition metal oxides have great application prospects in catalysis and adsorption due to their redox activity, variable valence states and good stability. In particular, the excellent oxidation-reduction properties of these oxides are attributed to the facile gain and loss of electrons in the d orbitals of transition metal ions. According to the catalytic decomposition mechanism of O₃, it is clear that the decomposition process of O₃ involves a redox process, so transition metal oxides show excellent O₃ decomposition performance. The physicochemical properties and O₃ decomposition performance of these oxides can be controlled by tuning their morphology, crystalline phase, size, dimensions and compositions. The development of transition metal oxides with excellent catalytic decomposition activity for O_3 can significantly reduce the cost in industrial application. Therefore, transition metal oxides have become the focus of catalytic O₃ decomposition research in recent years.

 O_3 decomposition activity of transition metal oxides reported in the literature is summarized in Tables 2–4. Details on specific transition metal oxides will be discussed in the following section.

3.1. Nickel oxides

Nickel oxide is a typical p-type semiconductor, and has been widely applied in catalysis, battery and semiconductor devices, and gas sensors. Among transition metal oxides, nickel oxide has excellent properties for catalysis of various oxidation reactions. Nickel oxide catalysts have been widely applied in the reduction of NO_x (Wang et al., 2015b), oxidation of CO (Xiao et al., 2011), oxidation of various organic compounds (Wang et al., 2018a), and electrocatalysis (Hoang et al., 2020). The nickel oxide catalysts have excellent O_3 decomposition activity and moisture resistance. Alumina-supported NiO catalysts with superior O_3 decomposition activity were prepared by a simple impregnation method, and



Fig. 2. Conversion of O_3 on Ni/NiO pH-7, pH-4, and pH-1 catalysts (O_3 inlet concentration = 1000 ppm, T = 25 °C, SV = 240,000 mL/(g•hr), dry air or RH = 90%). (Gong et al., 2020b).

their excellent catalytic performance was ascribed to the formation of NiAl₂O₄ spinel and the high dispersion of active sites over the alumina surface (Dan et al., 2007). An alumina-supported nickel oxide catalyst was also prepared by a deposition oxidationprecipitation method, and the catalyst had superior and stable O₃ decomposition performance even at temperatures below zero. The high content of active and mobile oxygen introduced to the catalyst surface during the synthesis process and the formation of highly active $Ni^{4+}O(OH)_2$ during the process of O₃ decomposition were the main reasons for the excellent O₃ decomposition activity (Stoyanova et al., 2006). Recently, Gong et al. (2020b) prepared Ni/NiO heterogeneous nanostructure catalysts with high catalytic activity and water resistance by a citric acid sol-gel method (Fig. 2), and concluded that their high catalytic activity could be attributed to the synergistic effect between metallic Ni and NiO, which is beneficial to electron transfer in the catalytic process and the desorption of water under high relative humidity. In addition, Ni was also combined with other transition metals to prepare composite oxides with excellent O₃ decomposition performance. Ni-Cu-Al samples were prepared by the co-precipitation method, and the effect of nickel content on the catalytic activity of O₃ decomposition, stability and mechanical strength of the catalysts was studied. The strong synergistic effect due to the formation of a NiO-CuO-Ag₂O-Al₂O₃ solid solution oxide with the optimal

 Ni^{2+}/Ni^{3+} ratio increased the adsorbed ability of O₃ molecules on the surface of catalysts and the low-temperature reducibility of catalysts (Batakliev et al., 2017). $NiMn_2O_4$ and $NiMnO_3$ catalysts were synthesized by introducing two metal ions into sites with octahedral coordination, and the $NiMnO_3$ catalyst with ilmenite structure had better catalytic activity for O₃ decomposition than $NiMn_2O_4$, which is attributed to more active oxygen species on the surface of $NiMnO_3$ (Mehandjiev et al., 2001).

3.2. Ferric oxides

Because of its abundant natural resources and excellent catalytic properties, iron oxides have been widely studied as catalysts. Mehandjiev and Naidenov (1992) prepared an α -Fe₂O₃ catalyst by calcining Fe(NO₃)₃ solid at 500 °C for 5 hr, and studied the catalytic O₃ decomposition performance of α -Fe₂O₃ at 23–65 °C. The catalyst had superior O₃ decomposition performance in the beginning, but its activity gradually decreased as the reaction went on, which was caused by the formation of NO_x in the O_3 generator. Mesoporous two-line ferrihydrite (M2LFh), a potential material for O₃ decomposition, was prepared for the first time (Mathew et al., 2011). M2LFh, with high surface area and ferrihydrite phase content, had more iron sites at or near the surface and an enhanced rate of mass transfer to the reactive iron sites than comparable materials. The superior O₃ decomposition activity of M2LFh was ascribed to abundant unsaturated iron sites on the catalyst surface and isolated FeO_x species. There has been little application of binary iron oxides in O₃ decomposition. In later work, Fe was added as an auxiliary agent into manganese oxides to improve their O₃ decomposition performance (Chen et al., 2020; Jia et al., 2017; Lian et al., 2015; Ma et al., 2017). The enhancement effect of Fe on the performance of manganese oxides will be described in detail in the subsequent section on modified manganese oxides.

3.3. Copper oxides

Copper oxides have the advantages of low cost, environmental friendliness, abundant resources and adjustable morphology. Therefore, they have been applied in gas sensors, lithium ion batteries, catalysis and other fields. In recent years, the research group of Yunfa Chen synthesized a series of copper oxide catalysts and applied them for the catalytic decomposition of O₃. Firstly, Cu₂O catalysts with different morphologies and different particle sizes (40-968 nm) were prepared by a simple reductive solution chemistry method, and cubic Cu₂O with 40 nm particle size exhibited the highest O₃ decomposition activity, the best moisture resistance and the longest stable lifetime (Fig. 3), which was attributed to the weak adsorption of O_2^{2-} on its surface (Gong et al., 2017). Then, Cu₂O/rGO composite catalysts with excellent O₃ decomposition performance were synthesized by a simple in-situ reduction method at room temperature, and the formation of highly reactive cuprous oxide nanoparticles on rGO promoted electron density transfer and the desorption of intermediate oxygen species (Gong et al., 2018a). The Cu₂O-CuO-Cu(OH)₂ layered nanostructure was also prepared by a mild solution reduction method (Gong et al., 2018b). The formation of the layered structure was ascribed to the synergistic effects of oxidative etching and acidic etching. The O₃ decomposition activity of the catalyst with reaction time of 3 hr was superior to that of catalysts prepared with other reaction times. Subsequent XPS and EPR characterization demonstrated that its high catalytic activity was mainly due to the formation of Cu₂O-CuO-Cu(OH)₂ hierarchical nanostructures with abundant delocalized holes, which accelerated the electron transfer from adsorbed intermediate oxygen species to the catalyst surface during the O₃ decomposition reaction. To meet the requirements of industrial applications, a high yield of ultrafine Cu₂O with high O₃ decomposition performance was successfully synthesized by a simple liquidphase reduction method (Gong et al., 2020a). The amount of NaOH in the synthesis process determined the particle size of Cu_2O . Cu_2O of small particle size was beneficial to the desorption of intermediate oxygen species, which was beneficial to the O₃ decomposition reaction. The intermediate oxygen species on the above modified copper oxide catalysts are more likely to lose electrons and desorb from the active site during O₃ decomposition than for unmodified catalysts, which means that the reduction capacity of the active site shown in Fig. 1 is improved. The results can be explained by the general reaction mechanism of O₃ decomposition, and provide insight into the reaction mechanism for O₃ decomposition.

