

Research progress on Mn-based catalysts for catalytic combustion of VOCs

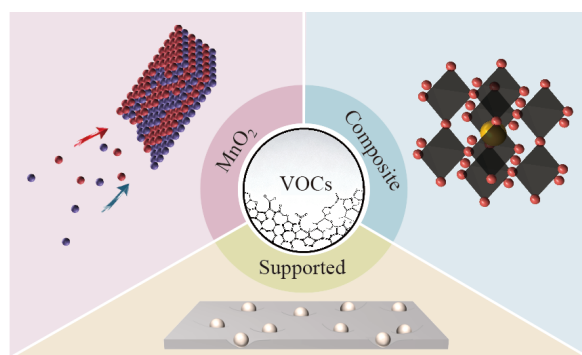
LUO Guangjun¹, CHEN Shuang^{1,*}, YIN Hong¹, ZENG Jia², XIE Hongmei^{2,*}, ZHOU Guilin^{1,2}

¹Chongqing Technology and Business University, Engineering Research Center for Waste Oil Recycling Technology and Equipment, Ministry of Education, Chongqing 400072, China;

²Chongqing Technology and Business University, School of Environment and Resources, Chongqing 400072, China

Abstract: Volatile organic compounds (VOCs) originating from diverse sources, exert a profound detrimental impact on the atmospheric environment and pose grave threats to human health. Manganese (Mn)-based catalysts, celebrated for their exceptional structural diversity and abundant redox versatility, are extensively employed in the catalytic combustion of VOCs. This review summarizes the catalytic performance of diverse Mn-based catalysts. It emphasizes strategies for preparing high-performance Mn-based catalysts and provides a systematic analysis of how the construction of active sites influences their catalytic combustion performance for VOCs. Furthermore, the catalytic oxidation mechanisms of VOCs are expounded in detail. This work offers valuable insights and practical guidance for the remediation of VOCs pollution.

Key words: Mn-based catalysts; catalytic oxidation; metal composite; metal support; reaction mechanisms



Volatile organic compounds (VOCs) denote organic chemicals that readily volatilize into the gaseous phase under ambient temperature and pressure^[1]. VOCs can infiltrate the human body and induce pulmonary diseases, while also serving as precursors to secondary organic aerosols (SOA) and ozone (O₃) in photochemical reactions, thereby exacerbating environmental pollution^[2–4]. Given the enormous market demand for VOCs control, there is an urgent need for treatment technologies that are stable, highly efficient, and economically feasible. Currently, common VOCs removal technologies include catalytic combustion, adsorption, biodegradation, and photocatalysis^[5–8]. Catalytic combustion exhibits superior application potential owing to its exceptional versatility and simple reaction process.

Among them, noble metal catalysts (e.g., Pt, Pd, Rh, Au and Ru) demonstrate excellent catalytic combustion activity at relatively low temperatures; however, their high cost and susceptibility to poisoning limit large-scale industrial application^[9–12]. Transition metal oxide catalysts, such as

MnO_x, Co₃O₄, CuO and CeO₂, have become research hotspots in catalytic combustion owing to their low cost, excellent thermal stability, and robust resistance to poisoning^[13–14]. Manganese oxides (MnO_x), with their variable valence states, diverse morphologies and crystal phases, and their capacity to yield multifaceted manganese-based catalysts, exhibit immense potential in catalytic combustion of VOCs. This review summarizes the effects of structural characteristics and surface chemical composition of manganese-based catalysts on their catalytic efficacy, outlines the deactivation mechanisms and anti-poisoning strategies, and compares various performance-enhancement approaches, including doping, composite formation, and support modification.

1 MnO_x-based catalysts

A wide variety of MnO_x materials exist, exhibiting multifaceted crystal facets, phases, and morphologies,

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* Corresponding author. Tel: +86-23-62769785, E-mail: chenshuang@ctbu.edu.cn, xiehongmei@ctbu.edu.cn.

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alongside configurations such as distorted coordination, multiphase mixtures, and amorphous structures. The five crystal-phase structures of MnO_2 and their subtypes possess advantages including low cost, structural versatility, strong reducibility, and abundant oxygen species, and—together with Mn_2O_3 and Mn_3O_4 etc.—exhibit exceptional potential in the catalytic combustion of VOCs. The morphology and crystal structure of manganese oxides can be precisely tailored through the selection of synthesis routes and optimization of preparation parameters, enabling the directional design of catalysts. For example, deliberate exposure of specific crystal facets or the controlled synthesis of designated crystal phases or morphologies (Figure 1) can effectively enhance the catalytic activity of the catalysts toward VOCs, as summarized in Table 1.

Crystal facets are an important factor governing catalytic activity. Rong et al.^[9] synthesized $\alpha\text{-MnO}_2$ nanowires with exposed {310} facets *via* a hydrothermal approach. Compared with the {110} and {100} facets, the {310} facet more readily promotes the formation of oxygen vacancies, thereby facilitating the generation of surface-active oxygen species and enhancing formaldehyde oxidation. Huang et al.^[10] synthesized $\alpha\text{-MnO}_2$ exposing {110}, {210} and {310} facets, and discovered that in the catalytic oxidation of toluene, the $\alpha\text{-MnO}_2$ enriched with {210} facets exhibited superior activity, achieving a t_{90} (temperature required for 90% conversion) of 109 °C, whereas the t_{90} values for the {110} and {310} facets were around 170 °C. This advantage arises from the unique surface electronic structure formed by the alternating arrangement of Mn and O atoms on the {210} facet, which promotes more uniform charge distribution between Mn^{4+} and O^{2-} and strengthens surface redox capability. Moreover, the adsorption energy

barriers for toluene (−0.451 eV) and O_2 (−0.200 eV) reach their lowest values on the {210} facet, indicating more favorable adsorption of both toluene and oxygen molecules. Another study revealed that $\delta\text{-MnO}_2$ exposing {310} facets can be synthesized *via* ultrasound assistance. During MnO_2 formation, ultrasonic treatment disrupts the thermodynamically stable facets, thereby promoting selective growth of the {310} facet and enhancing catalytic activity for toluene combustion; compared with the {001} facet, the t_{90} was lowered by 25 °C^[11]. In catalytic combustion reactions, facet engineering enables the selection of highly active exposed facets, allowing regulation of oxygen vacancy concentration and surface adsorption properties, which profoundly governs overall catalytic performance.

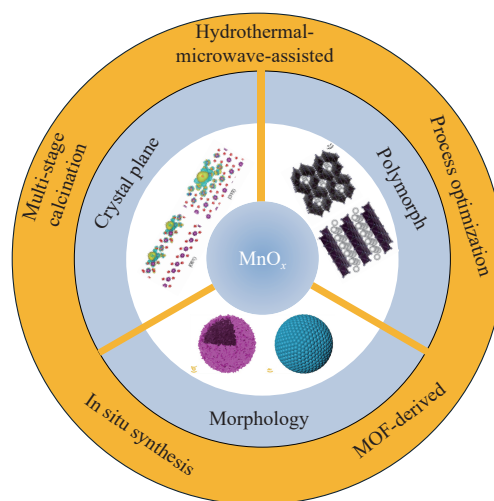


Fig. 1 Construction and synthesis method of manganese oxide

Table 1 Catalytic properties of manganese oxides

Type	Catalyst	VOCs type	Volume fraction/%	Air velocity/($\text{mL} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$)	$t_{90}/^\circ\text{C}$	Reference
Crystal plane	$\alpha\text{-MnO}_2(100)$	HCHO	0.01	60000	150	[9]
	$\alpha\text{-MnO}_2(110)$				130	[9]
	$\alpha\text{-MnO}_2(310)$				60	[9]
	$\alpha\text{-MnO}_2(110)$	toluene	0.05	15000	170	[10]
	$\alpha\text{-MnO}_2(210)$				109	[10]
	$\alpha\text{-MnO}_2(310)$				172	[10]
	$\delta\text{-MnO}_2(310)$	toluene	0.05	60000	163	[11]
	$\delta\text{-MnO}_2(001)$				198	[11]
Crystal phase	$\alpha\text{-MnO}_2$	toluene	0.1	60000	225	[12]
	$\beta\text{-MnO}_2$				295	[12]
	$\gamma\text{-MnO}_2$				260	[12]
	$\delta\text{-MnO}_2$				245	[12]
	$\alpha/\beta\text{-MnO}_2$	toluene	0.1	48000	210	[13]
	$\text{Mn}_3\text{O}_4/\text{Mn}_2\text{O}_3$	propene	0.05	20000	220	[14]
Morphology	nanosphere MnO_x	toluene	0.1	60000	258	[15]
	hollow ball MnO_x	toluene	0.1	60000	226	[15]
	spherical $\beta\text{-MnO}_2$	toluene	0.1	60000	240	[16]
	dice-shaped $\beta\text{-MnO}_2$				225	[16]
	peach-shaped Mn_2O_3				255	[16]
	bundle Mn_2O_3				240	[16]

Crystal structure determines the intrinsic properties of materials. Yang et al.^[12] synthesized α -MnO₂, β -MnO₂, γ -MnO₂ and δ -MnO₂ catalysts. The layered structure of δ -MnO₂ facilitates the formation of low-valence Mn species and provides more adsorbed oxygen species (O_{ads}), which promoting profound oxidation of toluene and achieving a t_{90} of merely 245 °C. In contrast, β -MnO₂ lacks sufficient O_{ads}, preventing the oxidation of large amounts of toluene and its intermediates. Another study revealed that the mechanism by which mixed-phase α/δ -MnO₂ or Mn₃O₄/Mn₂O₃ enhances catalytic activity differs between systems. The α/δ -MnO₂ catalyst benefits from the synergistic effect between the two phases: the α -phase provides abundant active sites, while the δ -phase, owing to its layered structure, facilitates oxygen migration. As a result, the t_{90} of α/δ -MnO₂ decreases to 210 °C, lower than 220 °C for α -MnO₂ and 245 °C for δ -MnO₂. In contrast, the lattice distortion at the heterojunctions of Mn₃O₄/Mn₂O₃ induces a higher density of oxygen vacancies, which also enhances catalytic performance^[13–14]. Zeng et al.^[17] conducted an in-depth investigation of the role of oxygen vacancies, demonstrating—using various α -MnO₂ samples rich in oxygen vacancies—that these defects profoundly modulate active oxygen species, surface structure, and reactant adsorption. In addition, directly designing defect engineering to regulate lattice defects has become another research focus for manganese oxides. Zeng et al.^[18] identified the critical role of the Mn 3d electronic structure in catalytic performance. Through experimental characterization and DFT calculations, they demonstrated that compared with Mn₂O₃ and Mn₃O₄, the interaction between Mn 3d and O 2p electronic states in MnO₂ weakens the Mn–O bond strength, thereby modulating catalytic activity. This study provides deeper insight into defect formation from the perspective of electronic structure. Bai et al.^[19] synthesized ϵ -MnO₂ with different degrees of lattice disorder, finding that the most disordered sample, MnO₂-R, displayed the weakest Mn–O bonds, which were more prone to break to form oxygen vacancies and generate more active oxygen species. It also exhibited superior low-temperature reducibility; consequently, its toluene t_{90} (222 °C) was 37 °C lower than that of the most ordered sample, MnO₂-H. In reactions involving mixed toluene and acetone gases, these two molecules share active sites and oxygen species, thereby enhancing their catalytic combustion. Similarly, MnO_x with low crystallinity prepared by Li et al.^[20] exhibited the strongest catalytic performance. Lattice defects exert a profound influence on catalytic activity, and the number of defects can be precisely tuned simply by adjusting the precursor ratio of (NH₄)₂CO₃ to Mn(NO₃)₂, resulting in excellent low-temperature reducibility. These findings collectively demonstrate that lattice disorder enhances both the low-temperature reducibility and oxygen-species activity of the catalysts.

