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Simple Thermocatalytic Oxidation Degradation of VOCs

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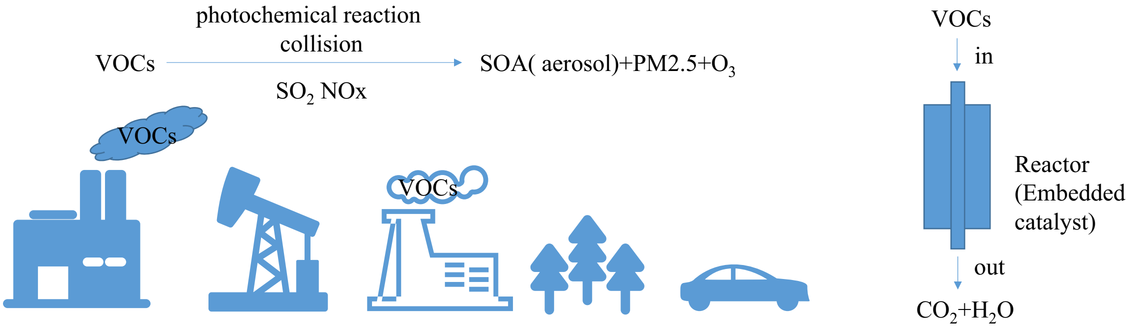
Abstract

Volatile organic compounds (VOCs) are a class of pollutants with many sources and harm humans and the environment. The application of noble metal catalysts and metal oxide catalysts in thermal catalytic oxidation degradation of VOCs was reviewed in this paper. Furthermore, the challenges of degradation of VOCs by thermal catalytic oxidation are listed and the prospects are put forward.

Graphic Abstract



Keywords VOCs catalytic oxidation · Supported noble-metal catalyst · Metal-oxide catalyst · Toluene degradation · MnO_x

1 Introduction

Volatile organic compounds (VOCs) are typical atmospheric pollutants. The World Health Organization defines VOCs as the general term of volatile organic compounds with a melting point lower than room temperature and the boiling point between 50 and 260 ℃ [1]. VOCs are a class of pollutants with numerous sources, involving almost all aspects of production and life. Industrial fixed sources, domestic emission source, and natural emission sources are regarded as the main emission. General industrial production, such as the Petrochemical industry, production of pesticides, pharmaceuticals, dyes, and so on are important components of industrial fixed sources. Domestic emission source mainly includes vehicle exhaust, kitchen fume, new house decoration, straw burning, etc. Natural emission source refers to volatile organic compounds (VOCs) from plants, especially in summer when vegetation grows vigorously. In addition,

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human skin is also an important source of VOCs, which can be identified by Zou et al. [2] that 37 kinds of VOCs could be emitted from humans' skin, with the emission of 0.8–86.3 μg/h. At present, there are more than 350 kinds of VOCs [3], most of which are toxic or pungent odors, which are extremely harmful to the environment and humans [4]. The main hazards of VOCs to the environment are the formation of complex pollutants and haze, and the hazards to humans are the effects of the respiratory system, skin, eyes, liver, and kidneys, which are teratogenic, carcinogenic, and mutagenic.

Zheng et al. [5] established three scenarios to forecast China's VOCs emissions in 2020, 2030, and 2050 based on the historical trends of China's VOCs emissions, population density, and geographic trends. The data shows that no matter what the model is, the emissions of VOCs are huge. Therefore, it is very important to take necessary measures to control VOCs. Countries around the world have issued relevant laws and regulations on the control of VOCs, and many countries have reached many consensuses. The Göteborg Agreement signed by EU member states is a good example. China's emission control of volatile organic compounds started relatively late, but it has gradually formed a complete system. The: 13th 5-Year Comprehensive Plan for Energy Conservation and Emission Reduction: (2017) stipulates that the total VOCs emissions by 2020 should be reduced by more than 10% compared with 2015. The treatment of VOCs is a systematic project, which should combine pollution source reduction, process control, and end treatment. The current industrial production could not able to fundamentally avoid the generation of VOCs, so the end treatment technology, which is regarded as the most effective processing method, has attracted the attention of researchers. The existing end treatment technologies are shown in Fig. 1 [6].

Source control can reduce VOCs emissions from the source. The improved reaction device can effectively prevent the escape of volatile organic compounds [7]. End treatment (additional control technology), such as membrane separation, catalytic combustion, etc. can effectively degrade VOCs.

Membrane separation [8] technology can selectively purify and enrich different VOCs. The advantage of membrane separation is simple operation, but high cost, poor stability, and limited flux, making it unsuitable for large-scale industrial applications. Absorption and adsorption [9, 10] are suitable for the removal of indoor VOCs, but these methods have inevitable shortcomings, such as difficulty in adsorbent treatment and easy to cause secondary pollution [11]. Low-temperature condensation [12] consumes energy and is only suitable for the treatment of volatile solvents. Biodegradation [13] has been regarded as an environment-friendly technology with low energy consumption and almost no secondary pollution. But this approach is extremely sensitive to the environment, even small change in temperature and concentration can lead to huge difference. Furthermore, biodegradation has a high degree of selectivity and the removal efficiency of hydrophobic VOCs is very low [14], and it is only effective for low weight and high solubility hydrocarbons. Thermal oxidation is another common technique to degrade VOCs, which is convenient and efficient but not economical. It requires a high reaction temperature, usually more than 800 ℃, and produces toxic intermediate products when incompletely burned. The non-thermal plasma [15]

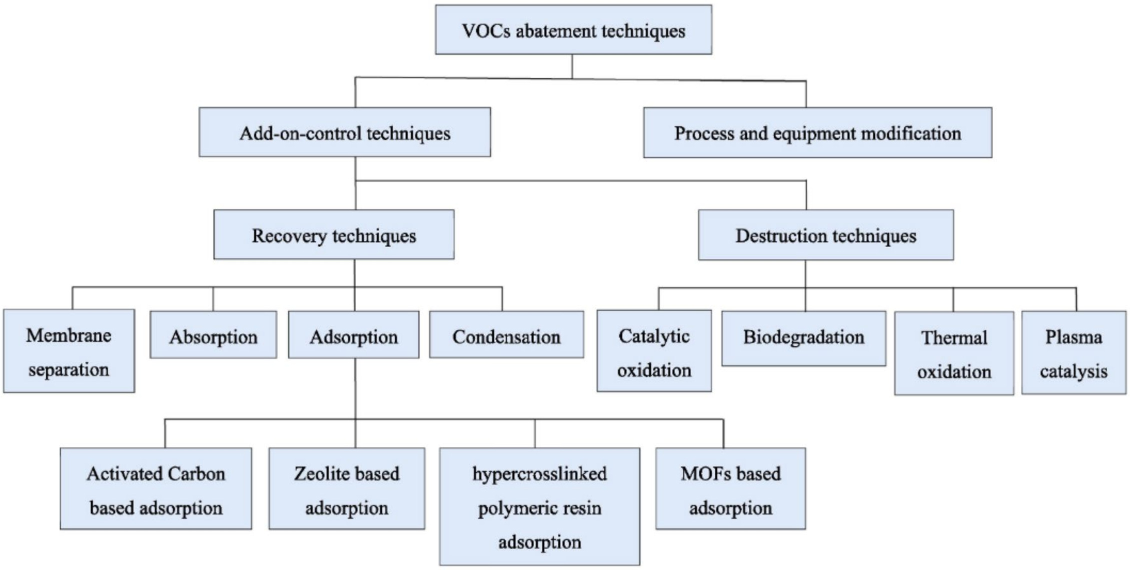

Fig. 1 VOCs removal method [6]

degradation of VOCs can achieve high-efficiency degradation of VOCs in a relatively short period of time and is generally considered to be a promising method in traditional degradation technologies. But its energy utilization rate is relatively low [16], and toxic intermediates will be produced. Photocatalysis [17] can overcome the barrier of activation energy without increasing the temperature [18], so the optically driven reaction can be carried out under mild conditions. Therefore, photocatalysis is regarded as an economical treatment method with a broad spectrum activity of activity. However, the quantum yield of photocatalysis is not high and the oxidation capacity is relatively limited. At present, delaying or avoiding the recombination of electron–hole [19], and improving the response range of photocatalysis in the visible light region [20] are regarded as keys to solving the problem of photocatalysis. Photothermal (PT)c [21] catalysis, including photocatalysis and thermal catalysis, can complete the oxidation of VOCs at a low temperature. Moreover, with the help of the photoinduced plasma effect of noble metals, the required potential barrier can be reduced, thus reducing the reaction energy consumption, but such catalysts are easy to be deactivated [22].