3.4. Cobalt oxides

Among the various transition metal oxides, cobalt oxides, with abundant resources and low cost, have also been applied in O_3 decomposition. Cobalt oxide catalysts were prepared by calcining at different temperatures (Tang et al., 2014). The CoO_x-350 catalyst with higher oxidation state cobalt ions (Co³⁺) and more adsorbed oxygen species had better O₃ decomposition performance than other cobalt oxides calcined at other temperatures.

3.5. Manganese oxides

The outer electron configuration of the manganese (Mn) atom is 3d⁵4s², so it has a variety of stable valence states, and forms a range of oxides (Mn₅O₈, MnO₂, Mn₂O₃, Mn₃O₄, MnO). Although there are many kinds of manganese oxides (MnO_x), the basic structural units in all MnOx are MnO₆ octahedra, in which the Mn atom is located at the center of the octahedron and the six oxygen atoms are located at each vertex. The MnO₆ octahedra can be arranged in hexagonal close packing or cubic close packing. Moreover, MnO₆ octahedra can be connected into single chains, double chains or multi-chains by sharing of common edges, and then tunnel structures, layered structures or three-dimensional structures can be constructed through sharing of common vertices between the chains. Because the MnO₆ octahedron has different stacking modes and MnOx can be composed of different chains, the crystal chemistry is complex and the crystal types are varied. Because of their low price, rich mineral resources, environmental friendliness, diverse structures, and simple preparation, MnO_x are widely employed in the field of catalysis. Catalysts for O3 decomposition have been studied for a long time. Early on, the studies mainly focused on supported catalysts and were mainly reported in patents. Among the catalysts, MnO_x are the most common active components, but there was no in-depth structure-activity relationship research. Dhandapani and Oyama (1997) impregnated various metal oxides (MnO₂, Co₃O₄, NiO, Fe₂O₃, Ag₂O, Cr₂O₃, CeO₂, MgO, V₂O₅, CuO, MoO₃) on γ -Al₂O₃, and then loaded the resulting MO_x/ γ -Al₂O₃ on cordierite foam. Then they found that MnO₂ catalysts have higher activity than those containing other metal oxides. After that, MnO_x became the hotspot of catalysis research. The catalytic O₃ decomposition activity of various MnO_x catalysts is summarized in Tables 3 and 4. Details of the research progress on MnO_x catalysts will be introduced in the following sections.

3.5.1. Supported manganese oxides

The O_3 decomposition performance of supported MnO_x catalysts was found to be influenced by the support, manganese precursor and the loading content of MnO_x . MnO_x was supported on Al_2O_3 , ZrO_2 , TiO_2 , and SiO_2 to study the effect of the support on the structure and the O_3 decomposition kinetics of MnO_x (Radhakrishnan et al., 2001). The Mn metal center on the Al_2O_3 support is mononuclear, while it grows in polynuclear forms on other supports. The support also affected the ease of charge



Fig. 3. (a) SEM images, high-resolution TEM images, and SAED patterns of Cu₂O crystals synthesized with various morphologies (a1-a3) cube, (b1-b3) octahedral, and (c1-c3) truncated octahedral (insets are corresponding TEM images); (b) O₃ conversion as a function of time over Cu₂O catalysts with different shapes at 25 °C. (O₃ inlet concentration 20 ppm, SV 60,000 mL g⁻¹ hr⁻¹); (c) O₃ catalytic decomposition on c-Cu₂O with different sizes. (O₃ inlet concentration 200 ppm, SV 60,000 mL g⁻¹ hr⁻¹). (Gong et al., 2017).

Table 3

O3 catalytic decomposition activity over supported manganese oxides^a.

Catalyst	Preparation method	O ₃ concentration (ppm)	Temperature (°C)	GHSV (hr ⁻¹)	RH (%)	Reaction time (hr)	O ₃ conversion (%)	Reaction rate (×10 ⁻⁶ mol/ (g·min))	Reference
0.44%MnO _x /AC	ISR	32	18	82,000	60	23.3	78	3.41	Jiang et al. (2013)
1.1%MnO _x /AC	ISR	21	25	82,000	60	23.3	83	2.33	Wang et al. (2014)
Mn ₃ O ₄ /CNTs	redox	50	25	$(1200 \ L \cdot g^{-1} \cdot hr^{-1})$	50	12	70	31.25	Ji et al. (2019)
5% wt% MnO/AC-700	IMP	30	25	$(1200 \ L \cdot g^{-1} \cdot hr^{-1})$	45	10	85.9	23.01	Yu et al. (2019a)
10Mn-Ti(A)	IMP	50	40	116,000	50	-	95	_	Kwon et al. (2017)
Ni-doped MnO _x /diatomite	thermolysis	16	RT	25,000	1	_	80	1.59	Rao et al. (2019)
Co-MnO _x (0.36)-Al	IMP	1000	25	$(48 \ L \cdot g^{-1} \cdot hr^{-1})$	50	12	67	23.93	Tao et al. (2019b)

^a CNTs: carbon nanotubes.

transfer from the adsorbed intermediate species to the active site, which would affect the desorption step for intermediate species (the reduction step of active sites in Fig. 1). The above conclusions also explain why the reducibility of catalysts had a great effect on their O₃ decomposition activity. MnO_x was also supported on various commercial TiO₂ materials to study the effect of the support on the structure and O₃ decomposition activity of the catalysts (Kwon et al., 2017). The Mn^{3+} ratio increased with the increase of O/Ti atomic ratio on the surface of TiO₂, and the catalyst of 10 wt% Mn with the highest Mn^{3+} ratio had the best activity for O₃ decomposition. In summary, the support will affect the electronic structure of active components on it, thus affecting the O₃ decomposition performance of the catalysts.

Because of its large specific surface area and strong adsorption capacity, activated carbon (AC) was often selected as the support material for MnO_x . Jiang et al. (2013) found that MnO_x/AC catalysts prepared with $KMnO_4$ had better performance than those prepared with manganese acetate or manganese nitrate precursors. The effect of the loading content of MnO_x on the structure and the O_3 decomposition activity of MnO_x/AC catalysts was also investigated (Jiang et al., 2013; Wang et al., 2014). Moderate loading content can

not only ensure a relatively high content of active species, but also ensure the formation of a porous structure, which is more conducive to O₃ decomposition. When the nominal loading content of MnO_x was between 0.44% and 1.1%, the MnO_x supported on the surface of activated carbon adopted a porous moss-like morphology, the oxidation state of Mn was between +2.9 and +3.1, and the crystalline phase was β -MnOOH with poor crystallinity. When the nominal load of MnOx increased to between 5.5% and 11%, the moss-like structure collapsed, most of the MnO_x formed compact nanospheres, the oxidation state of Mn increased to between +3.7and +3.8, and δ -MnO₂ appeared as the main crystalline phase. The 1.1% MnO_x/AC catalyst had the best activity, which was mainly attributed to its porous moss-like structure and relatively high Mn content. The 11%%MnOx/AC catalyst had the lowest activity, which mainly resulted from its dense MnO_x layered structure. Ji et al. (2019) immobilized amorphous MnO₂ nanosheets and crystallized Mn_3O_4 on carbon nanotubes (CNTs) by a facile redox method, and found that Mn₃O₄/CNTs, with higher reducibility and more oxygen vacancies, was more active than MnO₂/CNTs. Activated carbon (AC)-supported MnO nanoparticles with high O₃ decomposition catalytic activity were successfully prepared by the incipient

Table 4

O3 catalytic decomposition activity over non-supported manganese oxides^a.

