REVIEW ARTICLE

Catalytic removal of toluene over manganese oxide-based catalysts: a review

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Received: 23 August 2019 / Accepted: 11 November 2019 / Published online: 17 December 2019 © Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract



It is necessary to control the emissions of toluene, which is hazardous to both human health and the atmosphere environment and has been classified as a priority pollutant. Manganese oxide-based (Mn-based) catalysts have received increased attention due to their high catalytic performance, good physicochemical characteristic, availability in various crystal structures and morphologies, and being environmentally friendly and low cost. These catalysts can be classified into five categories, namely single manganese oxide, Mn-based composite oxides, Mn-based special oxides, supported Mn-based oxides, and Mn-based monoliths. This review focused on the recent progress on the five types of Mn-based catalysts for catalytic removal of toluene at low temperature and further systematically summarized the strategies improving catalysts, including improving synthetic methods, incorporating MnO_x with other metal oxides, depositing Mn-based oxides on proper supports, and tuning the supports. Moreover, the effect of coexisting components, the reaction kinetics, and the oxidation mechanisms toward the removal of toluene were also discussed. Finally, the future research direction of this field was presented.

Keywords Toluene · Manganese oxide · Catalytic removal · Catalyst modification · Reaction kinetics · Oxidation mechanism

Introduction

Toluene is one of the representative hazardous volatile organic compounds in the atmosphere. It was emitted mainly from petrochemical industries, chemical industries, processing industries, and transportation activities (Wang et al. 2013; Zhang et al. 2017). Exposure to toluene can lead to some health-related issues such as respiratory tract irritation and central lesion, and even induce carcinogenicity, reproductive toxicity, and mutagenicity (Hannigan and Bowen 2010; Hsu et al. 2006; Kamal et al. 2016). Besides, it possesses high photochemical ozone creation potential and high secondary organic aerosol formation potential (Derwent et al. 1996;

Responsible Editor: Santiago V. Luis

² Key Laboratory of Environmental Biology and Pollution Control, Ministry of Education, Hunan University, Changsha 410082, People's Republic of China Sun et al. 2016; Wu et al. 2017). Because of its being hazardous to air and human health, toluene has been classified as a priority pollutant. Therefore, the development of efficient technologies to reduce or even eliminate its emissions has become an important research field.

To date, various environmental technologies have been developed, such as absorption (Hariz et al. 2017), adsorption (Liu et al. 2018b), membrane separation (Cichowska-Kopczyńska et al. 2018), biodegradation (Mathur et al. 2007), catalytic oxidation/combustion (Rokicińska et al. 2017), plasma catalysis (Qin et al. 2016), and photocatalysis (Muñoz-Batista et al. 2018). However, each technology has certain limitations in practical application. For example, adsorption is only suited to treat highly diluted air pollutants and it may cause secondary hazardous pollutants during the regenerative process. Plasma catalysis can also lead to secondary pollutants including NO_x, organic small molecules, and many free radical species, which are produced during the discharge process; besides, it is with high energy consumption. Biodegradation has shortcomings such as concentration sensitivity, long residence time, complicated operation, and large area reactor. Among these technologies, catalytic oxidation/ combustion has been focused to be a very promising technology because of its high destruction efficiency, absence of

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secondary hazardous pollutants, safety, low operating cost, and wide application scope (Huang et al. 2015; Kamal et al. 2016). It is well known that the focus of catalytic oxidation/ combustion is to develop catalysts with high performance and low cost. Up to now, extensive studies have been devoted to the development of new catalysts for the removal of toluene. Typically, based on the active component, catalysts used in the removal of toluene can be classified into two major groups: noble metal-based catalysts (Pt (Peng et al. 2018), Pd (Zhao et al. 2016), Au (Tan et al. 2014), etc.) and nonnoble metal oxide catalysts (Mn (Kim and Shim 2010), Cu (Zhang et al. 2018), Co (Rokicińska et al. 2017), Ce (Hu et al. 2018a), Fe (Solsona et al. 2016), Ni (Meng et al. 2016), etc.). Noble metal-based catalysts commonly exhibit superior activity for toluene removal at relatively low temperatures; however, their widespread use is limited by high price, easy poisoning tendency, and low thermal stability (Spiveya and Buttb, 1992). Compared with noble metal-based catalysts, non-noble metal oxide catalysts, possessing sufficient activity, lower cost, better thermal stability, and good reducibility, have received increased attention (Li et al. 2009; Spiveya and Buttb, 1992).

Among the non-noble metal catalysts, Mn-based catalysts are considered as outstanding and promising catalysts (Xu et al. 2017). On the one hand, MnO_x is able to mobilize electrons to generate the mobile-electron environment which is beneficial to toluene removal (Durán et al. 2009). On the other hand, manganese is environmentally friendly and low cost. Many researches demonstrated that Mn-based catalysts showed better catalytic activity than other transition metal oxide-based catalysts for the removal of toluene (Du et al. 2012; Özçelik et al. 2009; Soylu et al. 2010; Suárez-Vázquez et al. 2018). Additionally, some researches revealed Mn-based catalysts possessed comparable catalytic activities with supported noble metals (Lahousse et al. 1998). In the past decade, many Mnbased catalysts with different structures and morphologies have been developed via various preparation methods. These catalysts are divided into five categories: (1) single manganese oxides, (2) Mn-based composite oxides, (3) Mn-based special oxides, (4) supported Mn-based oxides, and (5) Mn-based monoliths. Massive effort has been devoted to study their catalytic performance and catalytic behavior in the removal of toluene and significant progress has been made. Nevertheless, there are still few reviews concentrated on the removal of toluene over Mn-based catalysts.

Thus, this review focused on the recent progress on five categories of Mn-based catalysts for the catalytic removal of toluene at low temperature. Simultaneously, the strategies improving catalysts and the effect of coexisting components were systematically elaborated. Furthermore, the reaction kinetics and oxidation mechanism of removing toluene were also discussed. Finally, the future developing direction of this field was presented.

Newly developed Mn-based catalysts

Single manganese oxides

Single manganese oxides (MnO_x) , consisting of the basic structural $[MnO_6]$ octahedra, have been extensively investigated in the removal of toluene in the last years. Table 1(a) considers some newly developed MnO_x catalysts.

Manganese with electronic structure $3d^54s^2$ is a multivalent element, and it possesses variable valences $(-3 \rightarrow +7)$. In general, Mn₃O₄, Mn₂O₃, and MnO₂ are well-known high-performance MnO_r in the removal of toluene. Kim and Shim (2010) reported that the reactivity of MnO_x in toluene combustion showed an order of $Mn_3O_4 > Mn_2O_3 > MnO_2$, which was related to the oxygen mobility of catalysts. Piumetti et al. (2015) observed that the total oxidation activity of toluene on mesoporous MnO_x catalysts declined as follows: Mn₃O₄ > Mn_2O_3 > Mn_2O_3 - MnO_2 (mixture of Mn_2O_3 and MnO_2). Mn₃O₄ displayed the largest amount of surface electrophilic oxygen. Wang et al. (2016a) reported two MnO_x catalysts with similar textual properties: MnO2 as well as mixtures of Mn2O3 and Mn₅O₈. MnO₂ exhibited more superior activity and durability in the removal of toluene, which was correlated with average oxidation state of Mn, low-temperature reducibility, and the content of surface-adsorbed oxygen.

As we all know, MnO_x can show α -, β -, γ -, δ -, ϵ -, and λ -MnO_x crystal structures (Liang et al. 2008; Shi et al. 2012) and wire-like, rod-like, tube-like, flower-like, dumbbell-like, urchin-like, etc. morphologies (Li et al. 2014a; Shi et al. 2012; Wang et al. 2012) in different preparation environments. Different crystal structures and morphologies may lead to different specific surface areas, pore properties, active phases or facets, redox abilities, and active oxygen species, which can affect catalytic performance. Liao et al. (2017) reported that MnO_x polyhedron with hollow morphology was superior for toluene oxidation than the solid one owing to its high oxygen adspecies concentrations and high average oxidation state of Mn. Wang et al. (2012) compared toluene oxidation activity over three α -MnO₂ catalysts with different morphologies and found that the sequence was ranked as follows: rod-like α - MnO_2 > tube-like α -MnO₂ > wire-like α -MnO₂. Moreover, they also studied the activity for toluene combustion over three MnO₂ catalysts with a diversity of crystal structures and morphologies and found their activity decreased as follows: rod-like α -MnO₂ > flower-like ε -MnO₂ > dumbbelllike β -MnO₂ (Shi et al. 2012). The best activity occurred on the rod-like α -MnO₂ catalyst in both studies above, which was primarily connected with the quantity of adsorbed oxygen

Table 1 Catalytic removal of toluene over five types of Mn-based catalysts in recent literatures