Feng et al.^[15] synthesized hollow-sphere and nanospherical MnO_x and the former exhibited a larger specific surface area that exposed more active sites,

resulting in a t_{90} for toluene oxidation that was 32 °C lower than that of the latter. Mo et al.^[16] controlled the micro-morphology of manganese oxides by altering the precipitation method. Using ammonium bicarbonate in an ethanol-water solution as the mineralizer yielded a spherical MnO_x-ET catalyst, which had the largest specific surface area among diverse morphologies—including cubic, rough spheres, peach-like shapes, nanobundle, and carved bell-like structures—thereby exhibiting markedly superior catalytic activity (t_{90} = 225 °C). Moreover, the abundant oxygen vacancies on MnO_x-ET facilitated the formation of adsorbed oxygen and the activation of lattice oxygen. Through multiple reaction pathways (Figure 2), the surface-adsorbed-oxygen route follows: toluene → benzyl species → benzyl alcohol → benzoic acid → carbonates → CO₂ and H₂O; while the lattice-oxygen pathway advances *via*: benzoic acid → phenol → maleic anhydride, both contributing to deep oxidation of toluene. Zheng et al.^[21] enhanced the exposure of active sites by confining the particle size of MnO_x; carbon species derived from MOFs inhibited MnO_x agglomeration during N₂ calcination, thereby enabling the MnO_x nanoparticles to retain a small size. Zhou et al.^[22–23] further employed KIT-6 as a template to precisely regulate the structure of MnO₂-HT, thereby enabling MnO₂-HT to inherit the highly ordered mesoporous framework of KIT-6. The abundant mesopores facilitated the adsorption and diffusion of reactant molecules across the catalyst surface. Other studies have revealed that the precipitation rate in the precipitation method can profoundly influence the surface structure of catalysts. When urea was used as the precipitant, the relatively slow precipitation rate increased the proportion of Mn⁴⁺ and enhanced the activity of surface-active oxygen species in MnO₂, thereby dramatically enhancing its catalytic activity performance for toluene oxidation (t_{90} = 178 °C)^[24]. Additionally, both calcination temperature^[25] and precursor concentration^[26] emerge as important factors that profoundly modulate catalytic performance from multiple aspects.

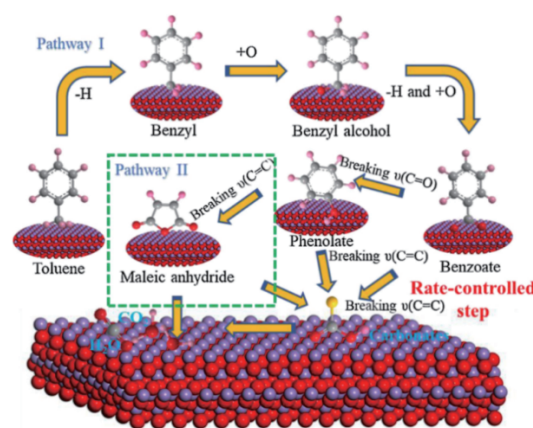


Fig. 2 Reaction mechanism of toluene on manganese-based catalyst^[16]
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In summary, the complex valence states and multifaceted morphologies of manganese oxides allow their catalytic performance to be improved through modulation of crystal facets, crystal structures, and morphological features. However, relying solely on manganese oxides makes it difficult to further enhance performance, and their stability still requires improvement. Challenges such as the scarcity of active sites and weak adsorption capacity also remain unresolved. To address these challenges, the strategic integration of manganese oxides with other metals has emerged as a highly strategy for catalyst design.

2 Composite Mn-based catalysts

Combining manganese-based catalysts with other metals is an important strategy for enhancing their catalytic activity toward VOCs, including but not limited to doping, composite formation, and supported structures. Transition metals are extensively employed to dope manganese oxides, and atomic substitution has been demonstrated to elevate the intrinsic catalytic activity of MnO_x , with several studies reporting notable achievements^[27–28]. Composite metal oxides can effectively modulate the morphology of manganese oxides and form distinctive structures or mixed phases such as solid solutions, spinels, or perovskites, thereby exhibiting superior catalytic performance. Table 2

summarizes the VOCs catalytic performance of composite manganese-based catalysts reported in recent literature.

2.1 Transition metal-doped Mn-based catalysts

Transition metal elements can substitute for or be incorporated into the original crystal lattice to form novel chemical bonds, thereby modulating the surface composition dominated by Mn–O bonds and ultimately optimizing the catalytic combustion performance of MnO_x toward VOCs.

Li et al.^[5] synthesized $\text{Cu}_x\text{-MnO}_2$ via a two-step hydrothermal doping approach. In the first hydrothermal step, $\delta\text{-MnO}_2$ with a unique hollow morphology was fabricated. In the second low-temperature hydrothermal step, this morphology was retained while Cu^{2+} was successfully incorporated into $\delta\text{-MnO}_2$. The Cu^{2+} ions substituted K^+ ions within the interlayers of $\delta\text{-MnO}_2$, triggering interlayer contraction, which induced periodic structural disruption and lattice distortion, resulting in the formation of oxygen vacancies. This, in turn, facilitated the adsorption and activation of oxygen species, with $\text{Cu}_{0.05}\text{-MnO}_2$ demonstrating the most significant effect, reducing the t_{90} for toluene to 190 °C. Similarly, Qiao et al.^[29] fabricated catalysts through hydrothermal synthesis, achieving deeper Mo incorporation into MnO_x .

Table 2 Catalytic performance of composite Mn-based catalysts

Type	Catalyst	VOCs type	Volume fraction/%	Air velocity/($\text{mL} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$)	$t_{90}/^\circ\text{C}$	Reference
Doping	$\text{Cu}_{0.05}\text{-MnO}_2$	toluene	0.05	36000	190	[5]
	0.3MoMnO_2	benzene	0.048	60000	235	[29]
	Fe_1Mn_5	toluene	0.1	30000	209	[30]
	$\text{Cu}_1\text{Mn}_1\text{O}$	toluene	0.1	60000	214	[31]
	10Co/OMS-2	toluene	0.2	60000	245	[32]
	Pd/OMS-2	toluene	0.1	90000	247	[33]
	Pd/OMS-2	acetone	0.1	90000	231	[33]
	Cu/OMS-2	acetone	0.1	90000	207	[33]
	Ir/OMS-2	dichloromethane	0.02	90000	293	[33]
Compositing	$\text{Co}_1\text{Mn}_1\text{O}$	toluene	0.4	24000	310	[34]
	5Co1Mn	toluene	0.1	60000	237	[35]
	CoMn_2O_x	toluene	0.1	40000	265	[36]
	$\text{Ce}_{0.25}\text{Mn}_{0.75}\text{O}_x$	propane	0.5	45000	350	[37]
	MC-TPAOH	toluene	0.1	60000	221	[38]
	$\text{MnCe-7\%}$	toluene	0.07	40000	195	[39]
		chlorobenzene	0.03		174	[39]
		toluene in mixture	0.07		240	[39]
		chlorobenzene in mixture	0.03		260	[39]
	LCMO	benzene	0.05	100000	240	[40]
		toluene	0.05	50000	207	[40]
		<i>o</i> -xylene	0.02	50000	227	[40]
	RCMO	toluene	0.05	50000	240	[40]
	GCMO	toluene	0.05	50000	280	[40]
	MnCu	toluene	0.1	40000	214	[41]

As shown in Figure 3, the resulting Mo-O_v-Mn active sites promoted oxygen adsorption on the catalyst surface and reduced the energy barrier for oxygen dissociation. However, excessive Mo doping led to the formation of Mo-O_v-Mo sites, where active oxygen species were difficult to release, thereby inhibiting catalytic activity. Therefore, an appropriate amount of Mo doping is necessary to balance oxygen adsorption energy and dissociation barriers, enhancing oxygen transfer efficiency. Co-precipitation methodologies can also uniformly incorporate Ce, Co, or Cu into MnO_x. Different transition metals exert varying influence upon MnO_x, generating additional oxygen vacancies that activate more active oxygen species, among which Ce exerts the most significant effect, markedly enhancing formaldehyde decomposition at room temperature^[42]. Beyond conventional synthesis routes, Fe_xMn_x catalysts have been prepared *via* a dichloromethane-induced layered interface followed by redox precipitation. In these catalysts, the incorporated Fe not only integrates into the δ-MnO₂ crystal structure but also forms a unique three-dimensional porous structure that increases the specific surface area and exposes more active sites. Simultaneously, the Mn-O bond strength is weakened, promoting the release of lattice oxygen; for the Fe₁Mn₅ catalyst, the t_{90} for toluene attains 209 °C^[30]. Conventional *in situ* hydrothermal Cu doping, although not producing special structures, can still increase the surface area and exposed active sites, enhancing gaseous oxygen adsorption and activation and accelerating lattice oxygen migration. Cu substitution also increases the proportion of Mn³⁺ ions, improving the redox properties of the catalyst^[31]. Dong et al.^[32] prepared Co-doped manganese octahedral molecular sieve (OMS-2) through a pre-incorporation method (Figure 4). After Co substituted some surface Mn atoms, the OMS-2 morphology was retained, but the surface electronic structure changed. Electrons from Co²⁺ transferred to Mn⁴⁺, lowering the valence state of Mn, increasing the Mn³⁺/Mn⁴⁺ molar ratio, and substantially enhancing low-temperature reducibility. The Mn-O bond was weakened, and the O_{ads}/O_{latt} molar ratio significantly increased, allowing more active oxygen to participate in reactions and effectively

enhancing catalytic performance. The t_{90} for toluene before and after doping was 280 and 245 °C, respectively. Furthermore, the incorporation of multiple metal elements (Pd, Ir, Cu) into OMS-2 has been explored (Figure 5) using a redox method, successfully substituting Mn sites in the octahedral framework. The incorporation of these heteroatoms strengthened the catalytic combustion of specific VOCs: Pd improved the reducibility and mobility of oxygen species; Cu ions promoted C-C bond cleavage; and Ir ions enhanced the bond-breaking ability of OMS-2. In the catalytic oxidation of different VOCs, this “metal doping-structure regulation-function orientation” logic explains the differential promotion effects of various metal dopants. Pd doping reduced the t_{90} for toluene and acetone to 247 and 231 °C, respectively, thereby improving OMS-2 performance by 10–20 °C. Cu notably enhanced acetone oxidation, and Ir significantly promoted dichloromethane oxidation, lowering the t_{90} to 207 and 293 °C, decreases of 44 and 82 °C, respectively^[33].