Catalyst	Preparation method	O ₃ concentration (ppm)	Temperature (°C)	GHSV (hr ⁻¹)	RH (%)	Reaction time (hr)	O ₃ conversion (%)	Reaction rate (×10 ⁻⁶ mol/ (g·min))	Reference
MnO _x -350	precipitation	1000	25	$(120 \text{ L} \cdot \text{g}^{-1} \cdot \text{hr}^{-1})$	_	48	97	86.61	Tang et al. (2014)
MnO _x +MnCO ₃	precipitation	14	25	460,000	dry	22	85	5.84	Jia and Zhang (2018)
OMS-Ac	hydrothermal	40	30	600,000	90	6	75	13.39	Wang et al. (2015a)
α -MnO ₂	hydrothermal	14	40	$(660 \ L \cdot g^{-1} \cdot hr^{-1})$	1	_	100	6.88	Jia et al. (2016b)
α -MnO ₂ -NFs	hydrothermal	23	25	$(880 \ L \cdot g^{-1} \cdot hr^{-1})$	45	2	82	12.05	Jia et al. (2016a)
$H-\delta-MnO_2$	ion-exchanged	200	30	$(600 \ L \cdot g^{-1} \cdot hr^{-1})$	dry	11	100	89.29	Gopi et al. (2017)
H-MnO ₂	ion-exchanged	120	25	$(600 \ L \cdot g^{-1} \cdot hr^{-1})$	50	5	58	29.26	Liu et al. (2018c)
KOH-4 h	hydrothermal	50	25	$(540 \ L \cdot g^{-1} \cdot hr^{-1})$	70	10	25	5.02	Zhu et al. (2018)
N-MnO ₂	ion-exchanged	115	25	$(600 \ L \cdot g^{-1} \cdot hr^{-1})$	50	60	60	30.80	Cao et al. (2019)
Ag-MnO _x -H	hydrothermal	40	25	420,000	60	6	90	22.5	Deng et al. (2019)
NaMn3	solid-state	45	25	660,000	30	6	92.5	20.55	Hong et al. (2019)
MnFe _{0.5} O _x	hydrothermal	10,000	25	$(12 \text{ L} \cdot \text{g}^{-1} \cdot \text{hr}^{-1})$	>90	8	90	80.36	Lian et al. (2015)
Fe-MnO _x	hydrothermal	100	25	$(660 \ L \cdot g^{-1} \cdot hr^{-1})$	60	6	72	35.36	Jia et al. (2017)
$W-MnO_2(0.06)$	hydrothermal	120	25	(660 L·g ⁻¹ ·hr ⁻¹)	65	4	50	29.46	Yang et al. (2018)
V-MnO ₂ (0.15)	hydrothermal	110	25	$(600 \ L \cdot g^{-1} \cdot hr^{-1})$	55	5	50	24.55	Yang et al. (2019)
C _{0.04} (FM) _{0.96}	CAS	21	25	$(480 \ L \cdot g^{-1} \cdot hr^{-1})$	65	6.5	63	4.88	Chen et al. (2020)
$Ce-MnO_2(0.28)$	hydrothermal	50-60	25	$(1200 \ L \cdot g^{-1} \cdot hr^{-1})$	dry	3	75	36.83	Liu and Zhang (2017a)
Ce-OMS-2	hydrothermal	40	25	600,000	90	6	90	16.07	Ma et al. (2017)
$Ce-\gamma-MnO_2$	hydrothermal	40	30	$(840 \ L \cdot g^{-1} \cdot hr^{-1})$	65	6	96	24	Li et al. (2018)
MnO _x -I	facile redox	20	25	$(600 \ L \cdot g^{-1} \cdot hr^{-1})$	50	11	100	8.93	Liu et al. (2018b);
									Yu et al. (2019b)
S-300	post heat	110-120	25	$(600 \ L \cdot g^{-1} \cdot hr^{-1})$	50	5	63	32.86	Liu et al. (2019)
	treatment					_			
OMS-2-0.7	hydrothermal	500	25	585,000	90	7	90	205.36	Peng et al. (2019)
Ce-OMS-2-80%	hydrothermal	40	30	600,000	45	528	91	16.25	Yang et al. (2020a)
Ce-OMS-2 (95 °C, 14 h)	hydrothermal	40	30	600,000	90	6	93	23.25	Yang et al. (2020b)
Ce-MnO ₂	hydrothermal	110-120	25	$(1200 \ L \cdot g^{-1} \cdot hr^{-1})$	dry	5	98	99.60	Liu and Zhang (2017b)
8%AgMnO _x	СР	40	30	840,000	65	6	81	20.25	Li et al. (2019b)
CeMn ₁₀ O _x	HP	40	30	$(840 \ L \cdot g^{-1} \cdot hr^{-1})$	65	6	94	23.5	Ma et al. (2020)

^a CAS: citric acid sol-gel, HP: homogeneous precipitation.

wetness impregnation method followed by calcination under nitrogen (Yu et al., 2019a). The calcination temperature had great influence on the particle size and surface oxygen species of the catalysts. The MnO/AC-700 catalyst had the smallest MnO particle size and the most surface oxygen vacancies, which was the main reason for its superior activity. In addition, lower loading of Mn was conducive to the stabilization of catalytic activity.

3.5.2. Supported bimetallic manganese oxides

In order to further improve the performance of MnO_x catalysts, other transition metals were added to improve MnO_x (Batakliev et al., 2008; Spasova et al., 2007). A series of doped MnO_x /diatomite composites with Ni, Fe, and Al were prepared by a simple thermolysis method, and doping with Ni, Fe, and Al could tune the oxygen vacancies and the average valence of Mn on the surface of MnO_x (Rao et al., 2019). Ni-doped MnO_x had the highest content of oxygen vacancies, so it had the best catalytic activity. A series of Co-MnO_x-Al composite oxide catalysts were prepared by the co-impregnation method (Tao et al., 2019b). The addition of CoO_x with appropriate Co/Mn molar ratio improved the interactions between CoO_x and MnO_x , enhanced the reducibility of MnO_x and promoted the formation of more Mn^{3+} and Mn^{2+} (oxygen vacancies), which are the key factors leading to enhanced activity, stability and moisture resistance in the Co-MnO_x-Al catalyst system.

To sum up, it can be seen that there are many factors affecting the performance of supported MnO_x catalysts, such as the type of manganese precursor and support, the loading content and the dispersion of MnO_x , the calcination temperature, and the preparation methods. Due to the complexity of the supported MnO_x system, many factors will affect the O_3 decomposition performance and physical and chemical properties, which makes it difficult to determine the key factors affecting the O_3 decomposition performance. For the same reasons, the supported catalysts are not a good choice for the in-depth study of the O_3 decomposition mechanism. Therefore, the research focus of MnO_x for O_3 decomposition shifted from supported MnO_x to non-supported MnO_x .