Catalyst		Reaction conditions	Catalytic efficiency		Ref.
			Conversion (%)	CO ₂ yield (%)	
a	MnO ₂ –SBA ₁₆ MnO ₂ –KIT ₆	1000 ppm toluene, toluene/ $O_2 = 1/400$, N_2 balance, 20,000 mL/(g h)	$T_{100} = 230 \text{ °C}$ $T_{100} = 230 \text{ °C}$		Du et al. (2012)
	MnO ₂	1000 ppm toluene, air balance, 15,000 mL/(g h)	$T_{90} = 230 \ ^{\circ}\text{C}$		Wang et al. (2016a)
	MnO_x -hollow	1000 ppm toluene, air balance, 32,000 mL/(g h)	$T_{100} = 240 \ ^{\circ}\text{C}$		Liao et al. (2017)
	Mn ₂ O ₃	1000 ppm toluene, 20 vol% O ₂ , N ₂ balance, 60,000 mL/(g h)	$T_{90} = 239 \ ^{\circ}\text{C}$		Yang et al. (2019b)
	$\alpha@\beta-MnO_2$	500 ppm toluene, 20 vol% O_2, N_2 balance, 30,000 h^{-1}		$T_{100} = 205$	Huang et al. (2018)
	γ -MnO ₂	120,000 mL/(g h)	$T_{90} = 252 \ ^{\circ}\text{C}$	C	Si et al. (2015)
	Mn ₃ O ₄	1000 ppm toluene, air balance, 180,000 h^{-1}	$T_{90} = 250 \ ^{\circ}\text{C}$		Li et al. (2016b)
b	Mn _{0.6} Ce _{0.4} O ₂	500 ppm toluene, 20 vol% O_2 , Ar balance, 22,500 h^{-1}	$T_{100} = 210 ^{\circ}\text{C}$		Du et al. (2018)
	$Mn_{0.85}Ce_{0.15}O_x$	1000 ppm toluene, air balance, 32,000 mL/(g h)	$T_{100} = 225 \ ^{\circ}\text{C}$		Liao et al. (2013)
	$CeO_x - \delta - MnO_2$	1000 ppm toluene, air balance, 15,000 mL/(g h)		$T_{90} = 277$ °C	Li et al. (2017a)
	Mn_2CeO_x	500 ppm toluene, 1.6 wt% H ₂ O, 20 vol% O ₂ , N ₂ balance, 40,000 mL/(g h)	$T_{90} = 215 \ ^{\circ}\text{C}$		Wang et al. (2018a)
	$Mn_{0.5}Ce_{0.5}O_x$	600 ppm toluene, 20 vol% O ₂ , He balance, $W/F = 0.072$ (g s)/cm ³		$T_{100} = 260$ °C	Delimaris and Ioannides (2008)
	$Mn_{0.5}Ce_{0.5}O_x$	1000 ppm toluene, air balance, 60,000 mL/(g h)		$T_{90} = 245$ °C	Tang et al. (2015)
	Mn_3CeO_x	1000 ppm toluene, air balance, 60,000 mL/(g h)	$T_{90} = 256 \ ^{\circ}\text{C}$	$T_{90} = 268$ °C	Chen et al. (2018)
	MnO _x -CeO ₂	1000 ppm toluene, 20 vol% O ₂ , N ₂ balance, 60,000 mL/(g h)	$T_{90} = 220 \ ^{\circ}\text{C}$		Sun et al. (2019)
	$Cu_{1.5}Mn_{1.5}O_4$	1000 ppm toluene, air balance, 46,154 mL/(g h)	$T_{100} = 240 \ ^{\circ}\text{C}$		Behar et al. (2012)
	CuMnO	1000 ppm toluene, 20 vol% O ₂ , N ₂ balance, 60,000 mL/(g h)	$T_{90} = 214 \ ^{\circ}\text{C}$		Hu et al. (2018b)
	CuMnO _x	800 ppm toluene, air balance, 30,000 mL/(g h)		$T_{90} = 190$ °C	Ye et al. (2018)
	CuO- δ -MnO ₂	1000 ppm toluene, air balance, 30,000 mL/(g h)	$T_{90} = 258 \ ^{\circ}\text{C}$	-	Li et al. (2017b)
	$MnCo_2O_x$	1000 ppm toluene, 20 vol% O ₂ , Ar balance, 30,000 mL/(g h)	$T_{100} = 250 \ ^{\circ}\text{C}$		Qu et al. (2014)
	MnCoO _x	500 ppm toluene, air balance, 96,000 mL/(g h)	$T_{100} = 240 \ ^{\circ}\text{C}$		Luo et al. (2018)
	Co ₃ O ₄ MnCo ₂ O _{4.5}	500 ppm toluene, 1.6 wt% H ₂ O, 10 vol% O ₂ , N ₂ balance, 30,000 h^{-1}		$T_{90} = 194$ °C	Wang et al. (2018b)
	Mn_2FeO_x	500 ppm toluene, 1.6 wt% H ₂ O, 10 vol% O ₂ , N ₂ balance, 50,000 h^{-1}		$T_{90} = 197$ °C	Wang et al. (2018c)
	Mn_5FeO_x	1000 ppm toluene, air balance, 20,000 mL/(g h)	$T_{90} = 147 \ ^{\circ}\text{C}$	$T_{100} = 215$ °C	Chen et al. (2017)
	$CuO_x - Mn_{0.5}Ce_{0.5}O_x$	1000 ppm toluene, air balance, 60,000 mL/(g h)	$T_{100} = 240 \ ^{\circ}\text{C}$		Hu et al. (2017)
	$CuMn_2Ce_4O_x$	5 g/m ³ toluene, air balance, 24,000 mL/(g h)	$T_{99} < 220 \ ^{\circ}\mathrm{C}$		Lu et al. (2015)
	MnMgAlO _x	600 ppm toluene, air balance, 84,000 mL/(g h)		$T_{90} = 273$ °C	Castaño et al. (2015)
	MnMgAlO _x	600 ppm toluene, air balance, 84,000 mL/(g h)	$T_{90} = 262 \ ^{\circ}\text{C}$	<i>T</i> ₉₀ = 290 °C	Castaño et al. (2013)
	CoMnMgAlO _x	1200 ppm toluene, 60,000 mL/(g h)	$T_{90} = 258 \ ^{\circ}\text{C}$	$T_{90} = 311$ °C	Aguilera et al. (2011)
c	Mn ₃ O ₄ -OMS-2	4000 mg/m ³ toluene, 16,000 h^{-1}		$T_{100} = 283$ °C	Santos et al. (2010b)
	OMS-2 _s OMS-2 _r	1000 ppm toluene, air balance, 200,000 $\rm h^{-1}$	$T_{100} > 300 \text{ °C}$ $T_{100} = 240 \text{ °C}$		Sun et al. (2011)

Table 1 (continued)