Besides transition metals, alkali metals such as Na and K are also commonly used in defect engineering of manganese-based catalysts. Wang et al.^[43] employed a molten salt method to insert Na, K and Cs into the interlayers of δ-MnO₂, mainly influencing the formation of oxygen vacancies. Among them, the formation energy of oxygen vacancies in CsMnO was 1.94 eV, lower than that of KMnO (1.97 eV) and NaMnO (2.07 eV), indicating that Cs insertion promotes the generation of abundant oxygen vacancies, thereby enhancing the adsorption and activation of active oxygen species in formaldehyde catalytic oxidation. The catalytic performance of formaldehyde combustion was consistent with these results: CsMnO (65 °C) > KMnO (90 °C) > NaMnO (100 °C). Zhao et al.^[44] incorporated Na and Cs into MnO_x *via* citric acid chelation, and the 5%Cs/MnO_x catalyst exhibited a t_{90} decrease of 28 °C. Cs existed as CsNO₃ on the MnO_x surface, increasing both the number and mobility of surface oxygen species. The doping of alkali metals is highly versatile and can also be applied to A-site substitution in manganese oxide perovskite structures. The substitution La in LaMnO₃ with alkali metals lowered the t_{90} for toluene by 10–30 °C^[45].

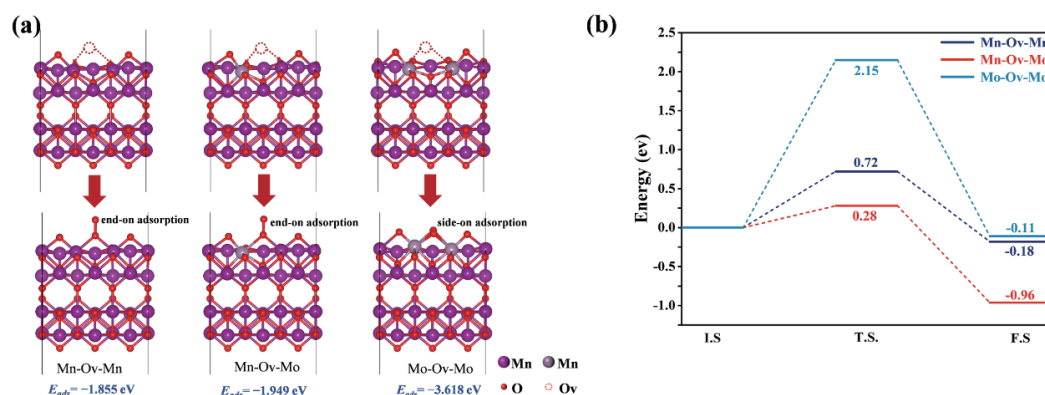


Fig. 3 (a) O₂ adsorption energy on the Mn-O_v-Mn, Mn-O_v-Mo and Mo-O_v-Mo sites of the MnO₂ surface; (b) O₂ dissociation energy profile calculation results for MnO₂ and xMoMnO₂ catalysts^[29] (with permission from Elsevier)

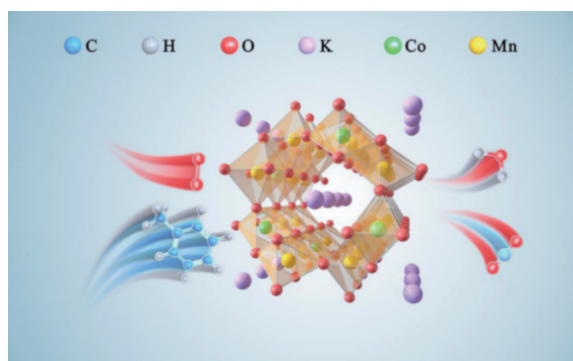


Fig. 4 Reaction mechanism of toluene catalytic oxidation over 10Co/OMS-2^[32]
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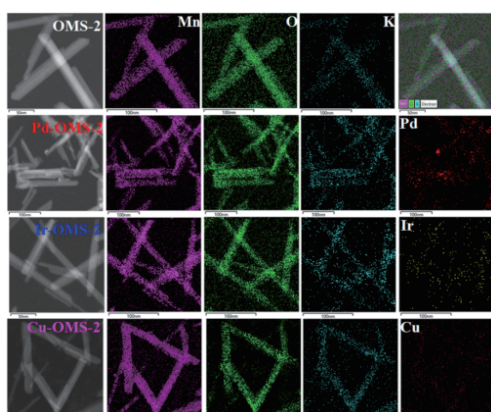


Fig. 5 Elemental mapping images of OMS-2 doped with Pd, Ir, Cu^[33]
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The doping method also affects MnO_x performance. Compared with exogenous doping methods such as impregnation, co-precipitation, and sol-gel, the endogenous doping achieved *via* hydrothermal synthesis generates more cryptomelane-type MnO_x , which enhances the redox capability of the catalyst and improves its catalytic combustion performance^[46].

Doping strategies provide a direct and effective approach to optimizing the catalytic oxidation of VOCs over manganese oxides. By altering the surface electronic structure or inducing lattice defects, catalytic performance can be enhanced. However, these methods typically induce only minor structural changes in the catalyst and often result in insufficient atomic utilization.

2.2 Composite metal oxide catalysts

2.2.1 Co-Mn system

Co and Mn have similar electronic structures, which facilitates the formation of composite oxides. Their multiple accessible oxidation states allow adaptation to diverse structures. Through the synergistic effect of the bimetallic

system, the redox cycles of Co and Mn ions are accelerated, thereby enhancing catalytic combustion performance by lowering the activation energy of the reaction. Consequently, researchers have long focused on optimizing catalytic performance and elucidating reaction mechanisms in Co-Mn systems.

Hu et al.^[34] synthesized CoMn spinel wherein electron transfer occurs between Co and Mn weakens the Mn–O bonds, thereby promoting the migration and activation of surface oxygen species. The CoMn spinel exhibited superior toluene conversion compared to monometallic oxides across the temperature range of 225–300 °C. This observation is consistent with kinetic modeling of toluene catalytic oxidation, which revealed that oxygen activation is the rate-determining step. Liu et al.^[35] synthesized hollow-structured CoMn composite oxides employing organic ligands as templates. The incorporation of Mn not only significantly increased oxygen vacancies but also effectively regulated the catalyst's micro-morphology. With increasing Mn content, the catalyst evolved from porous flower-like hollow microspheres to layered particle-stacked microspheres (Figure 6(b)). Changes in the dominant active oxygen species directly influenced the reaction pathway: when surface-active oxygen was abundant, toluene oxidation at 200–250 °C proceeded through the Langmuir-Hinshelwood (L-H) mechanism, whereas above 250 °C, lattice oxygen became activated, triggering the Mars-van Krevelen (MVK) mechanism (Figure 6(a)). The coexistence of multiple pathways is the main reason for the excellent catalytic performance. Li et al.^[36] synthesized CoMn hollow sub-nanospheres using carbon spheres as templates. Electron transfer from Mn^{3+} to Co^{3+} promoted the Co-Mn synergistic redox cycle, thereby accelerating lattice oxygen activation and regeneration. The CoMn_2O_x catalyst, exhibiting the strongest synergistic effect, attained a toluene t_{90} of 265 °C. Earlier, Zhou et al.^[47] successfully loaded CoMn spinel onto activated carbon *via* a simple impregnation method, achieving 90% and 87.9% degradation of toluene and ethylbenzene at 235 and 240 °C, respectively. Subsequently, Ren et al.^[48] employed urea to precisely construct oxygen vacancy engineering on CoMn spinel, investigating the roles of adsorbed oxygen and lattice oxygen and their activation in toluene catalytic oxidation. Structurally modified CoMn spinel enabled faster deep oxidation of toluene while maintaining dynamic equilibrium of oxygen species, significantly reducing the light-off temperature to a t_{90} of merely 230 °C, demonstrating excellent catalytic activity. Co-Mn composite oxides facilitate electron transfer or form new chemical bonds, and the strong synergistic effect of the Co-Mn system significantly enhances catalytic activity, thereby improving the performance of manganese-based catalysts. Song et al.^[49–50] synthesized a CoMn solid solution *via* a simple method. This unique structure exhibited excellent catalytic performance, achieving 97% toluene removal at 150 °C, comparable to that of some noble metal catalysts.

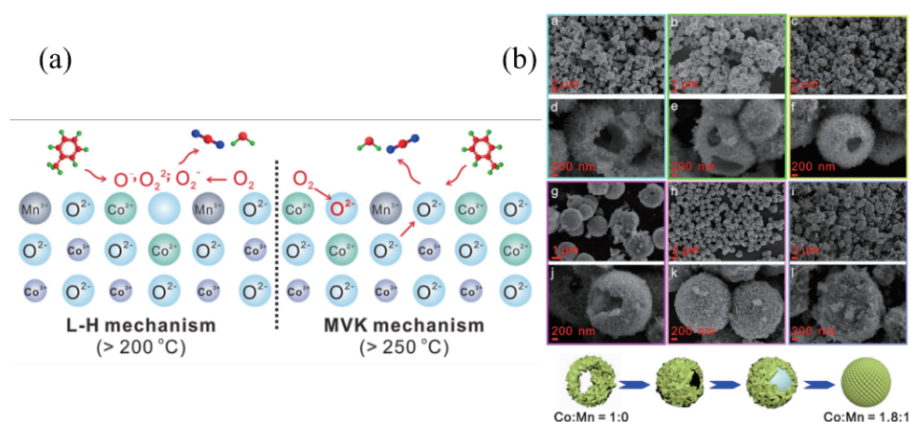


Fig. 6 (a) Reaction mechanism of toluene oxidation over 5Co1Mn; (b) SEM images of CoMn composite oxides samples^[35] (with permission from Elsevier)

2.2.2 Ce-Mn system

Ce has properties similar to Co and can improve the low-temperature catalytic activity and stability of manganese-based catalysts, thereby enriching their structural and functional diversity. In addition, cerium oxides possess exceptional oxygen storage capacity.