3.5.3. Manganese oxides

Initially, manganese oxides were synthesized by a simple method involving calcining $MnCO_3$ or other Mn precursors, and the effects of calcination temperature on the types of MnO_x and their O_3 decomposition performance were mainly studied (Tang et al., 2014; Tkachenko et al., 2007). Later, the crystal structure and morphology of MnO_x were regulated to improve catalytic performance, and the relationship between the structure of MnO_x and the O_3 decomposition performance was established by various characterization methods. Most importantly, the active sites of MnO_x catalysts were elucidated, which provided new ideas for the design and development of MnO_x catalysts.

Cryptomelane-type manganese oxide (OMS-2), which is a special type of α -MnO₂, is a manganese oxide with a one-dimensional tunnel structure with inside dimensions of 4.6 \times 4.6 Å that is composed of MnO₆ octahedra sharing common edges (2×2) and common vertices. Mn ions exist in the skeleton structure of OMS-2 in mixed valence states $(Mn^{2+}, Mn^{3+}, Mn^{4+})$. Potassium (K) ions with the same size as the 2 \times 2 channels are located in the channels of the OMS-2 structure to neutralize the excess negative charge, and also promote the formation of 2×2 channels in the synthesis of OMS-2. This pore structure gives OMS-2 large specific surface area, high catalytic activity and good stability. OMS-2 has been applied in the catalytic oxidation of VOCs, and its redox pairs of Mn⁴⁺/Mn³⁺, weak Mn-O bonds, reactive oxygen species and superior water resistance should also be beneficial to the O3 decomposition reaction (Genuino et al., 2012; Li et al., 2010; Luo et al., 2008; Peluso et al., 2008). In 2015, OMS-2 catalysts were first applied for O₃ decomposition by Wang et al. (2015a). A series of



Fig. 4. (a) Conversion of O_3 on OMS-2 catalysts and amorphous MnO₂ material (O_3 inlet concentration 40 ppm, temperature 30 °C, relative humidity 45%, weight space velocity 600,000 hr⁻¹); (b) XRD patterns of the OMS-2 catalysts. (Wang et al., 2015a).



Fig. 5. (a) O_3 conversion vs. temperature over α -, β -, and γ -Mn O_2 (O_3 inlet concentration: 14 ppm, weight space velocity: 660 L g⁻¹ hr⁻¹); (b) O_3 conversion by different nanostructured α -Mn O_2 samples (O_3 inlet concentration 23 ppm, temperature 25 °C, relative humidity 45%, weight space velocity 880 L g⁻¹ hr⁻¹). (Jia et al., 2016a, 2016b).

OMS-2 catalysts were successfully synthesized by the hydrothermal method, and the effect of the Mn^{2+} precursor on the structure of OMS-2 catalysts and the O₃ decomposition activity under high humidity conditions was investigated. The OMS-2-Ac catalyst prepared with MnAc₂ precursor had the best activity for O₃ decomposition (Fig. 4), which is mainly attributed to its high content of Mn^{3+} . The study clearly confirmed that a high content of Mn^{3+} is the key factor in the excellent activity of these manganese dioxide catalysts. However, when the relative humidity increased from 45% to 90%, the 6 hr activity of the OMS-Ac catalyst decreased from 100% to 80%, indicating that the water resistance of the catalyst had certain limitations. Then, the O₃ decomposition performance over manganese dioxides with different crystal structures (α -, β -, and γ -MnO₂) and α -MnO₂ with different morphologies (nanofibers, nanorods, and nanotubes) was studied, and it was found that α -MnO₂ with a nanofiber morphology had the best O₃ decomposition performance (Fig. 5) (Jia et al., 2016a, 2016b). These studies confirmed again that a high content of oxygen vacancies (Mn³⁺) was beneficial for increased activity in manganese dioxide catalysts. If Mn³⁺ is formed on manganese dioxide, an oxygen vacancy will be generated to maintain charge balance, so an oxygen vacancy and Mn³⁺ are essentially the same. The content of oxygen vacancies on the α -MnO₂ catalyst declined after reacting for 99 hr under O₃ atmosphere, which is attributed to the accumulation of intermediate oxygen species on the catalyst surface. The above phenomenon suggested that the oxygen vacancies on manganese dioxide catalysts were easily deactivated. Therefore, many researchers adopted various methods to modify manganese dioxides in order to improve the moisture resistance of the catalyst and regulate the content and properties of oxygen vacancies.

3.5.4. Modified manganese oxides

Manganese oxide catalysts are subject to deactivation under wet and dry atmospheres, so modification of the oxides was attempted from three aspects: increasing the content of oxygen vacancies; improving the stability of oxygen vacancies; enhancing the moisture resistance of the manganese oxides.

The methods to increase the content of oxygen vacancies on MnO_x mainly include: regulating the content and species of various ions in the channel of MnO_x ; doping with other metallic elements; deoxidizing MnO_x by vacuum reduction. Based on the tunnel characteristics of MnO_x , the ion species and content in the tunnel of MnO_x were regulated by replacing the original ions in the tunnel with H⁺, K⁺, NH₄⁺ and Na⁺ (Cao et al., 2019; Gopi et al., 2017; Hong et al., 2019; Liu et al., 2018c; Zhu et al., 2018). The process distorted the crystal cell of MnO_x and broke the charge balance in the tunnel, resulting in larger specific surface area, more lattice defects, and significantly increased oxygen vacancies. Therefore, the above modified MnO_x showed markedly enhanced O₃ decomposition activity. Besides, Fe, Ce, W or V metal elements were doped into the catalysts in the synthesis of MnO_x , which interfered with the normal growth of MnO_x and resulted in larger surface are-



Fig. 6. (a) The conversion of O₃ on the γ -MnO₂, M- γ -MnO₂, α -MnO₂, and physically mixed α -MnO₂/ γ -MnO₂ catalysts. Conditions: O₃ inlet concentration 40 ppm, temperature 30 °C, RH = 65%, weight space velocity 840 L g⁻¹ hr⁻¹; (b) XRD patterns of the γ -MnO₂ and M- γ -MnO₂ catalysts. (Li et al., 2018).



Fig. 7. O₃ decomposition rate over MnO_x and modified MnO_x.

eas and more oxygen vacancies (Chen et al., 2020; Jia et al., 2017; Lian et al., 2015; Yang et al., 2018, 2019). In particular, the effects of Ce doping on the structure and performance of MnO_x have been widely studied. In-situ doping of Ce in the process of hydrothermal synthesis had different effects on the formation of todorokite-type manganese dioxide (T-MnO₂), OMS-2, and γ -MnO₂, respectively. When Ce was doped in T-MnO₂, the modified MnO₂ had a larger surface area, and crystal boundaries formed between MnO₂ and CeO₂ (Liu and Zhang, 2017a). Doped Ce atoms successfully replaced K^+ in the tunnel and Mn^{4+} in the framework of OMS-2 (Ma et al., 2017). The addition of Ce made the original γ -MnO₂ starting material form mixed crystals (α -MnO₂ and γ -MnO₂) with larger specific surface area (Fig. 6) (Li et al., 2018). Although the addition of Ce has different effects on the structure of these three forms of MnO₂, it leads in all cases to the formation of more oxygen vacancies (Mn^{3+}) and surface defects on the modified MnO_2 . The addition of Ce into these MnO₂ catalysts significantly improved their O₃ decomposition performance, which showed that Ce is an excellent additive for MnO₂. In addition, more surface oxygen vacancies were introduced into α -MnO₂ nanofibers by the vacuum deoxidation method, causing a change in the charge distribution and marked improvement in the adsorption of O₃ on the catalyst surface (Zhu et al., 2017). The above methods all increased the content of oxygen vacancies on the surface of MnO₂ catalysts and significantly enhanced their O_3 decomposition activity (Fig. 7).