Catalyst		Reaction conditions	Catalytic efficiency		Ref.
			Conversion (%)	CO ₂ yield (%)	
	OMS-2 _S OMS-2 _h	1000 ppm toluene, 20 vol% O ₂ , N ₂ balance, 60,000 mL/(g h)	$T_{90} = 263 \text{ °C}$ $T_{90} = 311 \text{ °C}$		Sihaib et al. (2017)
d	LaMnO ₃ /TiO ₂ LaMnO ₃ /Y ₂ O ₃ -ZrO ₂	1000 ppm toluene, 20 vol% O_2,N_2 balance, 60,000 mL/(g h)	$T_{90} = 303 \text{ °C}$ $T_{90} = 248 \text{ °C}$		Giroir-Fendler et al. (2016)
	La _{0.8} Ce _{0.2} MnO ₃ /CeO ₂	300 mg/m^3 toluene, 12,000 h ⁻¹	$T_{90} = 240 \ ^{\circ}\text{C}$		Wang et al. (2016b)
	LaMnO ₃ -SG	1000 ppm toluene, 20 vol% O_2 , He balance, 15,000 mL/(g h)	$T_{90} = 213 \ ^{\circ}\text{C}$		Zhang et al. (2014)
	LaMnO ₃	1000 ppm toluene, toluene/O ₂ = 1/400, N ₂ balance, 20,000 h ⁻¹	$T_{90} = 220 \ ^{\circ}\text{C}$		Wang et al. (2014)
	SmMnO ₃	1000 ppm toluene, air balance, 24,000 mL/(g h)	$T_{100} = 240 \ ^{\circ}\text{C}$		Liu et al. (2018a)
	$SrTi_{1 - X}Mn_{X}O_{3}$	1000 ppm toluene, 20 vol% O_2,N_2 balance, 60,000 mL/(g h)		$T_{100} = 335$ °C	Suárez-Vázquez et al. (2018)
	3DOM LaMnO ₃	1000 ppm toluene, toluene/O ₂ = 1/400, N ₂ balance, 20,000 h ⁻¹	$T_{90} = 243 \ ^{\circ}\text{C}$		Liu et al. (2012)
	MnO ₂ /3DOM LaMnO ₃	2000 ppm toluene, 20 vol% $\rm O_2, N_2$ balance, 120,000 mL/(g h)		$T_{100} = 290$ °C	Si et al. (2016)
	MnO _x /3DOM LaMnO ₃	1000 ppm toluene, toluene/O ₂ = 1/400, N ₂ balance, 20,000 h^{-1}	$T_{90} = 215 \ ^{\circ}\mathrm{C}$		Liu et al. (2013)
e	MnO_x/Al_2O_3	1000 ppm toluene, air balance, 30,000 mL/(g h)	$T_{90} = 334 \ ^{\circ}\mathrm{C}$		Jung et al. (2015)
	MnO _x /Al ₂ O ₃ -HNO ₃	VOC: O_2 :He = 1:20.8:78.2, 20,000 mL/(g h)	$T_{80} = 310 \ ^{\circ}\text{C}$		Aguero et al. (2009b)
	MnO_x/α - Al_2O_3	1000 ppm toluene, air balance, 15,000 h^{-1}		$T_{90} = 289$ °C	Pozan (2012)
	$CuO-MnO/\gamma-Al_2O_3$ MnO-CeO_2/\gamma-Al_2O_3	1000 ppm toluene, air balance, $W/F = 0.018$ (g s)/cm ³	$T_{100} = 280 \text{ °C}$ $T_{97} = 280 \text{ °C}$		Saqer et al. (2011)
	$Cu_{1.5}Mn_{2.25}O_x/\gamma$ -Al ₂ O ₃	1000 ppm toluene, 30 vol% O_2 , N_2 balance, 120,000 h^{-1}	$T_{90} = 298 \ ^{\circ}\text{C}$		Wang et al. (2017)
	Cu–MnO _x / γ -Al ₂ O ₃	1000 ppm toluene, air balance, 21,000 h^{-1}	$T_{90} = 279 \ ^{\circ}\text{C}$		Kim et al. (2014)
	MnO _x -CeO ₂ /TiO ₂	1000 ppm toluene, 6 vol% O_2 , N_2 balance, 15,000 h^{-1}	$T_{100} = 240 \ ^{\circ}\text{C}$		Yu et al. (2010)
	CuCe _{0.75} Zr _{0.25} /TiO ₂	0.5 vol% toluene, air balance, 60,000 mL/(g h)	$T_{90} = 234 \ ^{\circ}\text{C}$		Zhao et al. (2019)
	Mn _{1.5} CoO _x /AC	10,000 ppm toluene, air balance, 66,000 mL/(g h)	$T_{93.5} = 235$ °C		Zhou et al. (2015)
	MnO ₂ /clinoptilolite	1000 ppm toluene, air balance, 15,000 h^{-1}		$T_{90} = 292$ °C	Soylu et al. (2010)
	NiO-Mn ₂ O ₃ /clinoptilolite	1000 ppm toluene, air balance, 10,000 h^{-1}	$T_{100} = 225 \ ^{\circ}\text{C}$		Ahmadi et al. (2017)
	MnO _x /H-Beta-SDS	1000 ppm toluene, air balance, 60,000 mL/(g h)	$T_{90} = 285 \ ^{\circ}\text{C}$		Peng et al. (2017)
	Cu-Mn/MCM-41	3500 ppm toluene, 8.8 vol% O_2 , Ar balance, 36,000 mL/(g h)	$T_{95.2} = 320$ °C		Li et al. (2008)
	MnO _x /HZSM-5	1000 ppm toluene, 20 vol% O_2 , He balance, 15,000 mL/(g h)	$T_{90} = 267 \ ^{\circ}\mathrm{C}$		Huang et al. (2016)
	MnO _x /HZSM-5	1000 ppm toluene, 20 vol% O ₂ , He balance, 15,000 mL/(g h)	$T_{90} = 261 {}^{\circ}\mathrm{C}$		Zhang et al. (2019)
	MnO _x /hydroxyapatite	800 ppm toluene, air balance, 30,000 mL/(g h)	$T_{90} = 210 \ ^{\circ}\text{C}$		Chlala et al. (2016)
	MnO ₂ /diatomite	200 ppm toluene, air balance, 8600 h^{-1}	$T_{90} = 380 \ ^{\circ}\text{C}$	$T_{90} = 380$ °C	Azimi Pirsaraei et al. (2016)
	MnO _x /diatomite	1000 ppm toluene, 20 vol% O ₂ , N ₂ balance, 30,000 mL/(g h)	$T_{90} = 267 \ ^{\circ}\text{C}$	$T_{90} = 279$ °C	Liu et al. (2017)
	Cu _{0.8} Mn ₂ Ce _{0.2} O _x /sepiolite	2000 ppm toluene, air balance, 10,000 h^{-1}	$T_{100} = 289 \ ^{\circ}\text{C}$		Niu et al. (2018)

Table 1 (continued)

Catalyst		Reaction conditions	Catalytic efficiency		Ref.
			Conversion (%)	CO ₂ yield (%)	
_	CoMn/Ce _{0.65} Zr _{0.35} O ₂	1000 ppm toluene, air balance, 12,000 h ⁻¹	$T_{100} = 242 \ ^{\circ}\text{C}$		Feng et al. (2017)
f	MnO _x /Ce _{0.65} Zr _{0.35} O ₂ /cordierite	1000 ppm toluene, air balance, 12,000 h^{-1}	$T_{100} = 250 \ ^{\circ}\text{C}$		Hou et al. (2018)
	Ce–MnO _x /ceramic	1000 mgC/m ³ toluene, air balance, 12,000 h^{-1}		$T_{100} = 370$ °C	Colman-Lerner et al. (2016)
	Cu _{0.15} Mn _{0.3} Ce _{0.55} /ceramic	Air containing toluene, 10,000 h^{-1}	$T_{99} = 240 \ ^{\circ}\text{C}$		Avila et al. (2005)
	$MnO_x/\theta-\delta-Al_2O_3$	4000 mgC/m ³ toluene, air balance, 10,000 h^{-1}	$T_{80} = 330 \ ^{\circ}\text{C}$		Aguero et al. (2011)

and low-temperature reducibility (Shi et al. 2012; Wang et al. 2012).

Moreover, surface defect (oxygen vacancy or manganese vacancy) also dramatically affects the catalytic performance of MnO_x . It has long been supposed that the active sites of heterogeneous catalysts are closely related to surface defects (Miao et al. 2019). The abundant vacancy defects benefit from the adsorption, activation, transfer, and replenishment of oxygen species, which has been widely recognized to be closely related with the catalytic activity for toluene removal (Yang et al. 2019b).

Improving synthetic methods to optimize several critical factors, including valence, structure, morphology, and surface defect, is a way to improve catalytic performance. The popular synthetic methods include the hydrothermal method (Huang et al. 2018; Liao et al. 2017; Yang et al. 2019b), redox method (Wang et al. 2016a), template method (Du et al. 2012; Zhou et al. 2014), sol-gel method (Wang et al. 2016a), selective atom removal method (Si et al. 2015), solution combustion method (Piumetti et al. 2015), etc. The synthetic conditions that can be adjusted include acid treatment, choice of reactant precursor, template, reactant ratio, pH, reaction time and temperature, calcination time and temperature, etc. Li et al. (2014b) found that the change of the reactant ratio of acetic acid (HAc) and manganese hydroxide could generate MnO_x catalysts with different morphology and crystal phase, and hereby significantly affected the content of reducible manganese oxide species and surface oxygen adspecies, as well as the activity of toluene oxidation. Yang et al. (2019b) reported acid treatment induced abundant vacancy defects in Mn₂O₃ catalyst synthesized by the hydrothermal method. The abundant vacancy defects facilitated the excellent surficial oxygen mobility and low-temperature reducibility, and thereby the catalytic performance was improved fundamentally. Si et al. (2015) selectively removed La cations from threedimensional (3D) ordered macroporous LaMnO₃ perovskites to synthesize γ -MnO₂-like catalysts with 3D macroporous and mesoporous. The 3D macroporous and mesoporous morphology allowed the accessibility of toluene to the catalyst. The γ -MnO₂-like structure enhanced the catalyst's oxygen mobility. Hence, the toluene conversion efficiency on the novel catalyst was much higher than traditional α -MnO₂, β -MnO₂, and δ -MnO₂. Huang et al. (2018) prepared a hierarchically $\alpha@\beta$ -MnO₂ nanocatalyst via the hydrothermal method, which exhibited higher toluene conversion efficiency and lower activation energy in toluene oxidation than pure β -MnO₂ and α -MnO₂ because of its mixed phase interfacial structure and higher oxygen vacancy concentration. The reaction might tend to take place at the interface of β -MnO₂ and α -MnO₂. As depicted in Fig. 1, β -MnO₂ was responsible for the adsorption of toluene molecules; α -MnO₂ and the activated adsorbed oxygen played a dominant role in providing oxygen species for reaction.