Shah et al.^[37] prepared a series of CeMn composite oxides employing a sodium carbonate co-precipitation method. The heterojunctions formed by Mn substituting CeO₂ and Mn₂O₃ were identified as the key active sites. The active sites in Mn₂O₃ adsorbed and activated gaseous oxygen, directly participating in VOCs catalytic combustion, while Mn substituting CeO₂ acted as a lattice oxygen reservoir. Under conditions of insufficient gas-phase oxygen or high reaction rates, lattice oxygen could be rapidly released to replenish the reaction sites, thereby synergistically facilitating the catalytic combustion of propane or naphthalene. Furthermore, using urea or nitrate grinding methods at 350 °C increased propane removal by 20%, effectively avoiding deactivation arising from Na atoms covering active sites. This indicates that the incorporation of extraneous atoms should be avoided during synthesis. Chen et al.^[38] modified CeMnO_x solid solutions employing diverse organic solvents. The MC-TPAOH catalyst (Figure 7) derived from modification with tetrapropylammonium hydroxide (TPAOH) solution, exhibited expanded interlayer spacing owing to TPA⁺ intercalation, while pore size slightly decreased and specific surface area increased. This structural adjustment increased the number of active sites and further enhanced oxygen species activity and redox performance, reducing the t_{90} for toluene to 221 °C, without incorporating extraneous atoms. Gao et al.^[39] synthesized MnCe catalysts *via* hydrothermal methods. Partial substitution of α -MnO₂ K⁺ and Mn sites by Ce triggered a Jahn-Teller effect, stabilizing Mn³⁺ and oxygen vacancies, thereby increasing the concentration of oxygen vacancies and acidic sites while further enhancing the deep oxidation of VOCs. In the catalytic combustion of mixed toluene and chlorobenzene gases, the two reactants

competitively adsorbed on the B acid sites of the catalyst, thereby significantly suppressing catalytic activity. Consequently, the t_{90} for toluene increased from 195 to 240 °C, while that for chlorobenzene increased from 174 to 250 °C.

Within the Ce-Mn system, Ce can directly substitute Mn within the manganese oxide lattice to form solid solutions, and it can also combine with Mn to form special structures such as perovskites. These structures enrich oxygen species, which, through defect engineering, actively participate in the catalytic combustion of VOCs, thereby improving the catalytic performance of manganese-based catalysts.

2.2.3 Cu-Mn system

Cu⁺/Cu²⁺ exhibits high electron-transfer activity and readily forms redox couples with Mn³⁺/Mn⁴⁺. Compared with other elements, such synergistic interactions occur more readily.

The morphology of catalysts has a significant impact on their catalytic performance. Wang et al.^[40] synthesized CuMn oxides with different morphologies *via* a hydrothermal method, embedding CuO nanoparticles into layered MnO₂. At the monoclinic-tetragonal (*m-t*) interface, abundant Cu²⁺-O²⁻-Mn⁴⁺ bonds were formed through oxygen bridges, promoting electron transfer from O²⁻ to Cu²⁺ and from Mn⁴⁺ to Cu²⁺.

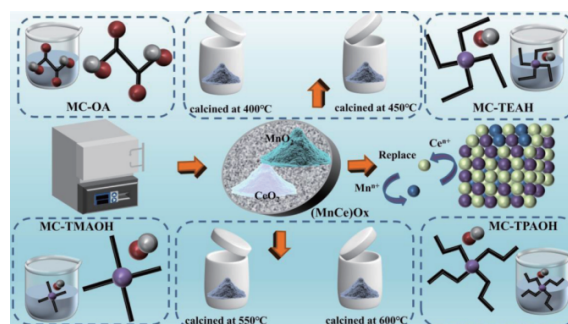


Fig. 7 MC series catalysts preparation process diagram^[38] (with permission from Elsevier)

This enhanced the activity of surface oxygen species and facilitated the redox cycle, which explains why layered CuMn oxides exhibited superior catalytic combustion performance for benzene, toluene, and xylene compared to rod-shaped and granular morphologies, with t_{90} values of 240, 207 and 227 °C, respectively. Cheng et al.^[41] synthesized CuMn_2O_4 and Mn_3O_4 via co-precipitation. Mechanical mixing of these two oxides improved catalytic activity for toluene combustion. As shown in Figure 8, oxygen vacancies formed at the $\text{CuMn}_2\text{O}_4/\text{Mn}_3\text{O}_4$ interface, effectively activating lattice oxygen within Mn_3O_4 , which subsequently migrated to the catalyst surface to participate in VOC oxidation. Replacing CuMn_2O_4 with CuCo_2O_4 or CuFe_3O_4 yielded similar t_{90} values (~240 °C), indicating that Cu significantly activates lattice oxygen species. However, not all composite oxides facilitate electron transfer; Ramstad et al.^[51] observed that Cu incorporated into OMS-2 tunnels merely produced coordination interactions, leaving the valence states of both Cu and Mn. Introducing composite oxides onto other supports also affects catalytic combustion performance. Rokicińska et al.^[52] impregnated CuMn spinel onto self-prepared dealuminated SiBEA zeolite, filling the interparticle gaps with spinel nanoparticles. During calcination, the Jahn-Teller effect induced partial oxidation-reduction of Cu^{2+} and Mn^{3+} to more stable Cu^+ and Mn^{4+} , thereby facilitating the reversible $\text{Cu}^{2+} + \text{Mn}^{3+} \leftrightarrow \text{Cu}^+ + \text{Mn}^{4+}$ redox cycle, lowering the reaction activation energy and generating abundant oxygen vacancies. Loading CuMn spinel improved both catalytic performance and economic efficiency. Many studies have concentrated on using diverse synthesis routes to yield varied catalyst structures. Li et al.^[53] synthesized CuMn bimetallic oxides (CM-MW, CM-SG, CM-CP) via microwave heating, sol-gel and co-precipitation, respectively, each manifesting the $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ active phase. CM-MW, with lower crystallinity, generated numerous oxygen vacancies, promoting oxygen species activation and migration, resulting in stronger oxidation ability and higher catalytic activity, achieving a toluene t_{90} of 213 °C, whereas CM-SG and CM-CP recorded t_{90} values of 235 and 268 °C, respectively.

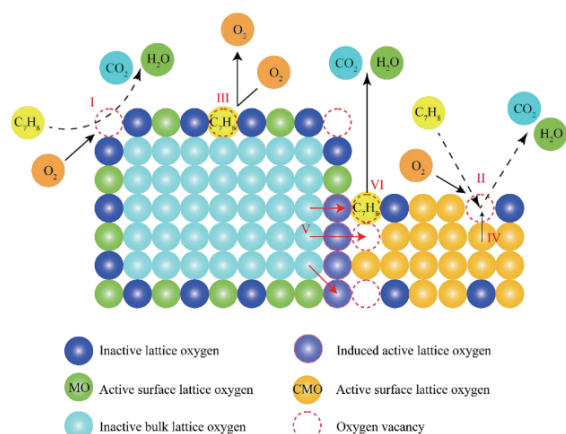


Fig. 8 Oxygen species migration mechanism^[41]
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Further, Xiang et al.^[54] prepared composite oxides with diverse morphologies through surface modification and hydrothermal methods. Surface modification induced interfacial electron redistribution and structural strain between CuO and MnO_2 , creating surface oxygen defects, while Cu^{2+} in hydrothermal CuMnO_x caused charge compensation and lattice distortion, generating bulk oxygen defects. Both types of oxygen defects enhanced toluene catalytic combustion, yielding t_{90} values of 238 and 259 °C, respectively, significantly better than $\alpha\text{-MnO}_2$ ($t_{90} = 287$ °C). Li et al.^[55] systematically studied the effects of CH_3COOH concentration, Cu/Mn molar ratio, and calcination temperature on catalyst morphology and structure, providing insight into active site formation. Optimal Cu and Mn distribution was achieved at low CH_3COOH concentration and Cu/Mn molar ratio of 1, while isolated CuO or MnO_2 weakened the synergistic effect. Appropriate calcination temperature stabilized the structure, resulting in a t_{90} of 214 °C.

The large difference in solubility products between Cu and Mn ions often leads to the formation of multiphase mixtures in the Cu-Mn system. The heterointerfaces between Cu and Mn enable synergistic interactions, profoundly modulating the electronic structure of surface-active sites and thereby enhancing catalytic performance. Additionally, special composite structures, such as spinels and solid solutions, not only maintain exceptional catalytic activity but also improve VOC adsorption, elevate catalytic efficiency, and further enhance catalyst stability.

3 Supported Mn-based catalysts

Although composite manganese-based catalysts exhibit good performance in the generation of active oxygen species and catalytic stability due to the synergistic effects among multiple metals, they still face limitations in terms of active component dispersion, precision in reaction site regulation, and the orderliness of interfacial structures. In contrast, supported manganese-based catalysts offer highly controllable structural design and allow mutual interaction between the active components and the manganese-based support, thereby enabling effective modulation of both dispersion and electronic structure of the active sites. Consequently, they have emerged as a key research direction in the field of VOCs catalytic combustion and have attracted widespread attention. Table 3 summarizes the catalytic performance of supported manganese-based catalysts reported in recent years.