Compared with the above-mentioned technologies, thermal catalytic oxidation has significant advantages such as economic efficiency, excellent stability, and relatively low temperature required in the degradation process, which rarely causes secondary pollution. It is an environmentally friendly treatment method and the primary choice for industrial degradation of VOCs [23–25]. Therefore, thermal catalytic oxidation is worthy of further study.

Herein, firstly, the three mechanisms of thermal catalytic oxidation degradation of VOCs were systematically summarized. Then the supported noble metal catalysts and metal oxide catalysts were introduced in different categories. The supported Pt catalysts and MnO_x were selected as the typical representatives of the two types of catalysts. Finally, the prospects and challenges of thermal catalytic oxidation for VOCs elimination were summarized.

2 Thermal Catalytic Oxidation Mechanism

Thermocatalytic oxidation to degrade VOCs generally meet the following mechanisms [26]:

(I) Mars van Krevelen (MVK) Mechanism

The MvK mechanism is the most common, and there are many reactions to satisfy this mechanism [27, 28]. When the reaction degrades VOCs according to the MvK mechanism, there may be two different reactions paths [29]. One is to oxidize VOCs through surface lattice oxygen, leaving oxygen vacancies. Then, the oxygen in the gas phase will replenish the depleted lattice oxygen, thereby generating active oxygen again. Another approach is to degrade contaminants by using adsorbed oxygen on the surface. The former approach is related to the amount of lattice oxygen, while the activity of the latter approach is closely related to the amount of oxygen adsorbed on the surface.

(II) Eley Rideal (E–R) Mechanism

The E–R mechanism is a reaction involving only one active state. The E–R mechanism can be summarized as the reaction between the adsorbed state and non-adsorbed state. The reactions that follow the E–R mechanism in VOCs degradation occur between adsorbed pollutants and gaseous oxygen or between adsorbed oxygen species and pollutants in the gas phase. The reaction model of this mechanism can be expressed by the following equation:

(i) Form adsorption state: $A + c = A{-}c$

(ii) Products generated: $A{-}c + B = P$

where A and B are reactants, c is the active species, A−c refers to the adsorption state, and P is products.

(III) Langmuir Hinshelwood (L–H) Mechanism

Corresponds to the E–R mechanism, the L–H mechanism can be simply summarized as a dual-active state mechanism, that is, both reactants participate in the reaction in an active state. The L–H mechanism can be summarized by the following equation:

(i) Form adsorption state: $A + c = A - c$

$B + c = B - c$

(ii) Products generated: $A{-}c + B - c = P$

where A and B are reactants, c is the active material, A−c and B−c are adsorbed reactants, and P is the product. For VOCs degradation reactions that follow the L–H mechanism, both pollutants and oxygen species exist in an adsorbed state.

The reaction schematic diagram of the above three mechanisms is shown in Fig. 2 [1, 30].

Thermocatalytic oxidation at present can be divided into supported noble metal catalysts and metal oxide catalysts. Both of them have different characteristics for the degradation of VOCs.

3 Supported Noble-Metal Catalysts

The supported noble metal catalyst is the earliest catalysts used for industrial waste gas treatment due to its good catalytic activity. The balance between excellent activity, high cost, and poor thermal stability of noble metal catalysts has always been a research hotspot in this field. To solve the above problems, many research groups have done a lot of work in this field. Table 1 lists the properties of noble metal catalysts used to degrade common VOCs. Only benzene, toluene, and xylenes (BTX) are selected as representative VOCs in this table.

The following is a list of efforts to ameliorate the adverse factors of eliminating VOCs on supported noble metal

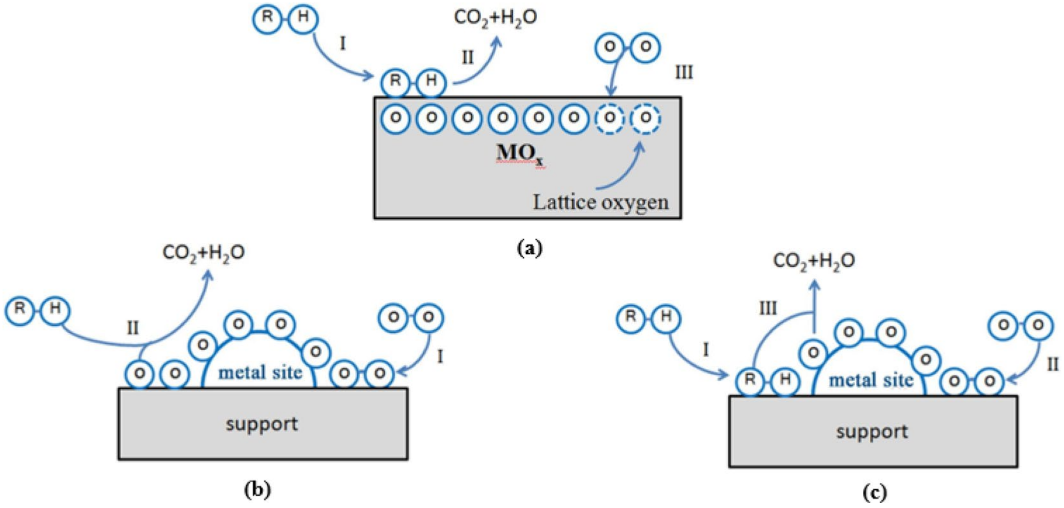

Fig. 2 Schematic diagram of mechanism [1, 30]; **a** MVK mechanism; **b** E–R mechanism; **c** L–H mechanism

Table 1 Associated properties of common noble metal catalysts used for BTX elimination

catalysts	M/wt% (M = Noble metal)	VOC	C/ppm	hourly space velocity mL/(gh)	Conver-sion rate/℃	stability	Ref
Pt-SDC-13	0.5	Toluene	1000	30,000	$T_{90\%}=228$	30 h, 230 ℃	[31]
Pt/3DOM Mn_2O_3	2.3	Toluene	1000	40,000	$T_{90\%}=194$	60 h, 200 ℃	[32]
Pt@ZSM-5	0.5	Toluene	1000	60,000	$T_{98\%}=176$	360 h, 230 ℃	[33]
Pt/CeO_2-1.8	0.25	Toluene	1000	48,000	$T_{90\%}=143$	60 h, 155 ℃	[34]
Pt/ZSM-5-OS	0.72	Toluene	1000	120,000	$T_{90\%}=164$	60 h, 175 ℃	[35]
Pd/MgO-Al_2O_3	0.5	Toluene	500	24,000	$T_{90\%}=209$	30 h, 230 ℃	[36]
Pd/Mn_3Ce_2-300	0.5	Toluene	1000	40,000	$T_{90\%}=185$	30 h, 185 ℃	[37]
Au/3DOM $LaCoO_3$	7.63	Toluene	1000	20,000	$T_{90\%}=202$	100 h, 200 ℃	[38]
Pt/Al_2O_3-11	0.8	Benzene	2800	32,000	$T_{99\%}=145$	100 h, 165 ℃	[39]
Pt/LaSPC (0.5:1)	0.2	Benzene	1000	20,000	$T_{100\%}=200$	100 h, 190 ℃	[40]
Pd/AlNi-PILC	0.2	Benzene	1000	36,000	$T_{100\%}=250$	1000 h,240 ℃	[41]
Pd–Pt(1:1)/10%Ce/γ-Al_2O_3	0.2	Benzene	1000	20,000	$T_{100\%}=200$	1000 h,190 ℃	[42]
Ag/Co_3O_4	2.0	Benzene	100	120,000	$T_{90\%}=201$	90 h, 202 ℃	[43]
Ag/NiOx-MnO_2	5.0	*o*-xylene	500	6000	$T_{100\%}=190$	60 h, 190 ℃	[44]
Pt/Fe_2O_3	0.22	*o*-xylene	1000	40,000	$T_{90\%}=215$	30 h, 230 ℃	[45]
Au–Pd–0.22Fe/3DOM Mn_2O_3	1.94	*o*-xylene	1000	40,000	$T_{90\%}=213$	60 h, 210 ℃	[46]
Au/*meso*-Co_3O_4	6.5	*o*-xylene	1000	60,000	$T_{90\%}=162$	60 h, 200 ℃	[47]

catalysts. Pt is mainly selected as an important introduction object.