Mn-based composite oxides

The incorporation of MnO_x with other metal oxides (X-MnO_x) is another way to enhance catalytic properties. The metallic elements used to incorporate MnO_x usually include Ce, Cu, Co, Fe, Ni, Zn, and Cr. Incorporating proper metal oxides with MnO_x can effectively suppress the growth of MnO_x crystal or cause noncrystallization (Durán et al. 2009; Saqer et al. 2011). Remarkably, the incorporation may facilitate the formation of Mn-based solid solutions (Du et al. 2018; Qu et al. 2014; Wang et al. 2018c) or other mixed-oxide phases (Behar et al. 2012; Zhang et al. 2014) and hereby cause the distortion of the MnO_x lattice, which can bring about abundant oxygen vacancies and enhance redox properties. Moreover, carbon deposits can also be oxidized efficiently by X-MnO_x at lower temperatures in comparison with the individual MnO_x and XO_x (Saqer et al. 2011). Therefore, X-MnO_x usually shows better catalytic activity than MnO_x due to synergistic effects.

The molar ratio between manganese and other metal elements is one of the main factors affecting catalytic performance directly. It usually influences the formation of a catalyst, determining the dispersion of Mn species, the crystalline state of Mn species, the crystal diameter of the catalyst, and the morphology of the catalyst, and hereby





affects the catalytic performance. Luo et al. (2018) found Mn/ Co molar ratio marginally affected crystalline phase and textural features of Co–MnO_x catalysts, while it played a crucial effect on the morphology. Liao et al. (2013) and Li et al. (2017a) reported that low content of Ce in Ce–MnO_x catalysts led to the best catalytic activity and high stability in toluene combustion. Niu et al. (2018) found the change of the doped atom content could lead to different surface oxidation/ reduction activation energies. The optimum performance will take place when the two surface activation energies are infinite near.

Up to now, great efforts have been devoted to construct novel Mn-based multimetal oxide catalysts (especially nanocatalysts) with special structure, well-defined morphology, and/or homogeneous distribution between different elements. As we all know, a catalyst with special structure and well-defined morphology usually shows better catalytic performance than corresponding bulk catalyst, and different structures and morphologies can lead to different catalytic performances. For multimetal oxide catalysts, an intimate intermixing of each component can ensure MnO_x in close interaction with dopants and, hence, enhance the catalytic combustion activity. Table 1(b) considers some newly developed *X*-MnO_x catalysts. Their catalytic behaviors, varying with the dopants would be discussed in detail as follows.

Mn-based bimetallic oxides

Ce is the most used element to incorporate with MnO_x because of its well-known oxygen storage/release ability and good redox property derived from Ce⁴⁺/Ce³⁺ redox couples (Kašpar et al. 1999). In the structure of Ce– MnO_x catalyst, Mn usually plays a dominant role in catalytic removal of toluene, whereas Ce maybe not directly take part in the reaction and it may facilitate the activation of oxygen species in MnO_{x} and increase the oxygen mobility of MnO_x (Torres et al. 2013; Wang et al. 2018a). At present, the removal of toluene over Ce-MnO_x catalysts has been reported in many papers (Chen et al. 2018; Delimaris and Ioannides 2008; Du et al. 2018; Li et al. 2017a; Liao et al. 2013; Sun et al. 2019; Tang et al. 2015; Wang et al. 2018a; Yu et al. 2010). Du et al. (2018) reported Ce acted a vital part in the adsorption of toluene, whereas Mn played a primary part in toluene oxidation in Mn_{0.6}Ce_{0.4}O₂ catalyst, which was prepared via combining the redox method and hydrothermal synthesis. Li et al. (2017a) developed a facile new self-propagated flaming technique to construct CeO2-doped \delta-MnO2 catalysts. Good low-temperature reducibility and high Mn⁴⁺/Mn³⁺ ratio, brought by the synergy of the highly dispersed CeO₂ nanoparticles and the δ -MnO₂ substrate, caused enhanced activity and good stability in toluene removal. More remarkable, this catalyst could maintain original crystal texture even after four reuse cycles as shown in Fig. 2. Sun et al. (2019) synthesized high-efficiency MnO_r CeO₂ catalyst by in situ pyrolysis of Ce/Mn-MOF-74 precursor. They found that incorporating Ce into MnO_x improved low-temperature reducibility and oxygen storage capacity due to the abundant oxygen vacancy and the strong interaction between cerium and manganese.

Cu–MnO_x catalysts have been extensively studied for toluene removal (Behar et al. 2012; Doggali et al. 2012; Hu et al. 2018b; Wang et al. 2017; Ye et al. 2018). For the Cu–MnO_x catalyst, $Cu_xMn_3 - _xO_4$ spinel was usually considered as the

Fig. 2 a Cyclical stability test of toluene conversion over CeO₂-doped δ -MnO₂ catalysts. **b** XRD patterns of fresh and used CeO₂-doped δ -MnO₂ catalysts (Li et al. 2017a)



main active phase (Ahn et al. 2017; Behar et al. 2012; Wang et al. 2017; Ye et al. 2018). The addition of Cu into $MnO_{\rm r}$ can give rise to abundant oxygen vacancies as well as good redox ability and hereby enhance catalytic property (Hu et al. 2018b; Morales et al. 2008). Their catalytic activity was demonstrated to root in a redox reaction: $Mn^{3+} + Cu^{2+} \Rightarrow Mn^{4+} + Cu^{+}$ (Papavasiliou et al. 2007). Behar et al. (2012) prepared nanosized Cu_{1.5}Mn_{1.5}O₄ spinel by using ionotropic alginate gel, which aggregated in small spheres (1 mm) and presented a homogeneous composition. It showed better activity than Cu_{1.5}Mn_{1.5}O₄/TiO₂ catalysts in the removal of toluene. Ye et al. (2018) found that CuMnO_x synthesized by the redoxprecipitation route showed much higher activity for toluene combustion in comparison with CuMn₂O₄ synthesized via the co-precipitation method and outperformed the commercial hopcalite over time on stream. The superior activity of the redox sample might be related to its better textural characteristics such as higher surface areas and amorphous state as well as structural disorder. Li et al. (2017b) reported layered δ -MnO₂ mixed with Cu, Co, Ni, and Zn oxides, synthesized by the self-propagated flaming technique. Except Nidoped catalysts, all the other catalysts showed better activity than pure δ -MnO₂ in toluene combustion, indicating that the self-propagated flaming method is a feasible method to fabricate nanocomposites. Among these, the CuO-δ-MnO₂ catalysts exhibited the highest activity and showed good catalytic stability during four reaction cycles and long-term stability test. Li et al. (2004) and Kim et al. (2014) got the same result that $Cu-MnO_x$ catalyst yielded the highest catalytic activity in toluene combustion among various X-MnO_x catalysts, revealing that Cu is an excellent element to modify MnO_x.

 Co_3O_4 has aroused attention as a p-type semiconductor with many electron deficiencies which benefit the formation of active oxygen species (Deng et al. 2018a). So Co is also considered as an ideal additive to modify MnO_x (Feng et al. 2017; Luo et al. 2018; Qu et al. 2014; Wang et al. 2018b; Zhou et al. 2015). Qu et al. (2014) firstly prepared nanocrystal-like $MnCo_2O_x$ solid solution via two-step hydrothermal method. This catalyst performed well for toluene removal due to its high porosity and surface area as well as reducible oxygen species concentration. Luo et al. (2018) obtained $MnCoO_x$ catalysts derived from $Mn_3[Co(CN)_6]_2 \cdot nH_2O$ nanocubes (metal–organic frameworks). Results showed that Mn, Co, and O species in this catalyst were homogeneously distributed. The catalyst exhibited excellent deep oxidation activity and cycle stability in the removal of toluene. Wang et al. (2018b) synthesized Co_3O_4 –MnCo₂O_{4.5} nanosheet by the redox-precipitation method. The catalyst showed good activity with 90% toluene conversion of 194 °C when 1.6 wt% H₂O existed in simulated flue gases. The active interface of Co_3O_4 and $MnCo_2O_{4.5}$ as well as the abundant oxygen electrophilic species (O^-/O^2^-) contributed to its high catalytic performance.

Except for Ce, Cu, and Co, Fe is usually used to modify MnO_x as well (Chen et al. 2017; Durán et al. 2009; Ma et al. 2013; Wang et al. 2018c). Wang et al. (2018c) reported homogeneous $MnFe_2O_x$ solid solutions prepared by the redoxprecipitation route showed high activity, water tolerance, and stability. Good low-temperature reducibility and high electrophilic oxygen concentration, which are brought by the homogeneous distribution of Fe, Mn, and O elements, resulted in the excellent catalytic property. Inspired by the redoxprecipitation route, Chen et al. (2017) designed a facile hydrolysis driving redox reaction route coupling two simultaneous reactions to rapidly prepare a homogeneous $Fe-MnO_x$. The route is depicted in Fig. 3. The catalyst showed better activity and higher TOF_{Mn} (turnover frequencies per unitage of Mn cations) for toluene combustion than $Fe-MnO_x$ prepared via the co-precipitation method, which was related to its homogeneous distribution of Mn and Fe, higher surface area, higher content of Mn³⁺ ions, higher amount of lattice defects and oxygen vacancies, and better low-temperature reducibility. Importantly, the catalyst was stable and renewable reflected by durability tests at GHSV of 240,000 mL/(g h) and high moisture.