Manganese oxides with high contents of oxygen vacancies were also synthesized by other synthetic methods. Amorphous mesoporous MnO_x was synthesized by a simple redox method, and asprepared amorphous mesoporous MnO_x and a sample calcined at 300 °C had more oxygen vacancies than MnO_x calcined at other temperatures, which provided a novel approach for enhancing the content of surface oxygen vacancies over MnO_x (Liu et al., 2018b; Yu et al., 2019b). A MnO₂ catalyst with high contents of oxygen vacancies and strong Lewis-acid sites was also prepared by calcining MnCO3 at 300 °C for 6 hr, and the catalyst had excellent O3 decomposition activity (Liu et al., 2019). In addition, the effects of hydrothermal synthesis conditions on the content of oxygen vacancies over OMS-2 catalysts were also studied. The molar ratio of KMnO₄/MnAc₂ influenced the oxygen vacancy content and the O₃ decomposition performance of OMS-2 (Peng et al., 2019). The oxygen vacancy content of the Ce-OMS-2 catalyst was tuned by altering the fill percentage and hydrothermal conditions during the hydrothermal synthesis process, and a Ce-OMS-2 catalyst with 80% fill percentage prepared at 95-100 °C and 8-24 hr had the most surface oxygen vacancies and best O₃ decomposition performance (Yang et al., 2020a; Yang et al., 2020b).

There have been a few studies on improving manganese dioxide catalysts from the perspective of enhancing their stability. The stability of oxygen vacancies was successfully improved by removing surface hydroxyl groups through calcining the catalyst

Fig. 8. Time dependence of O_3 conversion over pristine Ce-MnO₂ and Ce-MnO₂(300) catalysts at 25 °C. Conditions: O_3 inlet concentration 110–120 ppm, dry conditions, weight space velocity 1200 L g⁻¹ hr⁻¹. (Liu and Zhang, 2017b).

Fig. 9. Calculation results of adsorption energy on sp2 hybridized oxygen vacancy (sp2-O_{vac}) and sp3 hybridized oxygen vacancy (sp3-O_{vac}) on the α -MnO₂ (110) surface. (Li et al., 2020).

at 300 °C (Fig. 8), because surface hydroxyl groups can react with O₃ molecules to generate surface-adsorbed water, which will occupy the oxygen vacancies, resulting in catalyst deactivation (Liu and Zhang, 2017b). Subsequently, a similar phenomenon was also found for amorphous MnO₂ (Yu et al., 2019b). The above studies provide inspiration for improving the stability of catalysts in the future. Then, different types of oxygen vacancies on manganese oxides were identified. Two kinds of peroxide species (O_2^{2-}) were observed in in-situ Raman spectra of α -MnO₂, which might be associated with two kinds of oxygen vacancies with different chemical coordination environments (Jia et al., 2016a). Li et al. (2020) proved that two kinds of oxygen vacancies with different stability were present on the surface of MnO₂ catalyst through long-term activity tests, XPS measurements and DFT calculations (Fig. 9). Of these vacancies, sp3-Ovac (oxygen atom with sp3 hybridization) is beneficial for the adsorption of reactants and release of the product. Although the adsorption energy of sp3-Ovac for water was found to be lower than that of other vacancies and thus beneficial for water adsorption, the competitive adsorption of water molecules and O_3 molecules is inevitable for any type of oxygen vacancy. Most importantly, the deactivation effects resulting from competitive adsorption of water molecules and

 O_3 molecules are usually temporary and can be easily recovered by methods such as dehumidification. Inactivation caused by the accumulation of intermediate oxygen species is difficult to recover from and is the decisive factor in deactivation. Therefore, sp3- O_{vac} is more stable from the point of view of deactivation resulting from intermediate oxygen species aggregation, which provides guidance for improving the stability of oxygen vacancies.

The hydrophobicity of manganese dioxides could also be regulated by adding noble metals or improving the surface properties of catalysts. Deng et al. (2019) significantly improved the water resistance and humid O₃ decomposition activity of MnO_x by introducing the noble metal Ag, which was proved by water adsorption experiments. Li et al. (2020) removed the residual surface acid ions on the surface of Ce-modified γ -MnO₂ to enhance its hydrophobicity and humid O₃ decomposition by washing with deionized water (Fig. 10).

Li et al. (2019b) and Ma et al. (2020) also applied simple precipitation methods (the co-precipitation method and uniform precipitation method with urea) to precipitate manganese together with other elements (Ag and Ce) to prepare composite manganese oxides (AgMnO_x and CeMn_aO_x) with superior O₃ decomposition performance (Li et al., 2019b; Ma et al., 2020). The main reason for the excellent activity of Ag-modified manganese oxides (AgMnO_x) was the formation of the Ag_{1.8}Mn₈O₁₆ structure. The superior activity of the CeMn_aO_x catalyst is attributed to the formation of cerium-manganese complex oxides with large surface area.

3.5.5. Deactivation and regeneration mechanisms

Although MnO_x catalysts have been widely studied due to their excellent properties, they are prone to deactivation under both wet and dry atmospheres.

Manganese oxides will adsorb oxygen species after reacting under O₃ atmosphere, resulting in a higher valence state for manganese and decreased oxygen vacancies, which is the main reason for the deactivation of MnO_x under both wet and dry atmosphere (Fig. 12) (Jia et al., 2016b; Li et al., 2018; Yu et al., 2019b). Zhu et al. (2018) and Hong et al. (2019) also found that oxygen species adsorbed on the surface of MnO_x could completely desorb at high temperatures under inert atmosphere. However, whether the activity can be fully recovered depends on the regeneration capacity of the catalyst. For the OMS-2 (NaMn3) catalyst, activity was almost completely recovered (Fig. 11a). However, the activity of α -MnO₂ (KOH-4 h) could only be partially recovered (Fig. 11b). Although researchers have adopted various methods to improve MnO_x, the oxygen vacancies will still be deactivated to different degrees. The phenomenon can be attributed to the existence of different types of oxygen vacancies on the MnO_x materials (Fig. 12), which has been proved by Li et al. (2020). Therefore, oxygen vacancies need to be more precisely regulated in future studies to improve their stability.