3.1 Supported Pt Catalysts

Researches have shown that the degradation pathways of VOCs on various supported Pt catalysts are basically similar (Fig. 3a–c) [48–50]. The degradation of VOCs is realized by the synergistic effect of hydroxyl on the carrier surface and oxygen species adsorbed on Pt, such as the elimination of formaldehyde. Therefore, preparing a suitable carrier and improving the dispersibility of precious metal particles are of great help to catalyst activity.

To enhance the sinter-resistance and coke-resistance of supported noble-metal catalysts, Liu et al. [33] prepared Pt@ZSM-5 sandwich structure by loading monodisperse Pt onto ZSM-5 by impregnation method. The Pt clusters dispersed in the interlayer greatly improved the anti-sintering ability of the active components, which effectively enhanced the comprehensive performance of the catalyst. Pt@ZSM-5

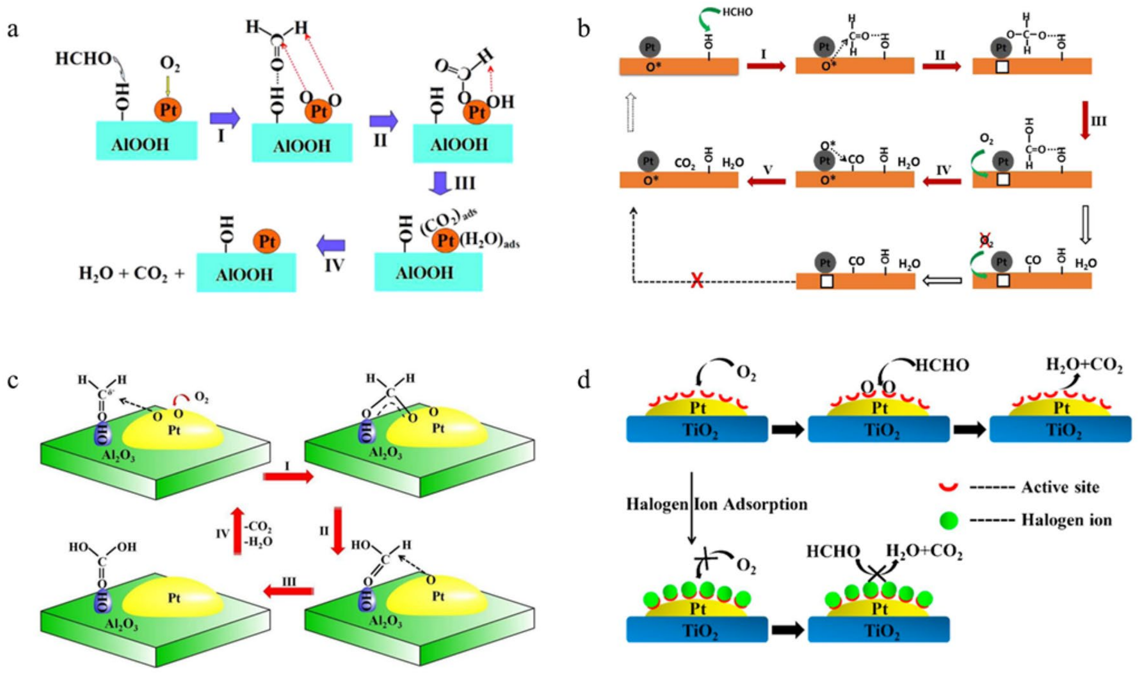

Fig. 3 Possible pathways for different Pt-based catalysts to degrade formaldehyde [48–50, 53]

Nanosheet can catalytic combustion of toluene at low temperature ($T_{5\%} = 146$ ℃, $T_{98\%} = 176$ ℃), and completely oxidize toluene at 230 ℃ for more than 360 h.

Adjusting the interaction between active components and supports is usually regarded as an effective approach to enhance the adsorption/desorption capacity of catalysts. Appropriate interaction can not only enhance the stability of catalysts but also ensure the high activity of noble metal catalysts [51]. Xu et al. [48] prepared Pt@AlOOH nanosheets by adjusting the type of support. This catalyst could degrade formaldehyde at room temperature and exhibited better performance than similar catalysts (Pt/Al_2O_3 and Pt/TiO_2). Sergio et al. [52] prepared different types of carbon nanomaterials including carbon nanocoatings and carbon nanofibers and studied the catalytic performance of such materials to degrade BTX when loaded with Pd or Pt. The strong interaction between the carbon nanomaterials and the active ingredients greatly improves the activity and stability of the catalyst. The catalytic performance of the above catalysts was evaluated using BTX and acetone as target pollutants. It was found that the catalyst could completely oxidized VOCs to CO_2 at temperatures below 190 °C. Sun et al. [49] also adjusted the interaction between the active ingredients and the carrier by changing the structure of the carrier to improve the overall activity of the catalyst. They prepared an ultra-thin Bi_2WO_6 nanolayer by a simple hydrothermal method, and loaded a small amount of Pt nanoparticles on it, effectively reducing the temperature of formaldehyde degradation to room temperature.

In addition to the above methods, selectively exposing specific faces of the support is also a favorable means to regulate the interaction between the carrier and active component of the catalyst. Zhu et al. [50] effectively regulated the activity of supported Pt catalyst by directional exposure the (110) crystal plane of the layered Al_2O_3 support, which was beneficial to the adsorption of the reactants and did not hinder the desorption of products, and finally realized the degradation of formaldehyde at room temperature.

Catalyst poisoning is one of the adverse reasons for the deactivation of supported noble metal catalysts, so improving the toxicity resistance of catalysts plays a decisive role. Zhu et al. [53] proposed a possible mechanism of halogen poisoning of noble metal catalyst by exploring the effects of different halogen elements on the degradation of formaldehyde by $Pt\text{-}TiO_2$. The mechanism indicated that halogen occupied the active site on the surface of the noble metal catalyst which hindered the reaction. The mechanism can be explained by Fig. 3d [53].

The competitive adsorption of water molecules and VOCs on the catalyst surface is an important reason for catalyst deactivation [54]. It is generally believed that ameliorating carriers and noble metal nanoparticles is an effective measure to improve the water resistance of catalysts. Song et al. [55] modified NaY with KNO_3 to support Pt, which improved the water resistance of the noble metal catalyst, greatly improved the stability of the catalyst. K-Pt/NaY directly promoted the reaction of active OH with HCHO, and Pt with a good low-temperature reduction on the catalyst ensured the rapid conversion of H_2O to OH, which could supplement the consumed OH. Therefore, K-Pt/NaY zeolite possessed satisfactory catalytic performance and water resistance, which maked it possible to degrade formaldehyde in moist environment at room temperature. The significance of the above work is also to change the factors (humidity) that easily deactivate the catalyst into favorable factors. In addition to modifying the surface electronic structure of the catalyst, regulating the spatial structure of the support and precious metals is also an effective measure. Pei et al. [32] partially embedded Pt nanoparticles into 3D Mn_2O_3. Due to the interaction between Pt nanoparticles and Mn_2O_3, the stability of the catalyst was greatly improved.