Mn-based multimetal oxides

To further enhance the catalytic performance, some ternary (Castaño et al. 2015; Hu et al. 2017; Lu et al. 2015; Niu





et al. 2018; Weng et al. 2011) or even guaternary (Aguilera et al. 2011) Mn-based composite oxides were often used to abate toluene. Hu et al. (2017) obtained homogeneous sponge-like $Mn_{0.5}Ce_{0.5}O_x$ solid solutions with the help of a third doped Cu atom exited as amorphous CuO via the surfactant-templated method, achieving complete conversion of toluene at 240 °C. The highly reducible oxygen species concentration was identified as the key factor affecting catalytic behavior. Lu et al. (2015) synthesized high-activity Cu-Ce-MnO_x catalysts with Cu/Mn/Ce molar ratio of 1:2:4 via the sol-gel method. The structure of the catalyst was the coexistence of Ce-based solid solution and Cu-MnO_x with high dispersion. The Ce-based solid solution played a vital role in transporting active oxygen, while Cu–MnO_x played a leading role in activating and oxidizing toluene. The synergetic interaction had a positive influence on the reducibility, oxygen mobility, and active oxygen species concentration. Castaño et al. (2013, 2015, 2017) studied the catalytic performance of Mn–Mg–AlO_x catalysts in toluene oxidation. These catalysts with distinct Mn²⁺/Mg²⁺ ratios and glycine/nitrate ratios were prepared via the autocombustion method (glycine as a combustible) at a very short time. Results showed the incorporation of Al and Mg into the structure contributed to better structural stability, larger surface area, lower size particle, and better redox properties (Castaño et al. 2017); Mn^{2+/} Mg²⁺ ratios and glycine/nitrate ratios affected the catalytic activity obviously, and the sample with $Mn^{2+}/Mg^{2+} = 1.0$ and glycine/nitrate = 0.56 was the optimal catalyst (Castaño et al. 2013, 2015). Additionally, they found the autocombustion catalysts outperformed the Mn-Mg-AlO_x catalysts prepared using hydrotalcite-type precursor in the mineralization of toluene, which was related to their smaller particle size and greater reducibility.

Mn-based some special oxides

Cryptomelane-type oxides: OMS-2

OMS-2 is 1D microporous potassium-containing manganese oxide octahedral molecular sieve, with the molecular formula of KMn₈O₁₆ $\cdot n$ H₂O. It has a 2 × 2 tunnel structure and the tunnel size is 4.6 × 4.6 Å. Its structural frameworks consist

of edge and corner-shared [MnO₆] octahedron and some K⁺ incorporate into the framework (Ching et al. 1997). Such structure contributes to some unique characteristics such as excellent electrical conductivity and porosity (Suib 2008). Additionally, Mn²⁺, Mn³⁺, and Mn⁴⁺ coexist in the OMS-2 framework. It is the mixed valences of manganese and the unique structure that facilitate the excellent catalytic performance of OMS-2 in toluene removal.

As depicted in Table 1(c), some attempts have been made in the removal of toluene over OMS-2 in the last years. Genuino et al. (2012) prepared OMS-2 via the refluxing method. Interestedly, it had better activity for toluene combustion than amorphous MnO_x and nanosized Cu-MnO_x. The reactivity and mobility of active oxygen were considered to be responsible for the catalytic activities. OMS-2 catalysts prepared via different synthetic routes were also compared. Sun et al. (2011) reported the catalytic performance for toluene combustion over OMS-2 synthesized via the solid-state reaction (OMS-2_S) and refluxing route (OMS-2_R). OMS-2_R with more available Olatt and better oxygen mobility exhibited higher activity. Sihaib et al. (2017) recently reported toluene combustion performance on OMS-2 prepared by solid-state reaction (OMS-2_s) and hydrothermal route (OMS-2_h). OMS-2_s showed higher activity than OMS-2_h, which was associated with its larger surface area as well as better low-temperature reducibility. Santos et al. (2010b) obtained the incorporation of Mn₃O₄ into OMS-2 obviously enhanced the toluene oxidation performance because of a better mobility and reactivity of lattice oxygen (O_{latt}), while the presence of Mn₂O₃ has an opposite effect. In later papers of the same group, the stability of OMS-2 in toluene oxidation was investigated (Santos et al. 2010a). The results showed a gradual deactivation at temperatures lower than 268 °C and there were carbon deposits retaining after isothermal tests. Moreover, the catalyst showed an unstable behavior at temperatures of 252-258 °C. The deactivation and instability were explained by that the porous structure of OMS-2 could strongly retain toluene up to high temperatures certified through temperature-programmed desorption experiments (TPD).

In the OMS-2 structure, framework Mn^{n+} ions and tunnel K^+ ions can be substituted by other metal cations, tuning the Mn valence, structure, and morphology, as well as lattice

parameters of OMS-2, and thereby, its catalytic performance may be improved. At present, various metal cations that modified OMS-2 samples have been constructed to remove various air pollutants (Ma et al. 2017; Sun et al. 2013; Wu et al. 2017). Unfortunately, there are few papers referring to the removal of toluene over the OMS-2 catalyst substituted by other metal cations. Future research can be devoted to the development of this type of catalyst.

Perovskite-type catalysts

Perovskite-type oxides are compounds of the general formula of ABO₃, where A-site can be a rare earth metal cation, an alkaline earth metal cation, or an alkali metal cation, and Bsite can be a transition metal cation, such as Mn cation (Peña and Fierro 2001). These catalysts have aroused lots of attention because of high activity, high thermostability, and low cost (Merino et al. 2005). Besides, A- and/or B-site cations can be substituted by other cations with similar oxidation state and ionic ratio (Seiyama 1992). The molecular formula can be noted as $AB_{\nu}B'_{1-\nu}O_3$, $A_xA'_{1-\nu}BO_3$, or $A_xA'_{1-\nu}B_{\nu}B'_{1-\nu}O_3$. Generally, A-site replacement can form vacancies of the crystalline bonds and stabilize the unusual oxidation states of the B-site cation, while B-site replacement can facilitate change of the redox ion couples and the active sites, as well as the stability of the crystalline structure (Merino et al. 2006). In the past decade, as shown in Table 1(d), Mn-based perovskitetype catalysts have been extensively explored in toluene removal (Deng et al. 2008, 2009, 2010; Giroir-Fendler et al. 2016; Liu et al. 2018a, 2019; Suárez-Vázquez et al. 2018; Wang et al. 2014, 2016b; Zhang et al. 2014).

Bulk perovskite-type oxides normally have very low specific surface area ($< 10 \text{ m}^2/\text{g}$) because the traditional preparation method demands a long time high-temperature calcination, usually > 500 °C. The very low specific surface area can weaken their catalytic performance and limit their practical applications. Therefore, producing perovskite-type oxides with high specific surface area is important for these materials in catalytic reactions. The simplest and most classic solution is loading perovskite-type oxides onto the support with high specific surface area. Giroir-Fendler et al. (2016) prepared LaMnO₃/TiO₂ and LaMnO₃/Y₂O₃-ZrO₂ (YSZ) catalysts via the citrate sol-gel method. Compared to pure perovskite, the two catalysts exhibited a better oxygen exchange activity and were more stable and efficient for toluene combustion. For LaMnO₃/TiO₂, the oxygen vacancies of the YSZ and the interaction between LaMnO₃ and YSZ support caused this improvement. For LaMnO₃/TiO₂, the activation of the support contributed to this improvement. Wang et al. (2016b) investigated the effect of morphology (polyhedron, cube, and rod) of nano-CeO2 in La_{0.8}Ce_{0.2}MnO3/CeO2 on toluene combustion. La_{0.8}Ce_{0.2}MnO₃/CeO₂ nanopolyhedra showed optimum activity due to its large surface area (94.9 $m^2 g^{-1}$), small particle size, highly reactive oxygen species, and many oxygen vacancies.

Besides, many efforts have been dedicated to prepare pure perovskite-type oxides with high specific surface area by adjusting structures and morphologies. Suárez-Vázquez et al. (2018) prepared dendritic SrTi_{1 – X}Mn_XO₃ with relatively high surface area via the one-pot hydrothermal route. Compared with SrTiO₃, SrTi_{1 – χ}Mn_{χ}O₃ expressed better activity and cyclical stability for toluene oxidation because of more surface oxygen adspecies and better low-temperature reducibility. Wang et al. (2014) prepared porous spherical LaMnO₃ and cubic LaMnO₃ nanocatalysts via the molten salt method. The cubic nanocatalysts showed better activity for removal of toluene than porous nanocubes because of its better lowtemperature reducibility and higher surface Mn⁴⁺/Mn³⁺ molar ratio. As shown in Fig. 4, the morphology transformation from porous spherical structure to cubic particle might follow "template formation" and "grain boundary grooving and dissolution followed by the Oswald ripening process" mechanism. Liu et al. (2012) obtained 3D ordered macroporous (3DOM) single-phase rhombohedral LaMnO3 with nanovoid skeletons through a surfactant-assisted PMMA-templating method. The 3DOM LaMnO₃ material displayed excellent toluene combustion activity because of the nanovoid-based 3DOM structure, large surface area, high oxygen adspecies concentration, and excellent low-temperature reducibility.