Under humid atmosphere, in addition to deactivation resulting from the accumulation of intermediate oxygen species, the causes of deactivation are more complex and varied due to the presence of water molecules. A significant decrease in the activity of MnO_x for O₃ decomposition under humid atmosphere was observed (Jia et al., 2017; Li et al., 2018; Ma et al., 2017; Tsai et al., 1998; Wang et al., 2015a; Zhu et al., 2017). Einaga et al. (2005) found that Mn in the MnO_x/Al₂O₃ catalyst was oxidized to a higher oxidation state under humid O₃ atmosphere, and concluded that the presence of water vapor in the O₃ decomposition process was necessary for changes in the structure of MnO_x. They also found that heat treatment in an O₂ flow can completely regenerate the catalyst. A pathway for the O₃-decomposition reaction involving water molecules was proposed, in which the water molecules form surface -OH₂⁺ through electrostatic forces and hydrogen bonding, and combine with the O₃ molecules to form a six-membered ring. Then

Fig. 10. (a) Six-hour conversion of O_3 on the pH = 2, 4 and 7 catalysts under different relative humidity and space velocity 300,000 hr⁻¹. Reaction conditions: O_3 inlet concentration 40 ppm, temperature 30 °C; (b) Surface adsorption of water and residual SO_4^{2-} on pH = 2, 4 and 7 catalysts. (Li et al., 2020).

Fig. 11. (a) Effects of regeneration conditions on O₃ conversion over the deactivated NaMn catalyst. Initial O₃ concentration = 45 ± 2 ppm, temperature = 25 ± 1 °C, space velocity: 660,000 hr⁻¹; relative humidity: 30%; (Hong et al., 2019) (b) O₃ removal rate of the KOH-4 h and regenerated KOH-4 h. Temperature: 25 °C; weight space velocity: 540 L g⁻¹ hr⁻¹; relative humidity: 22%; O₃ inlet concentration 50 ppm. (Zhu et al., 2018).

this unstable six-membered ring will release HO₃•, leaving a surface hydroxyl group to continue to react with O₃ (Zhu et al., 2017). This reaction path provides a new perspective on the role of water molecules in the O₃ decomposition reaction process. However, Jia et al. (2017) proposed that the adsorption of O₃ molecules on oxygen vacancies was inhibited by the presence of water molecules, which they demonstrated by in situ Raman spectra. Next, Zhu et al. (2017, 2018), Li et al. (2018), Yu et al. (2019b), Yang et al. (2020b) proved that the deactivation of MnO_x under humid atmosphere was mainly caused by competitive adsorption of water molecules and O₃ molecules by a switching experiment with alternate use of dry gas and humid gas (Figs. 12 and 13). The deactivation effect due to humidity is usually temporary and can be easily restored by dehumidification, which is different from the deactivation mechanism resulting from the accumulation of intermediate oxygen species. However, the humidity problem is inevitable under the conditions of actual applications. Therefore, the problem of deactivation under humid atmosphere still needs to be solved, and it is still necessary to explore more effective ways to improve the water resistance of MnO_x, or to develop other new materials with excellent water resistance.

4. Other materials

Some unconventional O_3 -decomposition catalytic materials have been developed, and researchers found that some of the materials exhibited activity phenomena different from those of conventional noble metals and transition metal oxides (Table 5). The O_3 decomposition performance of anatase TiO₂ (A-TiO₂) was studied, and oxygen vacancies were the active sites for O₃ decomposition (Ding et al., 2017). The high O₃ decomposition efficiency of aluminum-reduced $A-TiO_2$ (ARA-TiO₂) is mainly attributed to higher contents of oxygen vacancies. The O3 decomposition performance of zeolites was also studied and improved, and the acid sites on these materials are the active sites for O₃ decomposition (Brodu et al., 2013, 2018; Mohamed et al., 2017). The removal mechanism of O₃ on molecular sieves mainly involves adsorption and decomposition at Lewis acid sites (LAS). The adsorption of O3 molecules and the generation of peroxide and atomic oxygen species during the decomposition process were observed by DRIFTS experiments (Brodu et al., 2013; Valdes et al., 2012, 2020). The O_3 removal capacity was found to be directly proportional to the content of LAS. The Si-Al ratio, heat treatment, transition metal modification and ammonium ion exchange all have great influence on the content and dispersion of LAS on molecular sieves (Alejandro et al., 2011; Brodu et al., 2013, 2018; Mohamed et al., 2017; Valdes et al., 2011, 2012, 2020). Among these factors, reducing the Si-Al ratio, heat treatment, ammonium ion exchange and Co modification can increase the content of LAS, and ion exchange of Fe and Cu can increase the dispersion of LAS, which all can increase the O₃ removal capacity of molecular sieves. In addition, the skeleton structure of molecular sieves also has a great influence on the O₃ decomposition performance of catalysts. The content of compensating cations in molecular sieves can be reduced by ammonium ion exchange and heat treatment, and the diffusion resistance of O_3 in the skeleton can be reduced, so the O₃ removal capacity of molecular sieves can be increased

Fig. 12. Deactivation and regeneration mechanisms under dry and humid conditions.

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O3 catalytic decomposition activity over other materials^a.

Catalyst	Preparation method	O ₃ concentration (ppm)	Temperature (°C)	GHSV (hr ⁻¹)	RH (%)	Reaction time (hr)	O ₃ conversion (%)	Reaction rate (×10 ⁻⁶ mol/ (g·min))	Reference
T500/ARA-TiO ₂	reduction	8600	25	$(6 \text{ L} \cdot \text{g}^{-1} \cdot \text{hr}^{-1})$	90	72	95	36.47	Ding et al. (2017)
Zeolite-Co	ion-exchange	9000	20	$(30 \text{ L} \cdot \text{g}^{-1} \cdot \text{hr}^{-1})$	_	5	62	124.55	Valdes et al. (2020)
MIL-100(Fe)	hydrothermal	45	25	190,000	90	12	100	66.96	Wang et al. (2018b)
LaFeO ₃	sol-gel method	1000	25	$(240 \text{ L} \cdot \text{g}^{-1} \cdot \text{hr}^{-1})$	90	4	75	125	Gong et al. (2019)
LaFe _{0.95} Ni 0.05O3	-					4	93	167.86	
p-type Si nanowires	wet chemical etching	20	25	$(240 \ L \cdot g^{-1} \cdot hr^{-1})$	-	16	90	3.39	Li et al. (2019a)

^a ARA-TiO₂: Aluminum-reduced A-TiO₂.

Fig. 14. O_3 conversion on MIL-100(Fe) at \leq 5% RH, 20% RH, 30% RH, 40% RH, and \geq 90% RH, respectively. Experimental conditions: 0.03 g catalysts diluted with 0.27 g quartz sand, O_3 concentration = 45 ppm, flow rate = 1000 mL/min, room temperature. (Wang et al., 2018b).

Fig. 13. Durability of $Ce-\gamma$ -MnO₂ catalyst. Conditions: O₃ inlet concentration 40 ppm, temperature 30 °C, weight space velocity 840 L g⁻¹ hr⁻¹. (Li et al., 2018).