For the supported catalysts, the size of the supported metals has a great influence on the activity of the catalysts. Sun et al. [34] synthesized Pt nanoparticles with different sizes by polyol reduction method and loaded them on CeO_2. For Pt/CeO_2, the dispersion degree of Pt on the supported surface is inversely proportional to the particle size. The contents of Ce^{3+}, oxygen vacancies, and Pt-O-Ce bonds are proportional to the particle size. Therefore, appropriate particle size can make the catalyst performance tend to be optimal. Among them, Pt/CeO_2-1.8 showed excellent stability and certain water resistance. Under a slightly humid environment (Water Vapor = 5 vol%), Pt/CeO_2-1.8 complete combustion temperature of toluene can be reduced to 155 ℃ and can work continuously for 120 h. Wang et al. [56] evaluated the catalytic activity of Pt nanoparticles with various sizes on TiO_2 support and found that the optimal performance could be achieved when the size of Pt was 1.9 nm. Pt-1.9@TiO_2 could completely oxidize toluene and acetone at a temperature lower than 220 °C and could maintain good stability even under high water vapor content (Water Vapor = 5–10 vol%).

The activity of supported noble metal catalysts is also closely related to the properties of the support. The three-dimensional porous material [57] (3DOM) with many merits, such as good structure, good stability, large surface area, and suitable pore size are commonly used as support for noble metal nanoparticles besides to directly used for VOCs elimination. The interaction of 3DOM and precious metal nanoparticles can enhance the integral performance of the catalyst. Zhang et al. [58] used the hierarchical porous mordenite zeolites (HPMOR) treated with acid and alkali as a carrier and loaded the active component Pt. Pt/HPMOR effectively promoted the contact between active components and reactants, reduced the mass transfer resistance of reactants and products to a certain extent, and making Pt/HPMOR ($T_{10\%} = 152$ °C, $T_{50\%} = 175$ °C, $T_{90\%} = 190$ °C) had superior catalytic performance than Pt/MOR ($T_{10\%} = 165$ °C, $T_{50\%} = 195$ °C, $T_{90\%} = 210$ °C).

Therefore, choosing appropriate supports can not only improve the thermal and sintering resistance ability of noble metal catalysts but also improve the activity of the catalyst and reduce the cost.

3.2 Supported Au Catalysts

Gold has good corrosion resistance, stability, electrical conductivity, and thermal conductivity. In addition to being used as an international reserve, it is often used in industry and science, and technology. In the present study, gold is no longer a precious metal without catalytic activity. Many studies have shown that Au has good catalytic activity when it exists in the form of nanoparticles. Au has been widely used as an active component loaded on different carriers. With the development of research, the application of Au supported catalysts has been expanded. In addition to low-temperature oxidation of CO and epoxidation of propylene, supported Au catalysts are also extensively used to degrade VOCs.

Liu et al. [47] prepared three-dimensional mesoporous material Co_3O_4 with high specific surface area ($S_{BET} = 91–94$ m^2/g) by template method, and uniformly deposited Au nanoparticles with the size of 1–5 nm inside the pores to obtain *x*Au/*meso*-Co_3O_4 (x = 3.7–9.0 wt%). Through the evaluation of its degradation performance of BTX, it was found that 6.5Au/*meso*-Co_3O_4 had a large specific surface area and high concentration of adsorbed oxygen (Oads), which could degrade 90% benzene, toluene, and xylene at 189, 138, and 162 °C, respectively. Using CMC-48 as template, Ying et al. [59] synthesized mesoporous CeO_2 with a larger specific surface area and smaller particle size ($S_{BET} = 222$ m^2/g, D = 3.7 nm) than nanocrystalline CeO_2 ($S_{BET} = 53$ m^2/g, D = 9.3 nm). The dispersion of Au on CeO_2-48 was much higher than that on CeO_2-P, and its catalytic performance for benzene degradation was better. Chen et al. [60] prepared Au/α-MnO_2 by redox etching precipitation method. The Au nanoparticles in the catalyst were close to monoatomic distribution, which greatly improves the utilization rate of precious metals, and can degrade low-concentration formaldehyde at low temperatures (WHSV = 60,000 mL/(g h), $T_{100\%} = 75$ ℃). The research group also used the same method to disperse single-atom Au onto a particular surface of CeO_2 and applied it to removal of Cl-containing gas at low-temperature [61]. The results showed that Au/CeO_2 has good stability and catalytic activity, and can resist Cl poisoning to a certain extent.

The size of the active component and the type of the carrier are two major factors affecting the catalyst supported Au. Therefore, the preparation of appropriate Au nanoparticles and the selection of an appropriate carrier are of great help to improve the catalyst activity.

3.3 Supported Ag Catalysts

Supported Ag catalyst is a relatively cheap noble metal catalyst. Therefore, using Ag to replace Pt and Au is of great help to reduce the cost. Chen et al. [62] synthesized Ag/TiO_2 catalyst by loading Ag onto TiO_2 with different crystal forms. Ag/TiO_2 presented multiple active centers (surface oxygen vacancies, Ag_2O, Ag). The multiple active centers had a synergistic effect and can effectively promote the oxidation of formaldehyde. Qin et al. [63] loaded different contents of Ag species on linear MnO_2 to promote the deep oxidation of toluene. Among them, 4% Ag/MnO_2 showed the best catalytic activity, and the complete combustion of toluene could be achieved at 220 ℃. Liu et al. [64] loaded a small amount of Ag on CeO_2 by impregnation method, which improved the mobility of oxygen in the catalyst, and the catalytic activity was greatly improved compared with pure CeO_2. The comparison of the catalytic activity of naphthalene degradation, it was found that the temperature of complete combustion of naphthalene by Ag/CeO_2 was 240 °C, while $T_{100\%} = 300$ °C by pure CeO_2. To improve the mechanical strength and anti-poisoning of the catalyst, Zhu et al. [65] supported Ag nanorods on MnO_2 cordierite. The catalytic activity evaluation of degradation of toluene, ethyl acetate, and chlorobenzene showed that 90% conversion could be obtained at 275 °C, 217 °C and 385 °C, respectively. The catalyst exhibited good mechanical strength and catalytic performance at relatively high space velocity, indicating that the catalyst possessed the potential for industrial application.

In the above studies, Ag and its oxides were directly used as active ingredients and participated in the catalytic oxidation of various VOCs. However, Lin et al. [66] did not use Ag or its oxide as an active component directly involved in the degradation reaction. The research group used $AgNO_3$ as a catalyst in the synthesis process to synthesize α-MnO_2 nanospheres with a large number of oxygen vacancies and a large specific surface area. The X-ray diffraction (XRD) results of the catalyst showed that the catalyst did not contain anything Composition related to Ag. The research team believed that there might be two reasons for the lack of Ag in the XRD characterization. One possibility was that $AgNO_3$ only acts as a catalyst for the synthesis of mesoporous α-MnO_2 nanospheres, so it did not enter the product. Another possible reason was that the Ag content in the product was too small to be detected by the instrument. The microsphere α-MnO_2 catalyst synthesized by $AgNO_3$ can completely oxidize toluene in a relatively humid environment. This study proves that the silver reagent involved in the synthesis of the catalyst can also improve the activity of the catalyst to a certain extent.

3.4 Other Precious Metal Catalysts

Except for Pt, Au, and Ag, other precious metal catalysts [67–71] are widely used in VOCs degradation. In the degradation reaction of VOCs, a variety of precious metals are usually combined to achieve complete degradation of pollutants at low temperature [42, 72, 73]. Catalysts containing many kinds of noble metals can achieve complete combustion of VOCs at lower temperatures and their catalytic activity is greatly improved than that of a single noble metal catalyst, but their cost is also higher.

To save cost, a single-atom catalyst emerged, which can achieve the maximum atomic utilization, and reduce the load of precious metals. The catalytic activity and selectivity of monoatomic noble metal catalysts are greatly improved compared with nanometer catalysts due to their high surface energy and quantum size effect [74, 75]. In the process of single-atom catalysis, the agglomeration of precious metals is a common inactivation pattern, so it is very important to develop effective strategies to avoid or slow down the agglomeration.

Hou et al. [76] prepared a monatomic Pd-Co catalyst that could degrade benzene efficiently (GHSV = 40,000 mL/(g h), T90% = 250 °C). Pd and Co in the catalyst were dispersed on γ-Al_2O_3 in the form of single atom, and no obvious deactivation occurred in the continuous reaction for 25 h on-stream (GHSV = 40,000 mL/(g h), T = 250 °C). Moreover, the sulfur resistance of Pd_1Co_1/Al_2O_3 in the presence of SO_2 (25 ppm) was tested, and it was found that the catalyst with the double active site also showed excellent SO_2-resistant ability. Mar et al. [77] has prepared a thin film structure with nano-cavities by atomic layer deposition (ALD) to stabilize the single atom Pd1 catalyst. The existence of nano-cavities greatly improves the stability of single-atom catalysts. But as the reaction temperature increases, single-atom catalysts tend to aggregate to form nanoclusters.