Currently, catalytic removal of toluene utilizing 3DOM perovskite-type material is of intriguing interest. The PMMA-templating method is the most widely used and relatively mature synthetic strategy preparing the 3DOM perovskite-type materials. These materials can not only act as a catalyst alone to promote toluene catalytic reaction, but also act as a carrier supporting active components. Si et al. (2016) firstly obtained a MnO₂/LaMnO₃ catalyst by in situ selectively removing partial La cations from the chain-like 3DOM LaMnO₃ material. It showed high activity, good stability, and relative low apparent activation energy on toluene oxidation, which was related to abundant oxygen species and excellent O_{latt} mobility. Liu et al. (2013) synthesized $MnO_x/3DOM LaMnO_3$ catalysts by an in situ tryptophan-assisted PMMA-templating route. The catalyst expressed high TOF values and high performance for toluene removal because of its large amount of adsorbed oxygen species, optimal low-temperature reducibility, and strong interaction between MnO_x and 3DOM LaMnO₃.

Mn-based supported catalysts

Selecting proper carriers to load Mn-based oxides can also significantly improve catalytic performance. For one thing, proper carriers can disperse active components to prevent or retard particle aggregation. For another, they provide the space for catalytic reactions to occur. Additionally, some carriers, **Fig. 4** Pathway of the morphological transformation of LaMnO₃ from the porous spherical structure to the cubic particle in the molten salt (Wang et al. 2014)



such as single or mixed metal oxides, can also participate in the catalytic reaction. For the supported Mn-based catalyst, the activity mainly depends on the nature of the support, the metal-support interactions, and the loading amount of Mnbased oxides. Catalytic performance usually changes with the different support. For instance, Jung et al. (2015) found toluene combustion activity on supported MnO_x catalysts declined as follows: $MnO_x/\gamma - Al_2O_3 > MnO_x/SiO_2 > MnO_x/$ TiO₂, which related to the amounts of defect oxides. Li et al. (2011) observed the water resistance of supported Cu–MnO_x catalyst for toluene combustion following the trend: Cu- $MnO_{x}/cordierite > Cu-MnO_{x}/TiO_{2} > Cu-MnO_{x}/\gamma-Al_{2}O_{3}$ which resulted from different adsorption abilities of these catalysts toward water molecules. As shown in Table 1(e), various materials, such as Al₂O₃ (Aguero et al., 2009a, b; Kim et al. 2014; Pozan 2012; Wang et al. 2017), TiO₂ (Yu et al. 2010; Zhao et al. 2019), active carbon (Zhou et al. 2015), zeolites (Soylu et al. 2010), mesoporous silicas (Wang et al. 2018d), hydroxyapatite (Chlala et al. 2016, 2018), some natural material (diatomite (Azimi Pirsaraei et al. 2016; Liu et al. 2017), sepiolite (Niu et al. 2018), etc.), and composite carriers (CeO₂-ZrO₂ (Feng et al. 2017; Hou et al. 2018), Y₂O₃-ZrO₂ (Giroir-Fendler et al. 2016), etc.), have been applied as the supports to immobilize Mn-based oxide for removal of toluene. Among these supports, Al₂O₃ materials, especially γ -Al₂O₃, are the most used traditional catalytic carriers for

removal of toluene owing to their several properties, namely large specific surface area, certain surface acidity, good thermostability, simple shape control, and low price; zeolites and mesoporous silicas, including clinoptilolite (Ahmadi et al. 2017; Özçelik et al. 2009; Soylu et al. 2010), Beta zeolites (Li et al. 2006; Peng et al. 2017), MCM-41 (Li et al. 2006, 2008), ZSM-5 (Huang et al. 2016; Meng et al. 2013; Zhang et al. 2019), SBA-15 (Qin et al. 2019b), etc., are the most promising catalytic carriers which were widely used because of their unique physicochemical properties. Recently, two paths have been attempted to enhance catalytic performance of Mn-based supported catalysts: improving preparation methods and tuning the support.

Improving synthetic methods

The adjustment of synthetic conditions such as loading value (Liu et al. 2017), calcination temperature (Huang et al. 2012; Jung et al. 2015), and the counterion of Mn(II) precursor (Chlala et al. 2016) is a common way to improve catalysts. The loading value of the metal oxide was studied widely in the recent years. It has a significant impact on the dispersity of metal oxides, the specific surface area of the catalyst, and the surface oxygen species concentration, and hence, affects catalytic activity. Catalytic activity usually increases when the loading values increase up to a turning point, and then

decreases with the increase of loading value. Jung et al. (2015) evaluated the influence of calcination temperatures (500, 700, and 900 °C) on toluene combustion activity on MnO_{y}/γ -Al₂O₃ catalysts. The activity of these catalysts decreased as follows: $MnO_{y}/\gamma - Al_{2}O_{3} - 900 > MnO_{y}/\gamma - Al_{2}O_{3} - 500 > MnO_{y}/\gamma$ γ -Al₂O₃-700, which depended on the crystalline structure and the area ratio of defect oxides/lattice oxides affected by the calcination temperature. Chlala et al. (2016) examined the effects of counterion of Mn(II) precursor, manganese nitrate (Nit), and manganese acetate (Ac) over 10 wt% MnO_x/Ca^{2+} enriched hydroxyapatite (Hap) catalyst. NO3⁻ contributed to good reducibility and dispersion of Mn^{n+} ($n \ge 3$) species on the Hap surface. On the contrary, CH₃CO²⁻ mainly resulted in mixtures of large Mn₃O₄ nanocrystals and an amorphous Mn_5O_8 . So the $MnO_x(Nit)/Hap$ catalyst exhibited better activity.

Tuning the support

Tuning the support can modify some physicochemical properties of the support and thereby strengthen the interaction of active components with support and increase the dispersion of active species on its surface. The most common approach toward tuning the support is acid treatment. Research showed that diluted nitric acid treatment could alter porosity, specific surface area, isoelectric point, and surface acidity of Al_2O_3 (Aguero et al. 2009b). Compared with nature diatomite, H_2SO_4 -treated diatomite caused an increase in surface area and total pore volume, promoting uniform dispersion of active MnO_2 on diatomite (Azimi Pirsaraei et al. 2016). HCl treatment attained considerable enhancement in surface area and completely altered the crystalline texture of clinoptilolite (Yosefi et al. 2015).

Carrier structure and morphology optimization is also a common method. Pozan (2012) evaluated toluene combustion activity on supported MnO_x catalysts with Al₂O₃ of different crystalline structures as substrates. The catalytic activity followed the order: MnO_x/ α -Al₂O₃ (prepared from boehmite) > MnO_x/ γ -Al₂O₃ (prepared from boehmite) > MnO_x/ γ -Al₂O₃ (commercial), which was attributed to Mn state and oxygen species concentration. Qin et al. (2019b) investigated the effect of carrier morphology (rod-like, hexagonal, and fiberlike) on toluene combustion activity over three MnO_x/SBA-15 catalysts. MnO_x/rod-like SBA-15 catalysts with abundant surface O_{latt} and excellent oxygen mobility showed the best activity.

For zeolite materials, carrier performance can be enhanced by improving the ion exchange method and adjusting Si/Al ratios. Soylu et al. (2010) modified clinoptilolite (CLT) samples through ion exchange by varying ion exchangers (NaCl, NH₄NO₃, and NH₄Cl) and ion exchange times (1.5, 6, 12, 24, 48, and 72 h) and then prepared a series of MnO₂/CLT catalysts. The best catalytic activity occurred in the CLT treated with NH₄NO₃ for 48 h. Lewis acidity was identified as the determining factor. Peng et al. (2017) evaluated the removal of toluene on supported MnO_x modified via Al-rich Beta zeolites (Beta-SDS) with H-form (MnO_x/H-Beta-SDS) and K-form (MnO_x/K-Beta-SDS), pure siliceous Beta zeolites (MnO_x/Si-Beta), and Al₂O₃. The activity of these catalysts decreased in this order: MnO_{x}/H -Beta-SDS > MnO_{x}/K -Beta-SDS > MnO_{y}/K -Beta-SDS > $MnO_{y}/$ Si-Beta > $MnO_{x}/Al_{2}O_{3}$, which was ascribed to oxygen adspecies concentration. Zhang et al. (2019) evaluated the toluene conversion efficiency on supported MnO_x materials with HZSM-5 of different Si/Al ratios as carriers. These catalysts possessed similar textural and redox properties but different surface acidity, and a fin linear relation between turnover frequency (TOF_{Mn}) and total acidity of these catalysts was found, indicating zeolitic acidity was a crucial promoter for toluene oxidation.