(Valdes et al., 2012). Besides, the presence of a narrow pore size

similar to that of the O₃ molecule can promote the interaction

between the O₃ molecule and LAS, thus improving the O₃ removal

performance of molecular sieves (Brodu et al., 2018). The size

restriction effect of this structure is also beneficial to the O₃

decomposition reaction and the regeneration of LAS (Brodu et al.,

2018). Then, the iron-containing metal-organic framework (MIL-

100(Fe)) was synthesized, and its O_3 decomposition mechanism was different from that of porous adsorbents and transition metal oxides (Wang et al., 2018b). With the increase of humidity, the O_3 conversion of the catalyst increased, and it could achieve the complete removal of O_3 under relative humidity from 40% to more than 90% (Fig. 14). This study provides a new way to solve the water-resistance problem of catalysts for O_3 decomposition. In addition, the highly active and humidity resistive perovskite LaFeO₃ and LaFe_{0.95}Ni _{0.05}O₃ were prepared, and the two catalysts had stable structures and little O_2^{2-} accumulation, which was the main reason for their high activity under high RH (Gong et al., 2019). Li et al. (2019a) fabricated p-type Si nanowires exhibiting better O₃ decomposition activity than n-type Si nanowires, and they found that delocalized holes in p-type Si nanowires were conducive to electron release from intermediate oxygen species during O₃ decomposition, which contributed to the desorption of adsorbed oxygen species and O₃ decomposition. The above research shows that the development of other novel catalysts for O₃ decomposition also has great research prospects, which provides guidance for solving the problems of poor water resistance and deactivation of oxygen vacancies.

5. Monolithic catalysts

In order to meet the requirements of practical application processes, monolithic catalysts for O₃ decomposition have been developed. These monolithic catalysts can be applied in O3 removal from printer exhaust, air purifiers, aircraft cabins, and urban atmospheres. The main active components of many monolithic catalysts are transition metal oxides and noble metals, which are prepared by various methods, supported on various monolithic supports, and combined with different kinds of additives and binders to improve their physicochemical properties and O₃ decomposition performance. Supported catalysts composed of metal and/or transition metal oxide active components and foamed, open-pored organic polymer supports were invented, which showed superior activity for O₃ decomposition at ambient temperature (Falke and Sarauss, 1991). Dhandapani and Oyama (1997) impregnated a series of metal oxides (MO_x) on γ -Al₂O₃, and then loaded the resulting MO_x/γ -Al₂O₃ on cordierite foam (60 pores/cm² and 5.1 cm \times 5.1 cm \times 1.3 cm geometry). Under the conditions of 40 °C, linear velocity 0.7 m/s, inlet O₃ concentration 2 ppm, relative humidity 40% and gas flow rate 1.8 L/s, MnO₂ exhibited better O₃ decomposition activity than Co₃O₄, NiO, Fe_2O_3 , Ag_2O , Cr_2O_3 , CeO_2 , MgO, V_2O_5 , or CuO. Therefore, MnO_x as a superior active component is widely applied in monolithic catalysts. Natural manganese ore (NMO) was coated on honeycomb cordierite to study the effect of the dispersity of MnO_x on the O_3 decomposition performance of NMO. The number of exposed Mn sites on the catalyst surface had greater effect on the activity of catalysts than the initial oxidation state of Mn (Kim et al., 2013). Matumura et al. (2006) supported a combination of activated carbon, manganese oxide, and inorganic adhesive on a corrugated honevcomb substrate to obtain monolithic catalysts that can effectively remove the O₃ exhaust generated from printers. Cao et al. (2019), Jia and Zhang (2018) and Yang et al. (2019) loaded a series of MnO_x catalysts with excellent O₃ decomposition activity on nonwoven fabrics. These composite materials not only have the advantage of low pressure drop, but also exhibit excellent O₃ removal efficiency under the real space velocity of filtration. Therefore, these materials can be applied with O₃-producing air purifiers and real building ventilation systems. MnCO₃ coated on a ceramic monolithic support was treated under an oxidizing atmosphere at 150-400 °C for 1-5 h to obtain a series of supported catalysts comprising mostly MnO_x and a small amount of MnCO₃, and the obtained monolithic catalysts had excellent O₃ decomposition performance (Kitaguchi et al., 1993, 1994). Refractory inorganic oxides were also added during the preparation as a binder to increase the physical stability and the O₃ decomposition activity of catalysts.

In order to improve the O_3 decomposition performance of MnO_x , monolithic catalysts composed of mixed metal oxides have also been developed. A series of activated carbon-supported bimetallic oxides were deposited on cordierite foam substrates, and the Fe₂O₃-MnO₂ system had better O₃ decomposition per-

formance than other bimetallic oxide (Co₃O₄-Fe₂O₃, Co₃O₄-MnO₂, MnO₂-NiO, Fe₂O₃-NiO, Co₃O₄-NiO) systems, which was due to the interaction between MnO₂ and Fe₂O₃ (Heisig et al., 1997). Organic and inorganic binders were also introduced into the catalyst systems to increase the physical stability and activity of the monolithic catalysts. Nagano et al. (1990a, 1990c, 1990d, 1991, 1992a, 1992b, 1993a, 1993b) invented a series of Mn-based monolithic catalysts with excellent O3 decomposition performance, which were modified by adding components such as transition metal oxides, alkali metal oxides or activated carbon. Besides, they also prepared monolithic catalysts by impregnating transition metal oxides on zeolite-A and mordenite, and investigated the effects of the transition metals, molecular sieve supports, and the methods used to mix the transition metal salt solution and the support, on the O₃ decomposition activity (Nagano et al., 1990b). Fisher et al. (2004, 2007) invented a series of amorphous metal oxide catalysts containing MnO_x and, optionally, one or more of the oxides ZrO_x, $\text{SiO}_{x},\ \text{TiO}_{x},\ \text{and}\ \text{AlO}_{x}$ as active components. The mixed metal oxides were co-precipitated onto the support materials to obtain monolithic catalysts with superior O₃ decomposition performance.

Noble metals were also combined with metal oxides to enhance the O₃ decomposition activity of the monolithic catalysts. Fein and Kent (1979, 1981) assembled a cylindrical laminar catalytic device by depositing metallic silver on a copper substrate and a zirconia/manganese oxide composite, and the O₃ decomposition efficiency of the catalytic device was not affected by space velocity. Dardas et al. (2018, 2019) firstly applied an adsorbent containing a transition metal oxide or metal organic framework to obtain treated gas, and then decomposed O₃ in the treated gas with noble metal catalysts to obtain pure gas. Terui and Yokota (1992, 1993, 1994) invented a series of catalysts comprising Mn oxide, Pd metal and/or a Pd compound as the active components impregnated on a honeycomb lattice. When Mn oxide and Pd were combined and alumina sol was selected as a binder during preparation, the catalyst performance was markedly improved. Chang (1980) coprecipitated Pt, Pd, and MnO_x onto honeycomb ceramics to prepare efficient Pt/Pd/MnOx catalysts for O3 decomposition, and the activity of deactivated catalysts could be recovered after several hours of treatment in air. Carr and Chen (1982, 1983) combined platinum group metals (Pd, Rh or Pt) with nonprecious metal oxides or aluminates (CoO₂, CoAl₂O₄, CoO+Al₂O₃, Fe₂O₃ and NiO) to prepare monolithic catalysts on which platinum group metals were the main active components, which had superior O₃ decomposition activity.