The application of atom trapping technology can greatly reduce the agglomeration of precious metal particles. Jones et al. [78] anchored single-atom Pt on CeO_2 powders with different exposure surface facets at high temperature. This method can ensure that Pt atoms only occupy the most stable sites, thus effectively reducing the agglomeration of noble metal particles and improving the sintering resistance of the catalyst. The construction of structural defects on the supports surface is also an effective measure to stabilize single atom sites. Zhang et al. [79] used hydrothermal method to anchor monatom Pt on ultra-thin birnessite-type MnO_2 nanosheets with structural defects, which avoided agglomeration to a large extent and ultimately realized the effective degradation of toluene (GHSV = 48,000 mL/(g h), $T_{100\%} = 160$ ℃).

To sum up, the performance of supported noble-metal catalysts has been greatly improved in all aspects. However, due to the limited reserves of precious metals, the use of non-noble metal oxide catalysts to degrade VOCs can better meet the needs of large-scale exhaust treatment in the industry. At present, many researchers have gradually shifted their research attention to the metal-oxide-base catalysts with low cost, high activity.

4 Metal Oxide Catalysts

Metal oxide catalyst is regarded as a favorable substitute for noble metal catalyst, which has high catalytic activity, good thermal stability, anti-poisoning, economic and efficient. However, there is still a certain gap between the low-temperature reducibility of metal oxide catalysts and the noble metal supported catalysts. Therefore, many research groups are committed to improving the catalytic activity of metal oxide catalysts and lowering the reaction temperature to develop metal oxide-based catalysts with practical application value.

4.1 Single Metal Oxide Catalyst

4.1.1 MnO_x

Among all kinds of metal oxide catalysts, transition metals are widely used, among which the oxygen-containing compounds of Mn are more prominent. Manganese oxides are usually used to degrade VOCs because of their multiple coordination numbers, multiple oxidation states, diverse structures, and good oxygen storage capacity.

Figure 4a–e are five crystal phases in MnO_2 [80], which are a-MnO_2 (cryptomelane), β-MnO_2 (pyrolusite), t-MnO_2 (todorokite), γ-MnO_2 and δ-MnO_2, respectively. All crystal phases of MnO_2 are composed of [MnO_6] regular octahedral units (Fig. 4f).

Among the four crystal forms of MnO_2, a-MnO_2 (OMS-2) shows 2 × 2 channels and 4.6 nm pore size. It is composed of edge shared octahedron connected by four corners. Moreover, it has variable valence, high porosity, higher lattice defects, easy to release lattice oxygen, and mild acid sites. Therefore, it is widely used in the degradation of VOCs. Sihaib et al. [82] synthesized four kinds of manganese oxides by two methods, among which OMS prepared by solid-state method showed the highest catalytic activity in toluene degradation. The toluene degradation activity of OMSs was slightly lower than that of commercial Pd/Al_2O_3 (conversion rate > 40%), but the initial reaction temperature was lower ($T_{0\ (OMSs)} = 170$ ℃, $T_{0\ (Pd/Al2O3)} = 190$ ℃). Rong et al. [83] synthesized α-MnO_2 nanowires with exposed (310) facets by a simple hydrothermal method, which could completely convert 100 ppm formaldehyde to CO_2 and H_2O at 60 °C. Sun et al. [84] synthesized nanosized rod-like OMS-2 with uniform morphology by hydrothermal method. The catalyst contained a large amount of lattice oxygen, and can completely degrade toluene to CO_2 and H_2O at 240 ℃.

The same crystal exhibits different activities through different preparation processes. Zhu et al. [85] used different K-containing precursors to modify α-MnO_2. The

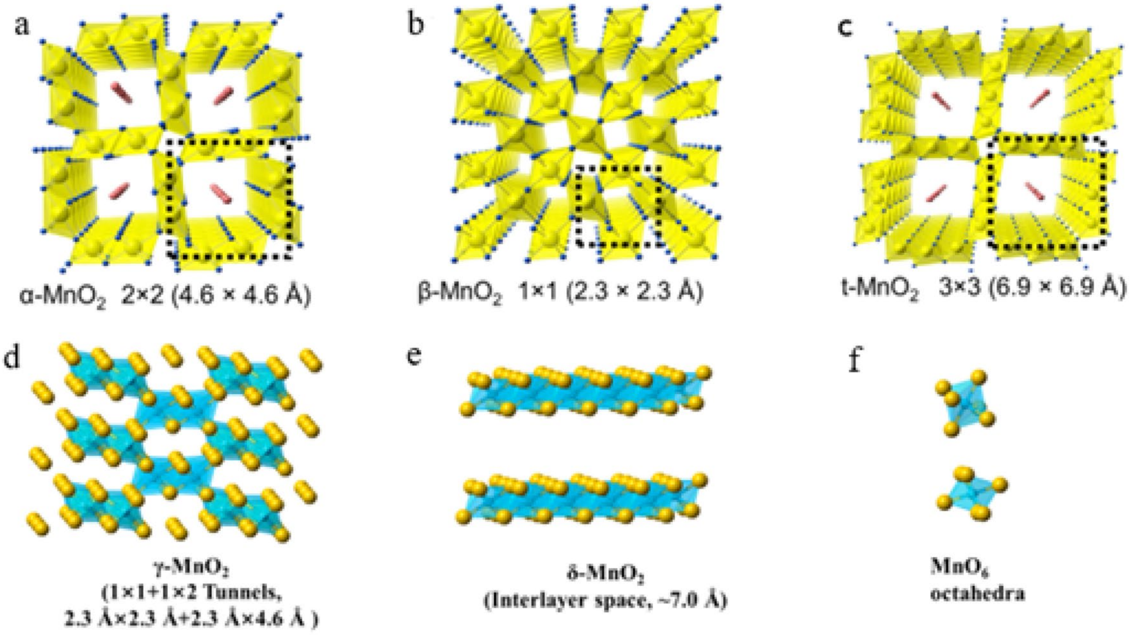

Fig. 4 Five crystal types of MnO_2 and their basic structural units [80, 81]. **a** a-MnO_2, **b** β-MnO_2, **c** t-MnO_2, **d** γ-MnO_2, **e** δ-MnO_2, **f** [MnO_6]

experimental results showed that α-MnO_2 modified by KOH presented higher catalytic activity than OMS-2 modified by other K-containing precursors. After modification, a larger specific surface area, suitable surface acidity, and suitable mobility can be obtained. When the toluene concentration was 1000 ppm, α-MnO_2 modified by KOH can degrade 90% contaminant at 226 ℃ ($T_{90\%} = 226$ ℃).

In addition to the types of K-containing precursors, the effect of K^+ concentration on the catalytic activity has also been studied. Hou et al. [86] studied the effect of different K^+ concentrations on the catalytic activity of rod-shaped OMS-2 for benzene oxidation. The results showed that the lattice oxygen activity of OMS-2 was different under different K^+ concentrations. The results exhibited that when K/Mn = 0.07, the catalyst showed the optimal catalytic activity, which degraded 50% and 90% benzene at 203 and 240 °C, respectively.

The influence of morphology on the performance of nanocatalysts can not be ignored [87, 88]. Wang et al. [89] studied the performance difference of toluene catalyzed by α-MnO2 with different morphologies (Fig. 5a–c). Compared with tube-like, rod-like, wire-like, and flower-like, the rod-shaped a-MnO_2 exhibited the best catalytic activity. When the weight hourly space velocity was 20,000 mL/(g h), Toluene can be degraded by 90% at 225 ℃ ($T_{90\%} = 225$ ℃).