Mn-based monoliths

Monolithic catalysts, formed by many narrow parallel channels, are a new type of catalyst developed in recent decades. Compared to traditional pellet catalysts, they possess lower pressure drop, uniform flow distribution, and higher mass transfer efficiency (Nijhuis et al. 2001). A monolithic catalyst usually consists of support, coating (the second support), and active species. The monolithic supports can be made of ceramic (mainly cordierite) or metal materials (stainless steel, metallic alloys, metal foams, etc.) with high-temperature resistance (Tomašić and Jović 2006). Table 1(f) considers some newly developed Mn-based monolithic catalysts in the removal of toluene.

Mn-based ceramic monolith has been widely employed in removal of toluene. Hou et al. (2018) studied toluene oxidation over MnO_x/mesoporous Ce_{0.65}Zr_{0.35}O₂/honeycomb cordierite monoliths with loading amount of 0, 5, 10, 15, and 20 wt%. Results exhibited 15 wt% MnOx/Ce0.65Zr0.35O2 monoliths showed the best activity and high stability owing to its well-dispersed MnO_x species, as well as better lowtemperature reducibility, more Mn⁴⁺ species, and more surface Olatt. Colman-Lerner et al. (2016) investigated the removal of toluene over Ce-MnO_x/ceramic monolithic catalyst prepared via directly impregnating aqueous precursor. The bimetallic catalyst performed better than the corresponding two monometallic catalysts. This was because of the synergism between Ce and Mn which improved the acidity, conductivity, and reducibility of the catalysts. Lu et al. (2011) found the activity of $Cu_{0.15}Mn_{0.3}Ce_{0.55}$ /cordierite monolithic catalysts was comparable to commercial Pd/ Al₂O₃ catalyst.

However, the applications of ceramic monolithic catalysts are partly affected by its thick wall and low thermal conductivity. Compared to ceramic monoliths, metallic monoliths have a higher cost, but possess higher mechanical resistance, lower pressure drop, better thermal conductivity, and thinner walls (Avila et al. 2005). So, they are also a good choice for the synthesis of monolithic catalysts. Aguero et al. (2010) studied the effect of the alumina layer acting as support of MnO_x metallic monoliths on the catalytic performance in toluene combustion. Supports used in this study include H₂SO₄anodized aluminum, H₂C₂O₄-anodized aluminum, colloidal alumina coating on FeCrAlloy, and θ - δ -Al₂O₃ coating on FeCrAlloy. Results revealed the sample using θ - δ -Al₂O₃ as carrier showed the best activity. In a follow-up study, they further optimized the preparation conditions of the optimum catalyst to get a well-adhered and homogeneous wash coating (Aguero et al. 2011). Results showed that using a 30-wt% solid content suspension and carrying out two immersions could lead to larger catalyst loading as well as more welladhered and homogeneous layer, and it was unnecessary to add a suspension stabilizer because suspensions are stable by themselves.

The effect of coexisting components

The effect of multi-VOCs

Generally, actual industrial exhaust gases usually contain a variety of VOCs, and different VOCs have different physical and chemical characteristics. The study on the catalytic performance of toluene does not represent the practical application of catalysts. Therefore, it is essential to test the catalyst performance in the removal of multicomponent mixtures. The "mixture effect" on catalyst performance mainly depends on the catalyst used and the composition of the reaction mixture. The presence of other components usually has an inhibiting effect for the removal of VOCs and rarely a promoting effect. Sager et al. (2011) reported inhibiting effects in different degrees during removal of propane-toluene mixtures on Cu- MnO_x/γ -Al₂O₃ catalyst and Ce-MnO_x/ γ -Al₂O₃ catalyst. For both catalysts, toluene oxidation was significantly suppressed by propane. However, propane oxidation was also significantly inhibited by toluene in the case of Ce–MnO_x/ γ -Al₂O₃ catalyst, while propane oxidation was weakly inhibited by toluene in the case of Cu–MnO_x/ γ -Al₂O₃ catalyst. Wang et al. (2018c) found the presence of methanol weakly affected the combustion of toluene over Fe-MnOx nanocatalysts, whereas the presence of toluene significantly inhibited methanol oxidation and this inhibition effect was irreversible. It may be clarified that toluene possesses higher affinity for the catalyst surface (Ordóñez et al. 2002). Aguero et al. (2009a) explored the removal of ethanol-toluene mixtures and ethyl acetatetoluene mixtures on MnO_x/Al₂O₃ catalyst. Toluene strongly inhibited ethyl acetate and ethanol oxidation because of the competition for the chemisorbed oxygen species on the catalyst and increased the concentration of yielded acetaldehyde. Toluene oxidation is also suppressed by ethanol and ethyl acetate. The inhibition was attributed to the influence of higher total VOC concentration in simulated flue gases.

Kim and Shim (2010) confirmed the mutual inhibitory effect between both compounds over 0.5 wt% Ca/Mn₃O₄ in toluene–benzene mixtures because of the competition for the same active sites. However, Wang et al. (2019) found benzene oxidation might produce some intermediates which could promote toluene oxidation over layered Cu–MnO_x catalysts. Wang et al. (2018b) observed toluene combustion was suppressed, while *o*-xylene combustion was enhanced dramatically in toluene–*o*-xylene mixtures over Co–MnO_x nanosheets. It may be because of the stronger adsorption of *o*-xylene on the catalyst and catalytic sites were blocked. Deng et al. (2018b) observed that the presence of toluene or xylene promoted benzene combustion over NiMnO₃/Ce_{0.75}Zr_{0.25}O₂/ cordierite monoliths, because the energy produced by toluene or xylene or xylene combustion could activate benzene.

Up to now, some robust catalysts with superior catalytic performance to remove mixed VOCs have been developed. Piumetti et al. (2015) reported Mn₃O₄/cordierite honeycomb has retained its good activity for complete removal of tolueneethylene-propylene mixtures over time on stream under alternating temperature conditions. Chen et al. (2018) studied the removal of mixed aromatic VOCs (benzene, toluene, o-xylene, and chlorobenzene) over Ce-MnO_x catalyst prepared through hydrolysis driving redox. As described in Fig. 5, Ce-MnO_x completely mineralized mixed aromatic VOCs into CO2 at 400 °C, and the major portion of VOCs was removed when 10 vol% H_2O existed, revealing Ce–MnO_x is a strong catalyst for the removal of mixed aromatic VOCs at simulated conditions. This superior performance was attributed to the homogeneous introduction of Ce into MnO_x contributing to better structural stability and reversible reducibility.

The effect of other coexisting components

 H_2O is one of the essential components in most of the exhaust, and so, much attention has been paid to study the effect of H_2O on toluene removal. Generally, the presence of H_2O could inhibit the activity of Mn-based catalysts due to the competitive adsorption of active sites (Hu et al. 2018b; Liu et al. 2017). The inhibition effect on the catalytic activity was various with reaction temperature. For instance, Hu et al. (2018b) studied the effect of H_2O on toluene conversion at different reaction temperatures over CuMnO hierarchical nanowire. The presence of H_2O only leads to a slight decrease on toluene conversion at 230 °C, while it leads to more and more obvious decrease with decreasing temperature. Besides, the inhibition effect was reversible in many cases (Luo et al. 2018; Qin et al. 2019a; Shan et al. 2019; Wang et al. 2016a; Yang et al. 2019a). Surprisingly, the presence of H_2O was





beneficial for toluene removal in some cases. García et al. (2019) reported that cavity-containing Mn_3O_4 achieved total conversion of toluene at only 150 °C in the presence of 4 mol% H₂O and at 175 °C in the absence of H₂O. Wang et al. (2018b) found H₂O was beneficial for toluene combustion over Co₃O₄–MnCo₂O_{4.5} nanosheets because of the promotion of intermediate formation or activation of O₂ molecules by H₂O. Hu et al. (2017) also observed that the presence of H₂O had a promoting effect on toluene combustion over sponge-like CuO–Mn_{0.5}Ce_{0.5}O_x. It was attributed to the fact that H₂O might strengthen the redox behavior of this catalyst.

 CO_2 is also an essential component in most of the exhaust, and SO₂, NO_x, CO, and mercury may coexist with toluene in some of the exhaust, such as thermal power plant flue gases, petroleum refinery flue gases, and automobile exhaust gases (Bonet et al. 2002; Lin et al. 2019). Unfortunately, there were still few reports referring to the simultaneous removal of toluene and these components, especially over Mn-based catalysts. García et al. (2019) observed that the addition of CO_2 could lead to a slight decrease of toluene conversion over a cavity-containing Mn₃O₄ catalyst. Wang et al. (2019) reported the presence of CO_2 did not affect the toluene conversion over layered Cu–MnO_x catalyst, whereas it had an inhibiting effect on granulated Cu–MnO_x catalyst. After adding CO_2 to the simulated feed, the surface active sites of granulated Cu- MnO_x could be gradually covered by the carbonate species and hereby decreased the activation adsorption of oxygen and/or toluene. In addition, the negative effect of SO2 on layered and granulated Cu-MnO_x catalyst in toluene oxidation was also revealed (Wang et al. 2019). It might be due do that SO₂ was adsorbed on the Cu-MnO_x surface to form abundant sulfates.