3.1 Nanoparticles (NPs) Mn-based catalysts

Mo et al.^[56] observed that H- MnO_2 (hollow spherical $\gamma\text{-MnO}_2$), $\gamma\text{-MnO}_2$, $\alpha\text{-MnO}_2$ and $\beta\text{-MnO}_2$ exhibited modest catalytic activity, achieving toluene t_{90} values of 230, 238, 263 and 275 °C, respectively. The incorporation of Pt significantly enhanced the catalytic performance of these

catalysts, as shown in Table 3. However, notable differences were observed among the catalysts due to variations in the strength of the strong metal-support interaction (SMSI) between Pt and different MnO₂ crystal phases. The intensity of SMSI is closely related to the structure of the support. Although low-crystallinity γ -MnO₂ readily promotes the formation of surface oxygen vacancies, its incomplete crystal planes weaken the electronic structure matching between metal particles and the support, thereby hindering effective SMSI. Strong SMSI profoundly improves catalytic activity. For Pt/ α -MnO₂ and Pt/ β -MnO₂, MnO₂ migration encapsulating Pt nanoparticles—a typical SMSI feature—was observed, whereas no such phenomenon appeared for Pt/ γ -MnO₂. Consequently, the t_{90} values followed the order Pt/ α -MnO₂ (170 °C) > Pt/ β -MnO₂ (180 °C) > Pt/ γ -MnO₂ (190 °C), consistent with the SMSI strength trend. The morphology and structure of manganese oxides are key factors influencing SMSI strength, and the loading method also affects SMSI. Hu et al.^[57] synthesized Pt/MnO₂-r-WI through deposition in an alkaline medium, resulting in smaller and more uniformly dispersed Pt nanoparticles. In contrast, Pt/MnO₂-r-IW prepared by conventional impregnation exhibited Pt NP agglomeration up to 1.3 nm. The highly dispersed Pt within Pt/MnO₂-r-WI maximized Pt utilization and generated stronger SMSI, thereby reducing toluene t_{90} to 224 °C, significantly lower than 250 °C for Pt/MnO₂-r-IW. Other factors also affect the catalytic performance of supported manganese-based catalysts. For example, the specific surface area exerts an important role. Li et al.^[58] employed acid etching to create pores in LaPdMO₃ (LPMO), selectively removing inert La sites and exposing Pd active sites, thereby substantially enhancing interfacial between Pd and MnO₂. As shown in Figure 9, the acid-etched catalysts increased the specific

surface area from 20 to 180 m²/g, providing abundant active sites and improving mass transfer, thereby reducing the toluene t_{90} from 248 to 200 °C. Xia et al.^[59] reported that the nanotubular morphology of α -MnO₂ in 0.91Au_{0.48}Pd/ α -MnO₂ could anchor a large number of noble metal nanoparticles, creating more active sites. Sun et al.^[60] discovered that Pt/Mn₃O₄-R exhibited superior catalytic performance compared with Pt/Mn₃O₄-C, attributable to the specific surface area of Mn₃O₄-R (138.2 m²/g) was over ten times that of Mn₃O₄-C (11.7 m²/g), thereby providing richer anchoring sites for Pt, better dispersion, and facilitating the formation of more Mn–O bonds. To further investigate the construction of active sites in supported manganese-based catalysts, Pan et al.^[61] synthesized Pt/Mn₂O₃. As shown in Figure 10, Pt embedded within the Mn₂O₃ surface induced lattice distorted, thereby weakening the Mn–O bonds and generating oxygen vacancies though dissociative oxygen activation. In contrast, Pt⁰ supported on Al₂O₃ participates in toluene catalytic combustion through adsorbed oxygen species (O_{ads}), indicating that the support properties influence the VOC reaction mechanism. At high temperatures, acetone can adsorb on Pt sites in Pt/Al₂O₃, thereby deactivating reaction sites; consequently, Pt/Al₂O₃ shows excellent catalytic performance only for toluene, with t_{90} values of 199 and 233 °C for toluene and acetone, respectively. Pt/Mn₂O₃, however, avoids deactivation and achieves efficient catalytic combustion of multiple VOC types, with t_{90} values of 201 and 169 °C.

Supported manganese-based catalysts realize low-temperature, high-efficiency catalytic oxidation of diverse VOCs through structural design and oxygen species regulation. The construction of active sites in supported manganese-based catalysts requires the synergistic optimization of morphology and noble metal dispersion.

Table 3 Catalytic performance of supported Mn-based catalysts

Catalyst	VOCs type	Volume fraction/%	Air velocity/(mL·g ⁻¹ ·h ⁻¹)	t_{90} /°C	Reference
Pt/H-MnO ₂	toluene	0.1	60000	180	[56]
Pt/ γ -MnO ₂				190	[56]
Pt/ α -MnO ₂				170	[56]
Pt/ β -MnO ₂				185	[56]
Pt/MnO ₂ -r-WI	toluene	0.15	40000	224	[57]
Pd/MnO ₂	toluene	0.1	60000	200	[58]
0.91Au _{0.48} Pd/ α -MnO ₂	toluene	0.1	40000	185	[59]
	<i>m</i> -xylene	0.1		200	[59]
	toluene in mixture	0.1	40000	212	[59]
	<i>m</i> -xylene in mixture	0.1		210	[59]
Pt/Mn ₃ O ₄ -R	toluene	0.1	48000	183	[60]
Pt/Mn ₃ O ₄ -C				226	[60]
Pt/Mn ₂ O ₃	toluene	0.1	120000	202	[61]
	acetone	0.1	120000	169	[61]
H ₂ -Pt ₁ /MnO _x -200	toluene	0.1	40000	219	[62]
Ag/HMO	benzene	0.02	23000	200	[63]
0.0383Pt ₁ /OMS-2	benzene	0.1	20000	189	[64]

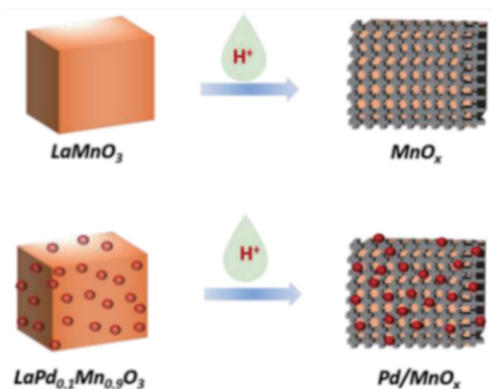


Fig. 9 Synthesis strategies of different catalysts^[58]
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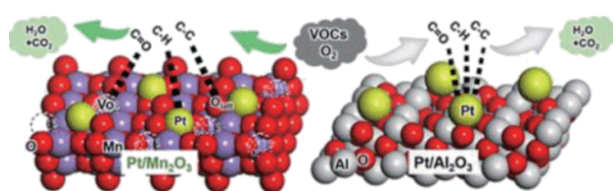


Fig. 10 Reaction mechanism^[61]
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The interaction between noble metal nanoparticles and the manganese oxide support constitutes a key factor in modulating catalyst activity. However, quantitative studies and clear structure-activity relationships regarding the influences of charge transfer, nanoparticle morphology, chemical composition, and SMSI on catalytic performance remain insufficient.

3.2 Single-atom Mn-based catalysts

Although the incorporation of noble metal nanoparticles significantly enhances the catalytic performance for VOCs, practical deployment remains limited by low metal utilization, activity degradation due to particle agglomeration, and unclear correlations between active site structure and reaction mechanisms in complex reaction pathways. To overcome the limitations of nanoparticles, single-atom catalysts anchor noble metals in an atomically dispersed form on the surface of manganese-based supports. This strategy not only maximizes metal atom utilization and prevents agglomeration but also provides well-defined geometric and electronic structures of active sites, thereby offering an ideal model for elucidating structure-activity relationships.

Li et al.^[65] employed a double-solvent method to anchor Pd atoms within the MOF structure of MnO, employing hydrophobic activated carbon as the support, successfully synthesizing Pd-0.5/Mn@C. Under room temperature and 50% humidity, the removal capacity for 53 mg/m³ hexanal reached 388.8 mg/g, which is 2.4 times that of commercial BPL activated carbon (162 mg/g) and 4 times that of lignite-based activated carbon (97.2 mg/g). For pollutant concentrations of 53 mg/m³ pentanal and 53 mg/m³ toluene,

the 99% removal capacities were 360 and 137.6 mg/g, respectively, thereby demonstrating high-efficiency removal of multiple VOCs (hexanal, pentanal, toluene). Single-atom catalysts exhibit exceptional catalytic performance in room-temperature oxidation and are also economically viable for low-temperature catalysis at higher reactant concentrations. Feng et al.^[62] employed a molten salt approach to anchor single-atom Pt on MnO₂ nanowires. The electronic interaction between Pt and Mn in Pt/MnO₂ effectively optimized the Mn oxidation state distribution, promoted Mn³⁺/Mn⁴⁺ cycling, weakened Mn–O bonds, and generated abundant oxygen vacancies, which enhanced lattice oxygen activity and mobility. Consequently, the toluene *t*₉₀ decreased significantly from 277 to 228 °C, and the reaction followed a MVK mechanism. In the catalytic oxidation of toluene and isohexane mixed gas, toluene adsorbed more strongly on the noble metal, with Pt^{δ+} causing over-adsorption and blocking active sites. H₂ reduction treatment diminished the Pt–O coordination number and disrupted the lattice order of manganese oxides, thereby increasing lattice oxygen mobility (Figure 11) and further reducing *t*₉₀ to 219 °C. Chen et al.^[63] anchored Ag atoms within the cavities of 4 nm hollandite-type MnO (HMO) particles, which significantly enhanced the activation and replenishment of lattice oxygen in adjacent Mn–O bonds. Similarly, Zhang et al.^[66] employed a one-pot synthesis to anchor single-atom Pt on sodium birnessite-type MnO₂ nanosheets, resulting in more active lattice oxygen. Hao et al.^[64] reported that OMS-2 catalysts incorporating Pt atom exhibited an increased O_{ads}/O_{latt} ratio, thereby effectively enhancing benzene catalytic performance (Table 3) and achieving over 90% benzene conversion at 189 °C. These studies reveal that the incorporation of noble metal single atoms effectively lowers reaction temperatures by enhancing oxygen species activity and other factors. Hao et al.^[67] first alkali-etched a KIT-6 template with NaOH to create a Na-doped MnO₂ phase, thereby enhancing the catalyst's sulfur resistance; however, excessive alkali doping inhibited molecular oxygen adsorption and activation. Notably, isolated Pt–Co dual-metal atoms were loaded, where Pt promoted lattice oxygen release and Co formed new redox electron pairs, enhancing Mn redox cycling. The synergistic effect of the two metals significantly promoted propane catalytic combustion.

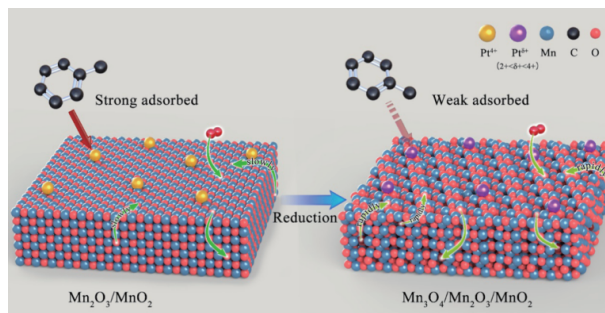


Fig. 11 Stability of Pt/MnO_x catalysts before and after H₂ treatment^[62]
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Single-atom catalysts enable more precise regulation of active site electronic structures, dynamic cycling of oxygen species, and the adsorption-activation balance of VOCs, achieving efficient and broad-spectrum VOC removal at low temperature with exceptional atom economy and practical applicability. However, current single-atom anchoring strategies still face challenges such as complex synthesis procedures, low efficiency, and constrained scalability, highlighting the need for the development of simpler synthetic methods to enable large-scale production.