In addition to the excellent catalytic performance of α-MnO_2 in the degradation of VOCs, the application of other crystal forms of MnO_2 in this field has also been reported. Yang et al. [90] studied the degradation of toluene by MnO_2 with different crystal forms. Compared with other crystal forms, the synthesized δ-MnO_2 with a nano-flower structure exhibited a large number of structural defects (Fig. 5d). At the same time, it contained a lot of adsorbed oxygen, showing the highest oxygen mobility and activity. When the catalyst was used to degrade toluene, $T_{90\%} = 245$ ℃ can be obtained. Li et al. [91] also gave a positive evaluation of the catalytic performance of δ-MnO_2 for toluene. In their research, layered δ-MnO_2 with excellent catalytic activity was prepared by simple redox precipitation method, and the reaction mechanism was clarified by in-situ characterization techniques such as online mass spectrometry and in-situ DRIFT. Toluene forms a series of oxygen-containing intermediates during the reaction and were eventually oxidized to CO_2 and H_2O. The possible reaction mechanism of toluene on layered δ-MnO_2 can be illustrated in Fig. 5f [91].

To obtain better catalytic performance, Huang et al. [92] synthesized two-phase MnO_2. The layered a@β-MnO_2(1:1) prepared by the simple hydrothermal method showed more active oxygen species and a larger specific surface area than a single-phase catalyst. The experimental results revealed that the reaction activity of the catalyst changed with the crystal phase under the same reaction conditions. An active interface favorable for toluene catalytic combustion was formed between heterogeneous phases. This interface was conducive to the formation of oxygen vacancies, while the existence of lattice distortion was also beneficial to the formation of reactive oxygen interface. The synergistic effect of a variety of factors made the a@β-MnO_2(1:1) biphasic catalyst exhibit high activity, and complete combustion of toluene can be achieved at 205 °C (GHSV = 30,000 h^{-1}). Liu et al. [93] treated birnessite MnO_2 with HNO_3 to increase the surface acidity and the amount of surface-active oxygen of the catalyst, thus promoting the adsorption and activation of benzene. And this green and facile treatment method can be used to treat other crystal forms of MnO_2 except for a-MnO_2.

Surface oxygen vacancy was another important factor affecting catalytic activity besides surface acid sites and surface reactive oxygen species. Wang et al. [94] introduced Mn^{3+} into the polycrystalline MnO_2 catalyst, which increased the oxygen vacancy content and the oxidation ability of the catalyst to polycyclic aromatic hydrocarbons.

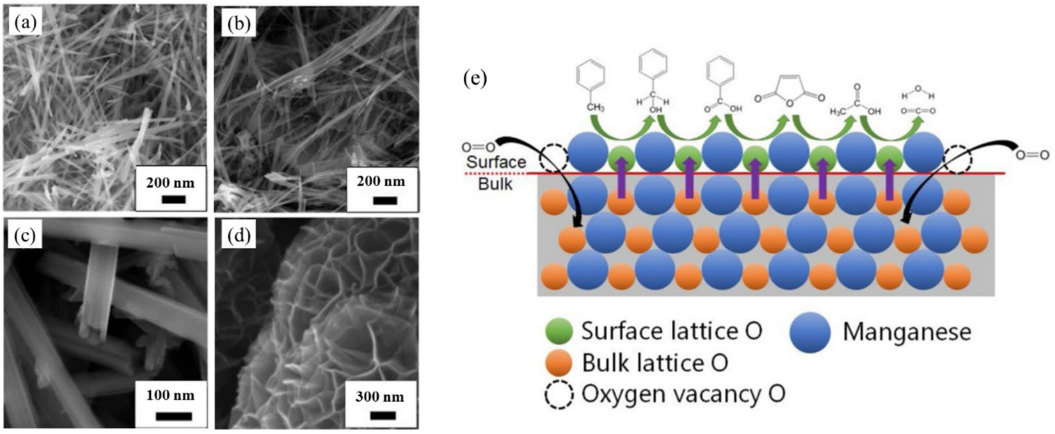

Fig. 5 SEM images of OMS-2 [89, 90], **a** rod-like, **b** wire-like, **c** tube-like, **d** flower-like, and possible mechanism of toluene degradation (**e**) [91]

Besides MnO_2, other oxides of Mn have been used to degrade VOCs. Yang et al. [95] used a facile method to grow MnO_2 on Mn_2O_3 and prepared the $Mn_2O_3@MnO_2$ heterojunction catalyst. Since the elimination of VOC mainly follows the MVK mechanism, the reaction tends to occur on the side with more surface adsorbed oxygen at lower temperatures, and on the other side with more lattice oxygen at higher reaction temperatures. For the $Mn_2O_3@MnO_2$ heterojunction, when the reaction temperature was low, the reaction occurred on the MnO_2 side, and when the reaction temperature was high, the reaction easily occurred on the Mn_2O_3 side. Generally, due to the existence of heterojunction, a large number of lattice defects would be generated, so the redox performance and oxygen storage capacity of the catalyst were improved. Piuitti et al. [96] synthesized three types of manganese oxides, of which Mn_3O_4 showed the highest catalytic activity with high CO_2 selectivity and thermal stability.

Thus, making full use of the advantages of MnOx with an open pore structure, high lattice oxygen mobility, and multiple surface active oxygen species can achieve efficient degradation of VOCs.

4.1.2 Other Single Metal Oxides

Besides Mn-based oxides, CoOx has been widely used in VOCs degradation. Luo et al. [97] studied the catalytic activity of CoOx supported on different carriers for toluene degradation. Compared with CoOx/SBA-15, CoOx/γ-Al_2O_3, and CoOx/AC, the CoOx supported g-C_3N_4 showed the highest catalytic activity, and 10% CoOx/g-C3N4 could degrade 90% toluene at 279 °C.

In addition to transition metal oxide catalysts, rare-earth-based metal oxide catalysts are also widely used in VOCs decomposition. Ce is the most abundant rare earth element. Ceria is an excellent oxygen storage material, which have good low-temperature reducibility and are easy to transform between redox states. Ce atoms can quickly obtain electrons from oxygen atoms, complete the reduction cycle, and generate oxygen vacancies. The Oxygen vacancy is equivalent to the moving active site, which is a powerful guarantee for the catalyst to exhibit good oxygen storage capacity.

Kong et al. [27] introduced oxygen vacancies into the CeO_2 catalyst through a simple treatment to promote the redox cycle. The treated catalyst showed both anti-carbon deposition performance and photocatalytic performance greatly improved. Additionally, the catalytic activity of CeO_2 is greatly affected by morphology. Yan et al. [88] prepared three morphologies of CeO_2 and explored the influence of which on the activity. The experimental results showed that CeO_2 with various morphologies exhibited good catalytic activity, especially the nanobelt CeO_2 with porous structure (WHSV = 60,000 mL/(g h), $T_{90\%} = 230$ °C). Besides, the catalyst showed good stability and can effectively degrade toluene for a long time, and no obvious deactivation was observed even under high concentrations of water vapor (water vapor = 5% vol.).

Furthermore, Ce-based materials can greatly resist Cl and S poisoning to a certain extent. Chen et al. [98] prepared polyoxometallates (POMs) -functionalized CeO_2 by a simple method. Compared with CeO_2 obtained by traditional methods, this material exhibited more structural defects, improved catalytic activity, and significantly increased anti-toxicity. Furthermore, the proper amount of POM modification would not cover the surface of CeO_2, and 5% HSiW/r-CeO_2 showed the optimal catalytic activity, which could degrade 80% chlorobenzene at 341 °C. Therefore, the catalyst not only showed a certain resistance to Cl poisoning but also exhibited high catalytic activity at a lower temperature. The research group also used in-situ analysis techniques including in-suit DRIFTS and on-line MS to explore the reaction mechanism. The synergistic degradation mechanism of CVOCs by POMs and CeO_2 was shown in Fig. 6 [98]. Due to the difference in chemical bond strength, the order of bond breakage was also different. C–Cl bond breakage was the first step for the catalyst to degrade CVOC.

These results show that metal oxides catalysts have potential application value to a certain extent.