To meet health standards, the environment in airplane cabins requires use of a monolithic honeycomb reactor to remove O_3 . Peak-hour O₃ levels decreased from 3–275 ppb to below 58 ppb after equipping the aircraft with O₃ decomposition catalysts (Bhangar et al., 2008). O₃ levels on the new aircraft with catalytic converters were much lower than those in cabins with older converters or without converters (Weisel et al., 2013). Therefore, new catalytic converters need to be widely developed. Currently, noble metals are the main active component applied in aircraft and can be combined with transition metal oxides to remove O₃. Heck et al. (1992) found that the catalytic efficiency of Pd for O_3 was higher than that of Pt, both in ideal pollution-free environments and in actual flight environments. Loading of Pd on an activated carbon fiber film (Pd/ACFs) was successfully developed to form a catalyst with effective O₃ conversion at temperatures of above 90 °C, exhibiting O_3 conversion of 98% at 150 °C for 37 ppm O_3 after 80 h of accelerated testing. Then, the Pd/ACFs catalyst with good O₃ removal efficiency was supported on a honeycomb reactor, and the activity test results indicated that the reactor could meet the O₃ flight requirements for 5000 hr (Fig. 15) (Wu et al., 2017). However, the pressure drop in the developed O3 converter was slightly high. Then, the configuration of the O₃ converter was optimized to

Fig. 15. (a) Honeycomb reactor body; (b) Variation of the O₃ concentration with time at different flow velocities and temperatures. (Wu et al., 2017).

reduce the maximum pressure drop to 1.9 kPa while still achieving an O₃ removal efficiency of 99% (Wu et al., 2019). Sheet-shaped α -MnO₂ with superior ultra-low-temperature O₃ decomposition activity was successfully developed, to assist the design of O₃ converters for conventional aircraft (Chen et al., 2018). The excellent performance of the catalyst is mainly attributed to the more abundant surface oxygen vacancies and the easier charge transfer between the intermediate oxygen species and the active sites.

From the aspect of O_3 removal in the atmosphere, a noble metal such as Pt or Pd is usually needed as the active component to improve the removal efficiency in practical application of monolithic catalysts. Wu and Kelly (1998) found that a Pd-only catalyst had superior O₃ decomposition efficiency and resistance to water vapor compared to Pt, Pd/Ni and Ni catalysts, and coated the catalyst on vehicle radiators to clean the air on city roads. Allen et al. (2004) prepared a series of Pt/Al₂O₃ and Pd/Mn/Al₂O₃ catalysts and coated them on vehicle radiators, which could effectively eliminate 8–50% of O_3 in the atmosphere. From the perspective of practical application, the researchers improved the adhesion properties of the catalysts by adding clay and/or silicone adhesives to make them adhere better to motor vehicle radiators (Heck and Hoke, 2001). A series of manganese-based monolithic catalysts $(Pd-MnO_{x}/SiO_{2}-Al_{2}O_{3})$ with high catalytic decomposition of O_{3} in ground-level air were developed (Ren et al., 2014; Yu et al., 2009a, 2009b). The catalysts with MnO_x content of 80%–90% had excellent activity and anti-deactivation ability. Under the space velocity of 660,000 hr^{-1} , the temperature at which O₃ is completely converted is 45-50 °C, which can meet the requirements of instantaneous contact temperature between air and the water tank of vehicles during operation. Under the conditions of 45 °C and 510,000 hr^{-1} , the monolithic catalyst could maintain O_3 conversion of over 90% for 95 hr, indicating that the catalyst had high ability to resist deactivation.

At present, the O₃-decomposition catalysts with excellent performance and application prospects mainly include Pd and MnO_x. Pd catalysts have excellent water resistance, anti-inactivation ability and long-term stable activity, but their price is excessive and the actual application cost is high. The cost of MnO_x catalysts is low, and their initial performance is excellent, but deactivation during long-term use and the poor water resistance are persistent problems. Therefore, a MnO_x catalyst with stable activity and excellent water resistance remains to be developed from the perspective of application prospects. It is also desirable to develop a mild and simple method of regenerating MnO_x.

6. Conclusions and outlook

Great efforts have been made to develop catalysts with high O_3 decomposition activity at room temperature, and even low temperature, high humidity, and high space velocity. Supported

noble metal and transition metal oxides are two common types of catalysts with excellent performance. Because of their low cost, transition metal oxides have been widely studied, among which manganese oxides (MnO_x) have the best O_3 decomposition performance. Mn^{3+} (oxygen vacancy) was identified as the active site on MnO_x for the catalytic decomposition of O₃. However, MnO_x catalysts are deactivated under wet and dry atmospheres, so researchers have worked to improve MnO_x from the following aspects: increasing the content of oxygen vacancies on MnO_x; enhancing the moisture resistance of MnO_x; improving the stability of oxygen vacancies on MnO_x. Under dry and humid atmospheres, the inactivation of MnO_x is due to the accumulation of intermediate oxygen species and competitive adsorption of water molecules and O3 molecules, respectively. Reactivation of deactivated catalysts can be achieved by treatment at high temperature under an inert atmosphere. However, the regeneration ability of catalysts is different due to differences in their physical and chemical properties. Based on the previous research results and shortcomings, the following research directions are suggested:

- (1) In recent years, studies on increasing the content of oxygen vacancies on the MnO_x have been abundant. The following methods have mainly been applied to increase the content of oxygen vacancies on MnO_x catalysts: regulating the content and species of various ions in the channel of MnO_x ; doping with other metallic elements; and deoxidizing MnO_x by vacuum reduction. However, the internal mechanism of different methods to increase the content of oxygen vacancies still needs to be further studied, which will be helpful to provide theoretical guidance for the improvement of catalysts in the future.
- (2) There are few studies on improving the stability of oxygen vacancies and the hydrophobicity of MnOx, and reliable methods to solve the problem of inactivation of MnO_x under dry and humid atmosphere have been not discovered. Therefore, more efforts should be made to solve the above problems from the perspective of practical application. Improving the stability of oxygen vacancies can be achieved by regulating the coordination environment of Mn atoms to accelerate the desorption of intermediate oxygen species. Improving the water resistance of MnO_x can be attempted by adding noble metals or introducing hydrophobic groups on the surface of MnO_x. In addition to developing catalysts with excellent properties that fundamentally prevent catalyst deactivation, some regeneration methods have already been successfully developed to solve the deactivation problem. Future research should also be aimed at developing gentler and easier regeneration methods for practical application.
- (3) Among noble metals, Ag and Pd have excellent water resistance and O_3 decomposition activity, so there has been

much research on them. However, the reasons for the differences in O_3 decomposition performance of different noble metal components (Ag, Pd, Au, and Pt) and the various factors influencing the O_3 decomposition performance of each noble metal remain to be studied.

- (4) In addition, new types of O_3 decomposition catalysts (metalorganic framework and perovskite) with superior activity and humidity resistance have been successfully developed, which provides a new direction for follow-up research on O_3 decomposition catalysts. New types of MOFs with excellent water resistance and O_3 decomposition activity can be further developed.
- (5) There is still a lack of definite evidence to clarify the detailed O_3 decomposition process and the properties of intermediate species on noble metal and transition metal oxide catalysts, which impedes the further understanding of the O_3 decomposition reaction to a large extent and is not conducive to obtaining theoretical guidance for the development of high-efficiency catalysts. With the development in-situ characterization methods and DFT calculations, more efforts should be devoted to study of the mechanism of O_3 decomposition in detail.
- (6) From the perspective of practical application, the combined control of O_3 and other indoor and outdoor pollutants is also a research direction. Because of its strong oxidizing ability, O_3 can provide intermediate oxygen species with stronger oxidizing ability, which may be conducive to the oxidative decomposition of pollutants such as VOCs. This also puts forward the requirements for the development of multi-effect catalysts with excellent performance.

Declaration of Competing Interest

None.

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