3.3 Supported Mn oxides

Manganese oxides or composite metal oxides are used as active components and supported on porous carriers such as Al_2O_3 , SiO_2 , TiO_2 and ZSM-5. The porous structure of the support facilitates uniform dispersion of the active components and enhances the atomic utilization of the catalyst.

Soltan et al.^[68] synthesized Fe-Mn/H-ZSM-5 catalysts through a two-step hydrothermal and precipitation method. The Fe-Mn bimetallic species loaded on H-ZSM-5 serve as the active components for toluene catalytic oxidation, while the support does not directly participate in the reaction. The t_{90} of the $\text{Fe}_2\text{-Mn}_1$ catalyst is 362 °C, but when supported on H-ZSM-5, the t_{90} markedly decreases to 232 °C. This improvement is attributed to the support promoting uniform dispersion of the Fe and Mn metals, stabilizing the active components against aggregation, and providing acidic sites coupled with an excellent pore structure that ensures efficient VOC adsorption and diffusion. Todorova et al.^[69] loaded Co-Mn bimetallic species onto hierarchical mesoporous silica (MMS). After loading, the catalyst retained the mesoporous structure of MMS; however, the CoMn-MMS catalyst exhibited lower activity compared to single-component catalysts. This difference is related to the location of the metal oxide particles: CoMn particles were confined within the mesopores, whereas single-component oxide particles were supported on the external surface, thereby facilitating superior reactant adsorption, diffusion, and interaction with active sites. Moreno-Román et al.^[70] loaded MnO_x on MCM-41 and SBA-15 and investigated the selective oxidation of toluene, isopropanol, and their binary mixture. The study revealed that reaction conditions, catalyst morphology, redox properties, and support acidity significantly influence catalytic activity and selectivity. On MCM-41, MnO_x aggregates on the external surface, making it more accessible to VOCs and actively participating in oxidation, whereas on SBA-15, MnO_x deposits within the larger pores (~9 nm). Zhang et al.^[71] applied Mn-Ce-*M* (*M* = Cu, Ni, Co) sol-gel coatings on cordierite, thereby achieving in situ loading that reduced preparation costs. The resulting catalysts exhibited excellent activity toward multiple VOCs. Beyond supports that enhance adsorption and diffusion, even inert supports can facilitate the formation of new structures with active components. Zhang et al.^[72]

synthesized $\text{MnO}_x/\text{SiO}_2$ composites with a Si-O-Mn hybrid structure, which weakened Mn-O bonds and facilitated the release of lattice oxygen. Consequently, the T_{90} decreased from 243 to 218 °C upon loading, indicating that the interaction between active components and inert supports can create novel structural features.

The loading of manganese oxides is typically controlled at 10%–20% to ensure high atomic utilization while allowing the support to provide optimal dispersion and stability, which is one of the primary factors enhancing the activity of such catalysts. Additionally, the newly introduced acidic sites from the support, coupled with its active participation in constructing catalytic centers, also contribute positively to the catalytic performance. Overall, these supported manganese-based catalysts amplify existing advantages to further enhance catalytic activity.

4 Deactivation mechanisms and poison-resistance strategies of Mn-based catalysts

Catalyst deactivation is one of the primary challenges limiting industrial applications. The main mechanisms of deactivation include chemical deactivation, physical deactivation, and loss of active components, which often act in combination.

Chemical deactivation includes sulfur poisoning, halogen poisoning, and hydrothermal deactivation. In the presence of sulfur-containing reactants, irreversible chemical reactions often occur between the sulfur species and the active sites during the reaction. Halogen elements strongly adsorb on the surface of active sites, blocking them and hindering the adsorption and activation of VOCs and oxygen species. Hydrothermal deactivation occurs because high-temperature, humid environments induce phase transitions in manganese oxides, thereby converting the catalyst into less active phases. Physical deactivation results from sintering, hydrothermal effects, and carbon deposition. Sintering causes small crystallites to migrate and aggregate into larger ones, thereby reducing the catalyst's specific surface area and the number of active sites, which is irreversible. Hydrothermal physical deactivation arises from competitive adsorption between water molecules and VOCs, while carbon deposition, caused by incomplete combustion of VOC molecules, obstructs the pores; both of these processes are reversible, with partial activity can be restored by reducing moisture content or high-temperature calcination. Additionally, active components can be lost as volatile compounds or physically eroded by gas flow. Zhang et al.^[73] reported that incorporating Fe into manganese-based composite oxides suppressed sulfate formation in sulfur-containing atmospheres, thereby protecting the MnO_x active sites. Qiao et al.^[29] demonstrated that moderate Mo doping in MnO_x decreased the formation of sulfates and sulfites, thereby alleviating chemical deactivation and enhancing sulfur resistance. Gao et al.^[39] synthesized CeMn composite oxides, where the synergy of Brønsted acid sites

and oxygen vacancies converted chlorine in chlorobenzene into easily desorbable HCl, preventing halogen species from covering active sites. Under extreme preparation conditions, MnO_2 can form thermodynamically more stable crystal planes or phases, which diminished catalytic activity^[9–10,12]; likewise, Xie et al.^[74] observed decreased adsorbed oxygen content in Mn_2O_3 particles after high-temperature hydrothermal treatment. Fan et al.^[25] reported that increasing the calcination temperature led to a rapid decrease in MnO_2 surface area and pore collapse. In manganese-based catalysts, water molecules generally compete with VOCs for adsorption. To address this, Bi et al.^[75] synthesized Mn-Na-1.0 *via* a non-thermally derived MOF method, which can activate and dissociate introduced water vapor into active adsorbed oxygen species.

In brief, the construction of special morphologies and the introduction of multiple metals can both suppress catalyst deactivation. However, in practical applications, catalysts should be designed specifically according to the nature of the target exhaust gases, while also simplifying the preparation processes.

5 Factors affecting the activity of Mn-based catalysts

The catalytic performance of manganese-based catalysts for VOCs combustion is influenced by numerous factors, which can be divided into intrinsic and extrinsic factors. Intrinsic factors include the catalyst's reaction energy barrier, oxygen vacancy concentration, redox properties, and adsorption capacity, all determined by the catalyst's morphology and structure. Extrinsic factors involve reaction conditions such as water vapor content, space velocity, and

the type of VOCs. Modification of manganese oxides often focuses on using novel synthesis methods to disrupt stable, regular crystal planes and phases, thereby generating multivalent manganese-rich interfaces and mixed-valence environments that facilitate the formation of oxygen vacancies and enhance the redox cycling of manganese ions. However, highly active structures are prone to degradation during reactions; for example, $\delta\text{-MnO}_2$ may collapse into $\alpha\text{-MnO}_2$ and $\gamma\text{-MnO}_2$ may transform into $\beta\text{-MnO}_2$. The unstable morphology of manganese oxides gradually transforms into thermodynamically stable states during prolonged reactions, leading to decreased surface area and pore collapse, which reduces catalytic activity. In composite manganese-based catalysts, the introduction of new metal elements disrupts the original lattice structure, either through doping with minor amounts of other metals or formation of new phases such as spinel, perovskite, or multiphase mixtures, then promoting oxygen vacancy formation. Newly incorporated metal ions such as Co, Ce and Cu synergistically interact with Mn, thereby enhancing redox cycling. Supported manganese-based catalysts can be prepared *via* two strategies: incorporation of noble metals or inert supports. Noble metal loading enhances catalytic activity primarily through strong metal–support interaction (SMSI) with the manganese oxide carrier, while the dispersion of active components significantly influences catalytic performance and efficiency. The introduction of porous supports further improves the dispersion of active species, thereby enhancing catalytic performance.

Based on the data summarized in Tables 1, 2 and 3, a visual summary is presented in Figure 12. The catalytic activity of manganese-based catalysts exhibits the following sequence: noble metal-supported > transition metal–composite > MnO_x .

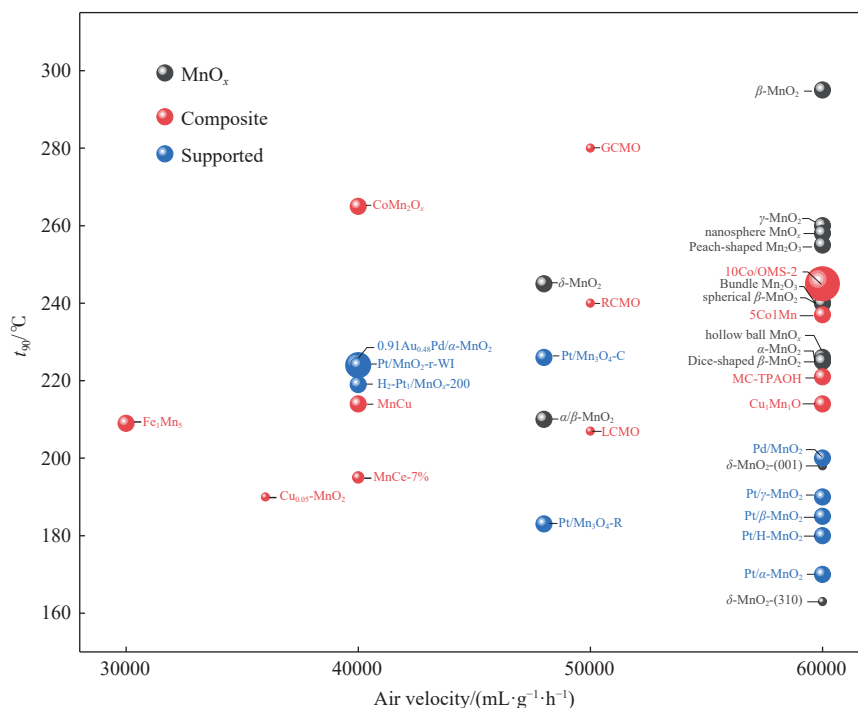


Fig. 12 t_{90} distribution of toluene catalytic combustion over manganese-based catalysts

Noble metal-supported catalysts exhibit the highest catalytic activity. Additionally, under low gas hourly space velocity (GHSV), some manganese oxides can achieve catalytic performance comparable to that of noble metal-supported catalysts. Both composite and supported catalysts maintain good catalytic activity even under high GHSV conditions.

6 Conclusions and outlook

VOCs are becoming increasingly complex, placing higher demands on catalysts, and manganese-based catalysts precisely meet the broad requirements for contemporary VOCs removal. Pure manganese oxides have simple composition and minimal toxicity, but their structural tunability remains inherently limited. Multimetallic composites, through synergistic effects, significantly enhance the redox ability of the catalyst, further improving catalytic performance. Meanwhile, diverse morphological structures such as spinel, solid solution, and perovskite exhibit stability under extreme conditions. Supported manganese-based catalysts not only exhibit excellent catalytic activity but also achieve substantial improvements in atomic utilization and cost efficiency.