4.2 Composite Metal Oxides

Metal oxide catalysts have good thermal stability, are more economical than supported precious metal catalysts, and have great application prospects. However, the activity of a single metal oxide as a catalyst is relatively low, and the reaction requires a large external energy supply. Therefore, taking appropriate methods to increase the activity and lower the reaction temperature has an excellent research prospect. The preparation of composite metal oxides is an important means to improve the activity of non-noble metal catalysts. Through the synergy between different metals, or lattice defects between the active interface to produce favorable factors for the degradation of VOCs. Compared with single metal oxide, the composite metal oxide display a greater improvement in the overall catalytic activity performance [99–101], showing better stability and activity. Table 2 lists some composite metal oxides used for highly efficient catalytic oxidation of toluene.

4.2.1 Binary Composite Metal Oxide

Transition metal type composite metal oxide is a kind of composite metal oxide catalyst which has been studied earlier. Deng et al. [108] used simple heat treatment to treat precursors of different metals (M = Co, Al, Fe, Cr) to prepare CoM composite metal oxides with uniform

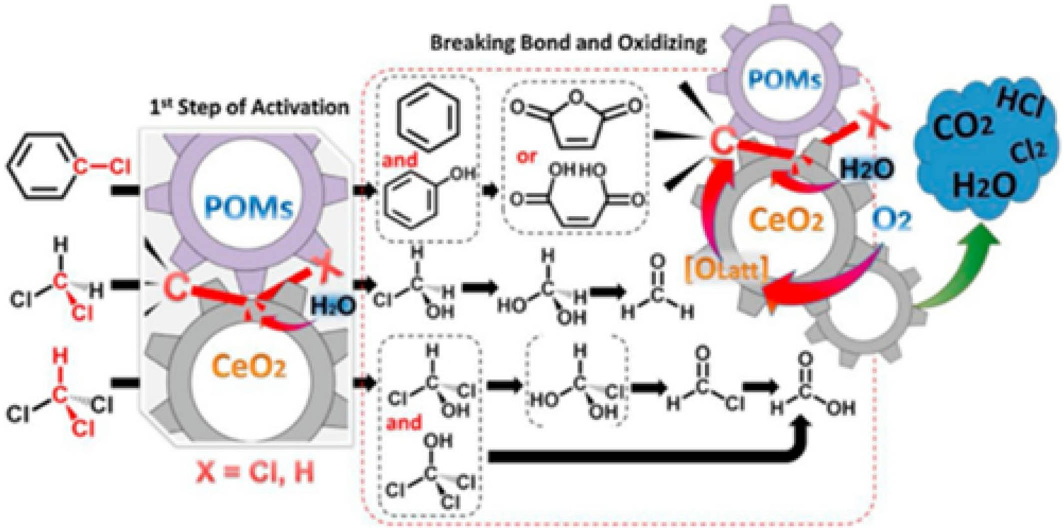

Fig. 6 POMs-functionalized CeO$_2$ to degradation CVOCs [98]

Table2 Composite metal oxides catalyze the oxidation of toluene

Catalysts	Morphology	Specific surface area m^2/g	C/ppm	Hourly space velocity mL/(gh)	Conversion rate/℃	Refs.
Cu1Mn1-500	Nanowire	45.9	1000	WHSV = 60,000	$T_{90\%}=214$	[102]
10Co-Ce/NF	Nanosheet		900	WHSV = 60,000	$T_{100\%}=268$	[103]
CoMn$_2$O$_4$	Nanoflower	124.4	500	WHSV = 60,000	$T_{90\%}=210$	[104]
Cu-doped Mn$_{0.5}$Ce$_{0.5}$Ox	Sponginess	82	1000	GHSV = 60,000	$T_{100\%}=240$	[105]
5Mn1Fe		191.8	1000	GHSV = 20,000	$T_{100\%}=215$	[106]
α-MnO$_2$@Co$_3$O$_4$	Layered nanostructure	54.9	1000	WHSV = 48,000	$T_{90\%}=229$	[107]

morphology and used the obtained catalysts for the degradation of chlorobenzene. Among the three mixed systems mentioned above, CoCr composite metal oxide exhibited excellent stability and catalytic activity. The catalyst can degrade 90% of CVOCs such as 1,2-dichloroethane, dichloromethane and 1,2-dichlorobenzene within 300 °C, and can stably degrade chlorobenzene at 300 °C for 50 h without obvious deactivation. Petar et al. [109] firstly prepared disordered mesoporous SiO$_2$ with different contents of Fe by a simple two-step method and then loaded a certain amount of Cu on the support by impregnation method. The research group compared the obtained catalyst with CuO and FeOx, in which the catalytic activity of toluene was increased by two times by Cu-oxo-Fe clusters catalyst supported on mesoporous SiO$_{2}$. The catalytic activity of the CuFe bimetallic catalyst was affected by the ratio of Fe/Si. For deep oxidation of Cl-containing volatile organic compounds (CVOCs), the deposition of toxic Cl containing by-products has always been the main reason for the deactivation of the catalyst.

Therefore, improving the resistance to Cl poisoning is of great importance to the improvement of the comprehensive performance of the catalyst.

Wang et al. [110] prepared FeMn composite metal oxide catalyst through a simple synthetic route. The catalyst exhibited good stability when degrading chlorobenzene, and only produces a small number of toxic by-products during the reaction. Sun et al. [111] made outstanding contributions in this regard. They modified Cu-HZSM-5 with Nb to obtain multiple active center catalyst. Nb can activate H$_2$O to H, and react with Cl adsorbed on the surface of Nb site to form HCl [112], avoiding the formation of CuClx from Cu and chlorine-containing by-products. Therefore, the presence of Nb sites can well protect Cu sites from the poisoning caused by electrophilic chlorination while participating in CVOCs oxidation. The above method provides a new idea for the degradation of CVOC. Besides constructing catalysts resistant to Cl poisoning, multiple active sites can be used to eliminate the accumulation of Cl-containing byproducts and reduce the side effects.

Among various transition metal oxides, MnOx has excellent properties [85, 113] and is widely used in combination with other metals to reduce the reaction temperature and increase the catalytic activity. Tang et al. [114] prepared a porous Mn-Co composite metal oxide catalyst for the removal of EtOAc and n-hexane. Compared with the single transition metal oxide catalyst, the catalyst exhibited higher activity and showed excellent catalytic performance at high space velocity. The degradation temperatures of 90% EtOAc and n-hexane by porous Mn-Co-based nanorods were 194 and 210 °C, respectively. Wang et al. [115] synthesized composite metal oxides with different valences (Co^{3+}, Mn^{4+}, Mn^{3+}) using the agar gel method. The catalyst has a large surface area and a high content of oxygen vacancies. Using this catalyst to degrade toluene, it could obtain higher catalytic activity than single MnOx or CoOx, and the catalyst still maintained good stability and activity at high water vapor content. Ren et al. [107] used the in-situ growth method to grow Co_3O_4 on a-MnO_2 to construct heterojunction with strong interaction. The performance of the catalyst obtained by this method is greatly improved than that of single a-MnO_2 and single Co_3O_4. Moreover, this method had certain practical significance and can be used to guide the preparation of other 1D MnO_2 materials. Dong et al. [116] used a new way to add Ni into a-MnO_2. The synergistic effect between NiOx and MnOx was used to reduce the reaction temperature of toluene degradation. The doped catalyst showed high catalytic activity and can degrade 90% of toluene at 199 °C ($T_{90\%} = 199$ °C).

In addition to studying the catalytic performance of the composite metal oxide catalyst formed by α-MnO_2 and other metals, the performance of other crystalline forms of manganese and different metal oxides for the degradation of VOCs has also been extensively studied.

It is generally considered that δ-MnO_2 has a large number of lattice defects and high oxygen mobility, which is conducive to the catalytic oxidation of VOC [90]. Dong et al. [117] evaluated the catalytic performance of δ-MnO_2 composite with different proportions of Cu in the catalytic degradation of toluene. The experimental results showed that the transition metal modified δ-MnO_2 can also obtain excellent catalytic performance. Wei et al. [118] synthesized a series of CuO, MnOx catalysts by template method at different temperatures, and applied them to toluene degradation. The catalysts calcined at 500 ℃ had the largest amount of surface lattice oxygen, making the complete degradation temperature of toluene as low as 230 ℃. Ma et al. [119] used the impregnation method to support Fe–Mn mixed oxide on cordierite and studied the effects of different ratios and calcination temperatures on the catalyst activity. Luo et al. [120] synthesized Cu-Mn composite metal oxide catalysts by a one-step hydrothermal method. Among them, Cu modification had the greatest promotion effect on the catalytic activity of the MnOx catalyst with a pore structure. When the space velocity is 10,000 h^{-1}, a 90% toluene conversion rate can be obtained at 169 ℃. Wang et al. [121] prepared Fe–Mn solid solution by precipitation method for toluene degradation and obtained composite metal oxide catalyst with high activity in a humid environment. The research results showed that the catalyst prepared by the redox precipitation method was more uniformly dispersed than the catalyst prepared by the co-precipitation method. Furthermore, the redox precipitation method can improve the activity and stability and can degrade toluene at a relatively low temperature in a close to a real complex environment.