Reaction kinetics and mechanism

A kinetic model is a helpful tool for simulating the toluene oxidation/combustion and evaluating the toluene removal efficiency in various operational conditions. There are three known kinetic models about removing toluene: power law model, Langmuir model, and Mars-van Krevelen (MVK) model. The power law model is just a math model, and it does not describe the chemistry of the reaction and has no direct connection to the reaction mechanism. The Langmuir model is based on the Langmuir-Hinshelwood mechanism (L-H) and the Eley-Rideal mechanism (E-R). L-H mechanism assumes that the reaction takes place between the adsorbed oxygen and adsorbed toluene molecules. The E-R mechanism assumes that the adsorbed oxygen reacts with gaseous toluene rather than adsorbed toluene. The MVK model exists based on the MVK mechanism. Firstly, the adsorbed toluene reacts with oxygen in the catalyst, and the metal oxides are reduced. Further, the reduced metal oxides are reoxidized by gasphase oxygen. It is a generally acknowledged mechanism to describe the toluene oxidation/combustion reaction over nonnoble metal catalysts.

In the past decade, only a few studies reported the kinetics of toluene removal over manganese oxide-based catalysts. Behar et al. (2015) investigated the kinetics of toluene oxidation on nanosized Cu_{1.5}Mn_{1.5}O₄ catalysts using the three models. Results exhibited that the MVK model fitted the experimental data best, suggesting this reaction follows the MVK mechanism. Sihaib et al. (2017) applied the power law model to investigate the kinetics of toluene removal over four different manganese oxide-based catalysts, including LaMnO₃ and Mn₂O₃ as well as OMS_s and OMS_h prepared by different methods. They found experimental data fitted this model well. The reaction was reported as the only ratelimiting step. Niu et al. (2018) chose two kinetic models to test on 20% CuMn₂O₄/sepiolite and 20% Cu_{0.8}Mn₂Ce_{0.2}O_x/ sepiolite catalysts. They found that the experimental data did not fit the power law model well, while it fitted well with the MVK model.

There are several reaction pathways of toluene removal over Mn-based catalysts based on the MVK mechanism. O_{latt} was considered to be a vital part in this process. Sun et al. (2015) found O_{latt} , being not only the adsorption site but also the active species, and the selectivity to CO_2 was



Fig. 6 Reaction mechanism for toluene oxidation over OMS-2 catalysts (Sun et al. 2015)

connected with the nature of replenished Olatt. Figure 6 shows the oxidation process: toluene firstly adsorbed through the C of the methyl group to Olatt of OMS-2 by abstraction of an H of the methyl group to produce benzoyl. Then, benzoyl transformed into benzaldehyde and benzoate when oxygen existed, while it was oxidized into benzoate in the absence of oxygen. Zhao et al. (2019) proposed a similar reaction path on CuCe_{0.75}Zr_{0.25}/TiO₂ catalysts when oxygen exists as exhibited in Fig. 7. Chen et al. (2017) pointed out completely removing toluene over Fe-MnO_x followed the MVK mechanism when the temperature was greater than 220 °C. The main active site was O_{latt} at the subsurface and migrating from the bulk toward the surface. The pathway for the evolution of toluene successively underwent generation of aldehyde, benzoic acid, maleic acid, and organic salts as well as MnCO₃ and finally conversion into CO₂ and MnO for the next cycle. Dong et al. (2019) reported benzyl alcohol, benzoate, anhydride, and acetate were the main intermediates for toluene oxidation over spinel CoMn₂O₄, and the conversion of the surface anhydride was the rate-controlling step. Wang et al. (2018a) reported that the adsorption form of toluene on Ce-MnOx nanosheet and Ce-MnOx nanorod was difficult as depicted in Fig. 8: toluene adsorbed perpendicularly (pe) and planarly (pl) on the bidimensional surface of Ce-MnOx nanosheets, as well as just adsorbed perpendicularly on the Ce-

Air Catalyst surface

Fig. 7 Reaction path for toluene combustion over $CuCe_{0.75}Zr_{0.25}/TiO_2$ catalysts (Zhao et al. 2019)

 MnO_x nanorod surface. Furthermore, the adsorbed toluene interacted with O_{latt} to form some intermediates including benzoyl oxide, benzaldehyde, benzoate, carbonate, enolic, formates, and acetates, which were oxidized to CO, CO₂, and H₂O at last. Du et al. (2018) observed the reaction process for toluene oxidation over Mn–Ce oxides. After toluene adsorbed on Mn–CeO_x, the oxidation reaction underwent the formation of benzyl alcohol and benzoic acid, further formed formate and carbonate species (or by-product phenol), and finally converted into CO₂ and H₂O.

Converting toluene into CO₂ is a multistep and complex process. Simply, the first step is the adsorption of toluene onto the catalyst surface through abstraction of an H of the methyl group to form benzoyl and then further generated intermediates with aromatic ring such as benzyl alcohol, benzaldehyde, and benzoate species. Then, active surface oxygen species attacked the aromatic nucleus of these intermediates to generate intermediates without aromatic ring such as maleic anhydride and carboxylate species, which were further oxidized to CO₂ and H₂O. In the entire process, the consumed oxygen could be replenished by gas-phase oxygen. What intermediates are produced during the reaction strongly depends on the nature of the catalyst. Studying the reaction kinetics and catalytic mechanism enables a deeper understanding of the reaction process and, hereby, guides effectively the improvement of catalyst performance. Further studies are needed to deeply and comprehensively clarify the reaction kinetics and mechanisms of removing toluene over more Mn-based catalysts.

Conclusions and perspectives

In this review, we give a brief survey of the catalytic removal of toluene over five types of Mn-based catalysts and summarized the strategies improving catalysts at first. Improving the synthetic method to optimize several critical factors of the catalysts or supports, such as valence, structure, morphology, surface defect, dispersion, metal-support interactions, and so on, is a common and efficient way to improve catalytic properties. Incorporation of MnO_x with other metal oxides such as CeO_2 , CuO, Co₃O₄, FeO_x, etc. has been successfully applied to enhance catalytic performance because of the synergy between active components. Loading Mn-based oxides on proper support (Al₂O₃, zeolites, mesoporous silicas, etc.) and tuning the support may obtain better catalytic performance compared with bulk Mn-based oxides because of larger specific surface area, better dispersion, and strong metal-support interactions. Then the effect of coexisting components was explored, and finally, the reaction kinetics and oxidation mechanism were discussed. The removal of toluene over Mn-based catalysts usually follows the MVK mechanism, and the reaction path can be simply divided into three steps: the adsorption of toluene to the catalyst surface to form



Ce-Mn oxide nanosheet

Ce-Mn oxide nanorod

intermediates with aromatic ring, the opening of the aromatic ring to form intermediates without the aromatic ring, and finally, the generation of CO₂ and H₂O. Although significant achievements have been obtained in these fields, there are still some challenges. Future researches may refer to the following aspects: Firstly, actual industrial application requires catalysts with high combination performance, low cost, and simple synthesis procedure. At present, it is still a big challenge to synthesize catalysts with the abovementioned advantage. Exploitation of simple synthesis process to construct novel MnO_x nanocatalysts or Mn-based composite nanocatalysts with special structure, well-defined morphology, and abundant surface defect is becoming a promising research direction. Besides, tuning the support through some simple methods to obtain strong metal-support interactions and excellent dispersion of Mn-based active component is also a promising research direction.

Secondly, more efforts need to be made to study the structure–activity relationships and the synergistic effect of the Mn-based catalysts in depth, which is beneficial to clearly reveal several issues. What is the role of doped metals or supports? Why do different structures and morphologies usually result in diverse catalytic performance? Why do different doped metals or supports usually lead to diverse catalytic performance? How does the strong interfacial interaction work? How do catalytically active sites activate the VOC and intermediate species?

Thirdly, the fundamental reason of the effect of H_2O and other VOCs on Mn-based catalysts is still a worthy subject to study in-depth the different catalysts. Besides, future efforts also should pay more attention to the effect of CO_2 , SO_2 , NO_x , CO, and mercury on toluene removal as well as the development of robust catalysts to remove toluene and coexisting components simultaneously. These coexisting components usually inhibit catalytic activity and rarely promote it. Carrying out more relevant researches and clarifying the internal mechanism of the suppression or promotion effect is useful in the later design of Mn-based catalyst with excellent durability.

Finally, reaction kinetics and oxidation mechanisms of removing toluene or even VOC mixtures over Mn-based catalysts should be explored deeply and comprehensively with the aid of in situ technologies, isotopic tracer techniques, real-time monitoring techniques, and analog computation. At present, there are few researches involved in this subject, and the mechanisms proposed are still unclear. The deeper study of catalytic behaviors helps in obtaining a molecular or even an atomic level view of toluene oxidation/combustion, such as where and how do the bonds of toluene and intermediates break? How do toluene and intermediates bond with the active site of the catalyst? What is the rate-controlling step? We believe that these issues may become hot research topics over the next few years.

Funding information This work was supported by the Key Research and Development Program of Hunan Province in China [2018SK2032] and the National Key Research and Development Program of China [2016YFC0204100].

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