Although manganese-based catalysts exhibit outstanding performance in catalytic combustion, they still face several challenges. First, industrial waste gases contain complex mixtures of VOCs, yet current research on the catalytic oxidation of multi-component systems and complex pollutants is limited, often focusing only on performance comparisons employing toluene as a probe. The reaction mechanisms for multi-component VOC oxidation remain inadequately understood. Second, broadening the applicability of manganese-based catalysts requires enhanced resistance to poisoning. More studies are needed on the adsorption and deactivation mechanisms induced by sulfur, chlorine and other elements. The long-term stability and regeneration strategies of catalysts under extreme conditions, such as high particulate concentrations and humidity, also require further exploration. Third, reliance on precious metals is a limitation. While manganese-based catalysts modified with precious metals show superior activity, their instability and high cost restrict industrial applications.

Researchers have largely focused on comparing catalytic performance, often neglecting the complexity of VOCs in practical production. Therefore, it is necessary to develop multiple evaluation metrics to enrich the catalyst performance assessment system. With their multifaceted advantages, manganese-based catalysts serve as an ideal platform for establishing a comprehensive catalyst performance evaluation framework.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] MOZAFAR A, ZHANG Y-L. Atmospheric volatile organic compounds (VOCs) in China: A review[J]. *Curr Pollut Rep*, 2020, 6(3): 250–263.
- [2] KYLE L A, NARESH K. Pulmonary health effects of indoor volatile organic compounds-A meta-analysis[J]. *Int J Environ Res Public Health*, 2021, 18(4): 1578.
- [3] MOZAFAR A, ZHANG Y-L, FAN M, et al. Characteristics of summertime ambient VOCs and their contributions to O₃ and SOA formation in a suburban area of Nanjing, China[J]. *Atmos Res*, 2020, 240: 104923.
- [4] LI Q, SU G, LI C, et al. An investigation into the role of VOCs in SOA and ozone production in Beijing, China[J]. *Sci Total Environ*, 2020, 720: 137536.
- [5] LI X, WANG Y, CHEN, D, et al. A highly dispersed Pt/copper modified-MnO₂ catalyst for the complete oxidation of volatile organic compounds: The effect of oxygen species on the catalytic mechanism[J]. *Green Energy Environ*, 2023, 8(2): 538–547.
- [6] FU X, LIU Y, DENG J, et al. Intermetallic compound PtMn_x-derived Pt-MnO_x supported on mesoporous T CeO₂: Highly efficient catalysts for the combustion of toluene[J]. *Appl Catal A: Gen*, 2020, 595: 117509.
- [7] XU Z, MO S, LI Y, et al. Pt/MnO_x for toluene mineralization via ozonation catalysis at low temperature: SMSI optimization of surface oxygen species[J]. *Chemosphere*, 2022, 286: 131754.
- [8] LI J, XU Z, WANG T, et al. A versatile route to fabricate Metal/UiO-66 (Metal = Pt, Pd, Ru) with high activity and stability for the catalytic oxidation of various volatile organic compounds[J]. *Chem Eng J*, 2022, 448: 136900.
- [9] RONG S, ZHANG P, LIU F, et al. Engineering crystal facet of α -MnO₂ nanowire for highly efficient catalytic oxidation of carcinogenic airborne formaldehyde[J]. *ACS Catal*, 2018, 8(4): 3435–3446.
- [10] HUANG J, FANG R, SUN Y, et al. Efficient α -MnO₂ with (2 1 0) facet exposed for catalytic oxidation of toluene at low temperature: A combined in-situ DRIFTS and theoretical investigation[J]. *Chemosphere*, 2021, 263: 128103.
- [11] Dai J, WANG R, SHI Z, et al. Modulating the steric effect over high-index facet of MnO_x catalysts to enhance toluene oxidation[J]. *Chem Eng J*, 2024, 486: 150328.
- [12] YANG W, SU Z, XU Z, et al. Comparative study of α -, β -, γ - and δ -MnO₂ on toluene oxidation: Oxygen vacancies and reaction intermediates[J]. *Appl Catal B: Environ*, 2020, 260: 118150.
- [13] LIU L, LIU J, GUO M. One-pot synthesis of dual-phase manganese dioxide for toluene removal: Effect of crystal phase blending level on oxygen species and activity[J]. *J Environ Chem Eng*, 2022, 10: 107448.
- [14] FIGUEREDO M J M, COCUZZA C, BNEAID S, et al. Catalytic abatement of volatile organic compounds and soot over manganese oxide catalysts[J]. *Materials*, 2021, 14: 4534.
- [15] FENG F, ZENG Y, YAN D, et al. Construction of hollow sphere MnO_x with abundant oxygen vacancy for accelerating VOCs degradation: Investigation through operando

- spectroscopy combined with on-line mass spectrometry[J]. *J Colloid Interface Sci*, 2024, 673: 746–755.
- [16] MO S, ZHANG Q, LI J, et al. Highly efficient mesoporous MnO₂ catalysts for the total toluene oxidation: Oxygen-Vacancy defect engineering and involved intermediates using in situ DRIFTS[J]. *Appl Catal B: Environ*, 2020, 264: 118464.
- [17] ZENG J, XIE H, ZHANG H, et al. Insight into the effects of oxygen vacancy on the toluene oxidation over α -MnO₂ catalyst[J]. *Chemosphere*, 2022, 291(3): 132890.
- [18] ZENG J, SONG S, CHEN S, ZHANG G, et al. Comparative study of Mn oxides catalysts on toluene oxidation: The effect of Mn valence electronic structures[J]. *J Environ Chem Eng*, 2024, 12(3): 112780.
- [19] BAI B, HUANG Y., CHEN J, et al. Ultrathin MnO₂ with strong lattice disorder for catalytic oxidation of volatile organic compounds[J]. *J Colloid Interface Sci*, 2024, 653: 1205–1216.
- [20] LI J, CHEN J, ZENG J, et al. Tuning the crystallinity of the MnO_x catalysts to promote toluene catalytic oxidation[J]. *Environ Technol*, 2025, 46(1): 98–110.
- [21] ZHENG Y, LIU Q, SHAN C, et al. Defective ultrafine MnO_x nanoparticles confined within a carbon matrix for low-temperature oxidation of volatile organic compounds[J]. *Environ Sci Technol*, 2021, 55(8): 5403–5411.
- [22] ZHOU G, LAN H, WANG H, et al. Catalytic combustion of PVOCs on MnO_x catalysts[J]. *J Mol Catal A: Chem*, 2014, 393: 279–288.
- [23] ZHOU G, LAN H, WANG, H, et al. MnO_x catalysts for the catalytic elimination of benzene compounds in the air and their preparation methods: CN201310137519. X[P]. 2013-04-19.
- [24] PAN T, DENG H, KANG S, et al. A simple strategy to tune α -MnO₂ and enhance VOC oxidation via precipitation rate control[J]. *Appl Surf Sci*, 2022, 576: 151823.
- [25] FAN C, CHEN S, ZENG J, XIE H, et al. Nano-MnO_x prepared by redox method for toluene oxidation removal from air[J]. *J Phys Chem Solids*, 2025, 196: 112379.
- [26] ZENG J, XIE H, LIU Z, et al. Oxygen vacancy induced MnO₂ catalysts for efficient toluene catalytic oxidation[J]. *Catal Sci Technol*, 2021, 11: 6708–6723.
- [27] XIE H, YV Y, CAO S, et al. Cobalt manganese composite oxide catalyst for eliminating benzene series volatile organic compounds in the air and Their preparation method: CN201510434338.2[P]. 2015-07-22.
- [28] XIE H, YV T, DU Q, et al. NiMn composite oxide catalyst for removing benzene series volatile organic compounds in the air and Their preparation method: CN201510433924.5 [P]. 2015-07-22.
- [29] QIAO Y, YANG S, SUN X, et al. Tailoring local environment of oxygen vacancies by molybdenum doping on MnO₂ for enhanced catalytic oxidation of VOCs[J]. *Chem Eng J*, 2024, 481: 148703.
- [30] YANG S, QI Z, WEN Y, et al. Generation of abundant oxygen vacancies in Fe doped δ -MnO₂ by a facile interfacial synthesis strategy for highly efficient catalysis of VOCs oxidation[J]. *Chem Eng J*, 2023, 452: 139657.
- [31] HU J, LI W B, LIU R F. Highly efficient copper-doped manganese oxide nanorod catalysts derived from CuMnO hierarchical nanowire for catalytic combustion of VOCs[J]. *Catal Today*, 2018, 314: 147–153.
- [32] DONG N, CHEN M, YE Q, et al. Promotional effect of cobalt doping on catalytic performance of cryptomelane-type manganese oxide in toluene oxidation[J]. *J Environ Sci*, 2023, 126: 263–274.
- [33] DENG H, LU Y, PAN T, et al. Metals incorporated into OMS-2 lattice create flexible catalysts with highly efficient activity in VOCs combustion[J]. *Appl Catal B: Environ*, 2023, 320: 121955.
- [34] HU Z, TANG Z, ZHANG T, et al. Synergism between manganese and cobalt on Mn–Co oxides for the catalytic combustion of VOCs: A combined kinetics and diffuse reflectance infrared fourier transform spectroscopy study[J]. *Ind Eng Chem Res*, 2022, 61(14): 4803–4815.
- [35] LIU P, LIAO Y, LI J, et al. Insight into the effect of manganese substitution on mesoporous hollow spinel cobalt oxides for catalytic oxidation of toluene[J]. *J Colloid Interface Sci*, 2021, 594: 713–726.
- [36] LI M, LIU X, NIU X, et al. Regulating the mobility of lattice oxygen on hollow cobalt-manganese sub-nanospheres for enhanced catalytic oxidation of toluene and o-xylene[J]. *J Colloid Interface Sci*, 2024, 671: 192–204.
- [37] SHAH P M, BAILEY L A, TAYLOR S H. The Influence of cerium to manganese ratio and preparation method on the activity of ceria-manganese mixed metal oxide catalysts for VOC total oxidation[J]. *Catalysts*, 2023, 13(1): 114.
- [38] CHEN Z, ZHOU J, ZHUGE X, et al. Catalytic oxidation of toluene using layer-modified Mn-Ce solid solution with high specific surface area[J]. *J Environ Chem Eng*, 2023, 11(6): 111427.
- [39] GAO H, SONG Z, MAO Y, et al. Tight coupling of oxygen vacancies and acidity on α -MnO₂ through cerium doping engineering for efficient removal of multi-component VOCs[J]. *Appl Catal B: Environ*, 2025, 362: 124745.
- [40] WANG Y, YANG D, LI S, et al. Layered copper manganese oxide for the efficient catalytic CO and VOCs oxidation[J]. *Chem Eng J*, 2019, 357: 258–268.
- [41] CHENG Y, ZHU J, WANG Z, et al. Revealing oxygen transfer between Mn₂O₄ and CuMn₂O₄ and its effect on enhanced catalytic oxidization of VOCs[J]. *Surf Interfaces*, 2023, 41: 103242.
- [42] GONG S, WANG W, CHEN K, et al. Effect of metal ion dopants on decomposition formaldehyde room-temperature catalyzed by oxygen-deficient M-MnO_x (M=Ce, Co and Cu) materials[J]. *J Environ Chem Eng*, 2022, 10(3): 107571.
- [43] WANG Y, LIU K, WU J, et al. Unveiling the effects of alkali metal ions intercalated in layered MnO₂ for formaldehyde catalytic oxidation[J]. *ACS Catal*, 2020, 10(17): 10021–10031.
- [44] ZHAO H, LIU H, LIU Y, et al. Alkali metal doped MnO_x catalysts for formaldehyde oxidation[J]. *Catal Lett*, 2025, 155(1): 40.
- [45] XU Y, DHAINAUT J, DACQUIN J P, et al. La_{1-x}(Sr, Na, K)_xMnO₃ perovskites for HCHO oxidation: The role of oxygen species on the catalytic mechanism[J]. *Appl Catal B: Environ*, 2021, 287: 119955.