At present, there are a lot of researches on the degradation of VOCs by composite metal oxides containing rare earth elements [122–125]. Among them, the composite metal oxide-containing CeOx is a typical representative of this type of catalyst [28, 113]. Li et al. [126] synthesized Cu-Ce-based composite metal oxidation catalyst with high activity by simple hydrothermal method. The catalyst exhibited a hollow structure and good low-temperature reducibility and can realize efficient oxidation of toluene. The hollow microporous CeaMnOx [127], synthesized by Zhao et al., was added an appropriate amount of Ce to MnOx. The catalyst displayed a large amount of surface adsorbed oxygen and Mn^{4+}, as well as good stability, and also has good toluene oxidation activity ($T_{100\%} = 226$ °C). Yang et al. [128] prepared $LaCoO_3$ perovskite-type catalyst with a large surface area and a high content of surface oxygen vacancies by the traditional sol–gel method. $LaCoO_3$ can obtain the best catalytic performance when the weight hourly space velocity is 60,000 mL/(g h) ($T_{90\%} = 223$ ℃). Feng et al. [129] prepared CeO_2 crystals with different morphologies for toluene degradation. The hollow spheres obtained exhibited the best performance ($T_{90\%} = 207$ ℃) and certain stability and reusability in a humid environment. Yang et al. [130] prepared mesoporous composite metal oxides which combined rare earth with transition metal by coprecipitation and used it to degrade chlorine-containing VOCs. The strong interaction between CeO_2 and MOx (M = V, Cr, Mn, Fe, Co, Ni, Cu) greatly enhanced the catalytic activity, among which 4Ce1Cr showed the best performance.

However, the catalyst was prone to coking and deactivation in the early stage of the reaction. The further work of the research group is to load the obtained 4Ce1Cr on the zeolite [131]. Firstly, the pollutants were adsorbed by the strong acid sites on the zeolite, and then the CVOCs were deeply oxidized by (Ce, Cr)xO_2. Dai et al. [132] studied the oxidation activity of VOx/CeO_2 catalysts for 1,2-dichloroethane degradation through various characterization methods. The results showed that the composite metal oxide catalyst exhibited good stability in a wide temperature range when used for the degradation of 1,2-dichloroethane. And 6%VOx/CeO_2 exhibited good catalytic activity and stability for a variety of CVOCs. Jing et al. [103] modified the Co-based composite metal oxide catalyst with Ce and deposited it on the nickel foam. The best toluene degradation effect can be obtained by adjusting the ratio of Co to Ce. 10Ce-Co can completely combustion toluene at high space velocity and low temperature (GHSV = 30,000 mL/(g h), $T_{100\%} = 268$ ℃). In addition to cerium, the use of other rare earth elements to degrade VOCs have also been extensively studied [133–136].

4.2.2 Multi-component Composite Metal Oxide Catalyst

Through the study of many transition metals and rare earth elements, it is found that the composite metal oxides formed by Cu, Co, Mn, Ce, Cr, and other elements have a good catalytic effect on the catalytic oxidation of VOCs [137–142]. Li et al. [143] synthesized multiple composite metal oxides containing Cu, Co, and Fe, and the formation of $CuyCo_{3-y}FeOx$ promoted the activity and stability of the catalyst. The synergistic effect between different components of the composite metal oxide and the interaction between the heterogeneous phases greatly promoted the catalytic combustion of toluene. In this work, Cu1Co2Fe1Ox showed the best activity, which can degrade 50% toluene at 224 °C, and the catalytic combustion of 90% toluene was only 238 °C. Deng et al. [144] doped different proportions of Co into Mn-Ce solid solution to prepare multiple composite metal oxides and evaluated the activity, stability, and CO_2 selectivity of the catalyst. The $CoxMn_{1-x}CeO_{\delta}$ catalyst was prepared by a simple co-precipitation method, which can degrade 1000 ppm of benzene efficiently at a WHSV of up to 90,000 mL/(g h). When the doping amount of Co is 0.25, benzene can be completely degraded at 250 ℃, and the activity of the catalyst is higher than that of some noble metal catalysts.

Therefore, multiple composite metal oxides are regarded as an effective substitute for noble metal catalysts and have high application value. Many studies have shown that the formation of composite metal oxides can effectively increase the activity of catalysts, but it is impossible to obtain high activity catalysts by simply combining different metals.

He et al. [145] prepared CuCeOx composite metal oxide catalyst by simple self-precipitation method for the oxidation of toluene. Compared with the single oxygen-containing compounds of Cu and Ce, the surface area and overall catalytic activity of the catalyst were enhanced. Mesoporous $Cu_{0.3}Ce_{0.7}O_x$, with the largest surface area ($S_{BET} = 162.8$ m^2/g), can decompose 90% propanal and toluene at 192 and 212 °C (GHSV = 36,000 h^{-1}), respectively. Zeng et al. [146] prepared Ce–Cu composite metal oxide catalysts by doping CuO into CeO_2, but the catalytic activity was not significantly enhanced after doping.

Thus, the controllable synthesis of composite metal oxides and the factors affecting catalytic performance are worthy of further study. Although the activity of some metal oxide catalysts is comparable to that of precious metals, in general, further research is still needed to expand the advantages of metal oxide-based catalysts and avoid the shortcomings of such catalysts to the greatest extent.

5 Conclusion and Prospect

In this review, the application of supported noble metal catalysts and metal oxide catalysts in VOCs degradation is introduced. Pt and MnOx are selected as representatives of supported noble metal catalysts and metal oxide catalysts to give an important introduction respectively, and other common catalysts are also briefly introduced. Supported noble metals catalysts have excellent catalytic activity, but they are expensive and easy to deactivate. Although monoatomic catalysts save the cost of supported noble metal catalysts, the complex preparation process and unavoidable agglomeration making such catalysts lack practical application value. Transition metal oxides and rare earth elements are effective substitutes for precious metal catalysts. They exhibit excellent thermal stability and cheap, but the low-temperature reducibility needs to be further improved. This paper reviews the catalytic degradation performance of supported noble metal catalysts and metal oxides for volatile organic compounds including toluene. Moving forward, it can be concluded that the thermal catalytic oxidation on VOCs has made great progress, there are still some aspects to be resolved:

(i) There is a gap between laboratory research and development and industrial production needs. The diversity and complexity of industrial tail gas increase the difficulty of catalyst optimization. At present, there are few catalysts with low cost and high stability for industrial tail gas treatment. Therefore, future research should focus on the development of catalysts with universal applicability to meet industrial needs.
(ii) The cost of thermal catalytic oxidation of VOCs can be reduced by using metal oxide catalysts rather than noble metal catalysts. However, the activity of metal oxide catalysts should be further improved to reduce the ignition temperature and save energy consumption.
(iii) At present, the treatment of industrial tail gas cannot be directly removed in the production process. The study of catalyst molding helps to solve the chemical pollution problem directly in chemical equipment, avoiding the high cost of tail gas collection and other processes. Therefore, more effort should be devoted to catalyst molding.

(iv) VOCs after thermal catalytic oxidation were directly discharged into the, which did not realize the reuse of resources. Reasonable methods should be developed to collect and utilize the gases generated by degradation and maximize the utilization of resources.

In short, thermal catalytic oxidation degradation of VOCs has been widely used in industrial waste gas treatment. Based on the summary of previous work, we expect that the use of metal oxide-based catalysts to degrade VOCs can make a new breakthrough.

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