- [46] HUANG Z, LI H, ZHANG X, et al. Catalytic oxidation of toluene by manganese oxides: Effect of K^+ doping on oxygen vacancy[J]. *J Environ Sci*, 2024, 142: 43–56.
- [47] ZHOU G, HE X, LIU S, et al. Phenyl VOCs catalytic combustion on supported CoMn/AC oxide catalyst[J]. *J Ind Eng Chem*, 2015, 21: 932–941.
- [48] REN Y, SONG C, WANG H, et al. Accelerated dual activation of lattice oxygen and molecule oxygen over $CoMn_2O_4$ catalysts for VOC oxidation: Promoting the role of oxygen vacancies[J]. *ACS Catal*, 2024, 14: 4340–4351.
- [49] SONG S, Qu Q, XIE H, et al. High performance CoMn solid solution oxide catalyst prepared by simple co-precipitation method for toluene low temperature oxidation removal from air[J]. *Inorg Chem Commun*, 2025, 179: 114678.
- [50] XIE H, SONG S, ZHANG J, et al. A CoMn solid solution composite oxide catalyst, preparation method and application: CN202411074622.9[P]. 2024-08-07.
- [51] RAMSTAD A L, MIKKELSEN Ø. Structural characterisation of copper-containing manganese oxide octahedral molecular sieve (Cu-OMS-2) materials by X-ray absorption spectroscopy and cyclic voltammetry[J]. *J Mol Struct*, 2004, 697(1/3): 109–117.
- [52] ROKICIŃSKA A, MAJERSKA P, DROZDEK M, et al. Impact of Mn addition on catalytic performance of Cu/SiBEA materials in total oxidation of aromatic volatile organic compounds[J]. *Appl Surf Sci*, 2021, 546: 149148.
- [53] LI M, ZHANG W, ZHANG X, et al. Influences of different surface oxygen species on oxidation of toluene and/or benzene and their reaction pathways over Cu-Mn metal oxides[J]. *J Colloid Interface Sci*, 2023, 630: 301–316.
- [54] XIANG W, LIU W, LIU G, et al. Decoding the role of oxygen defects in MnO_2 -based catalysts for enhanced VOCs oxidation[J]. *Mater Today Chem*, 2025, 44: 102604.
- [55] LI J R, ZHANG W P, LI C, et al. Insight into the catalytic performance and reaction routes for toluene total oxidation over facilely prepared Mn-Cu bimetallic oxide catalysts[J]. *Appl Surf Sci*, 2021, 550: 149179.
- [56] MO S, ZHANG Q, ZHANG M, et al. Elucidating the special role of strong metal-support interactions in Pt/ MnO_2 catalysts for total toluene oxidation[J]. *Nanoscale Horiz*, 2019, 4: 1425.
- [57] HU J, GAO X, FAN Q, et al. Facial controlled synthesis of Pt/ MnO_2 catalysts with high efficiency for VOCs combustion[J]. *RSC Adv*, 2021, 11: 16547.
- [58] LI L, YAN J, JI W. Engineering the microenvironment of Pd nanoparticles on porous MnO_x matrix to improve catalytic toluene combustion[J]. *Appl Catal A: Gen*, 2023, 649: 118947.
- [59] XIA Y, XIA L, LIU Y, et al. Concurrent catalytic removal of typical volatile organic compound mixtures over Au-Pd/ α - MnO_2 nanotubes[J]. *J Environ Sci*, 2018, 64: 276–288.
- [60] SUN Y, FAN J, CHENG H, et al. Investigation into the roles of different oxygen species in toluene oxidation over manganese-supported platinum catalysts[J]. *Mol Catal*, 2021, 507: 111569.
- [61] PAN T, BAI S, ZHANG X, et al. In-depth understanding of the oxidative compatibility of volatile organic compounds with Mn_2O_3 and Pt-loaded catalysts[J]. *Environ Sci Technol*, 2024, 58(21): 9381–9392.
- [62] FENG Y, WANG C, WANG C, et al. Catalytic stability enhancement for pollutant removal via balancing lattice oxygen mobility and VOCs adsorption[J]. *J Hazard Mater*, 2022, 424: 127337.
- [63] CHEN Y, HUANG Z, ZHOU M, et al. Single silver adatoms on nanostructured manganese oxide surfaces boost oxygen activation for benzene abatement[J]. *Environ Sci Technol*, 2017, 51(4): 2304–2311.
- [64] HAO X, DAI L, DENG J, et al. Nanotubular OMS-2 supported single-atom platinum catalysts highly active for benzene oxidation[J]. *J Phys Chem C*, 2021, 125: 17696–17708.
- [65] LI Y, ZHANG P, LIU Y. Single atom Pd anchored-MnO confined in porous carbon matrix for low-level VOCs removal at room temperature[J]. *Appl Catal B: Environ*, 2024, 355: 124139.
- [66] ZHANG H, SUI S, ZHENG X, et al. One-pot synthesis of atomically dispersed Pt on MnO_2 for efficient catalytic decomposition of toluene at low temperatures[J]. *Appl Catal B: Environ*, 2019, 257: 117878.
- [67] HAO X, DENG J, LIU Y, et al. Mesoporous Na_xMnO_y -supported platinum–cobalt bimetallic single-atom catalysts with good sulfur dioxide tolerance in propane oxidation[J]. *ACS Sustainable Chem Eng*, 2022, 10: 8326–8341.
- [68] SOLTAN W B, PENG J, CAO Z, et al. Bimetallic Fe-Mn loaded H-ZSM-5 zeolites for excellent VOCs catalytic oxidation at low-temperatures: Synergistic effects and catalytic mechanisms[J]. *Chem Eng J*, 2023, 475: 146251.
- [69] TODOROVA S, BLIN J L, NAYDENOV A, et al. Co-Mn oxides supported on hierarchical macro-mesoporous silica for CO and VOCs oxidation[J]. *Catal Today*, 2021, 361: 94–101.
- [70] MORENO-ROMÁN E J, CAN F, MEILLE V, et al. MnO_x catalysts supported on SBA-15 and MCM-41 silicas for a competitive VOCs mixture oxidation: In-situ DRIFTS investigations[J]. *Appl Catal B: Environ*, 2024, 344: 123613.
- [71] ZHANG X, WU D. Ceramic monolith supported Mn-Ce-M ternary mixed-oxide ($M=Cu, Ni$ or Co) catalyst for VOCs catalytic oxidation[J]. *Ceram Int*, 2016, 42: 16563–16570.
- [72] ZHANG B, ZHOU L, QI M, et al. Outstanding stability and enhanced catalytic activity for toluene oxidation by Si-O-Mn interaction over MnO_x/SiO_2 [J]. *Ind Eng Chem Res*, 2022, 61: 1044–1055.
- [73] ZHANG Q, HE S, ZHANG Z, et al. Low-temperature selective catalytic reduction of NO_x and anti-toxicity of $MnO_x-FeO_y/TiO_2-ZrO_2-CeO_2$ [J]. *Chin J Eng*, 2020, 42(3): 321–330.
- [74] XIE M, ZENG Y, CUI K, et al. The effect of hydrothermal aging on Mn_2O_3/Cu -SSZ-39 composite catalysts for selective catalytic reduction of NO_x by NH_3 [J]. *Catal Today*, 2024, 430: 114557.
- [75] BI F, FENG X, ZHOU Z, et al. Mn-based catalysts derived from the non-thermal treatment of Mn-MIL-100 to enhance its water-resistance for toluene oxidation: Mechanism study[J]. *Chem Eng J*, 2024, 485: 149776.

锰基催化剂用于 VOCs 催化燃烧的研究进展

罗光峻¹, 陈 爽^{1,*}, 殷 宏¹, 曾 嘉², 谢红梅^{2,*}, 周桂林^{1,2}

(1. 重庆工商大学 废油资源化技术与装备教育部工程研究中心, 重庆 400072; 2. 重庆工商大学 环境与资源学院, 重庆 400072)

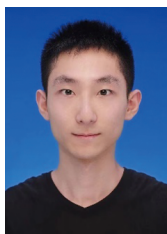
摘 要: 挥发性有机物 (VOCs) 来源广泛, 对大气环境影响突出, 可对人体健康造成严重危害。锰 (Mn) 基催化剂因其结构多样、类型丰富, 在 VOCs 催化燃烧领域应用广泛。本综述总结了多种锰基催化剂的催化性能, 重点讨论了高性能锰基催化剂的制备策略, 解析了活性位点的构筑对锰基催化剂催化燃烧性能的影响, 并阐述了 VOCs 的催化氧化机理, 对 VOCs 的污染治理具有一定的借鉴作用。

关键词: 锰基催化剂; 催化燃烧; 金属复合; 金属负载; 反应机理

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作者简介:



罗光峻(2001), 硕士, 研究方向为 VOC 的催化燃烧, 2023357003@ctbu.edu.cn。



陈爽(1991), 博士, 博士后, 助理研究员。研究方向包括纳米材料的可控制备、异相催化以及生物质转化, chenshuang@ctbu.edu.cn。