常温下 $\text{MnO}_2/\text{Al}_2\text{O}_3$ 催化剂催化臭氧氧化甲苯反应龙丽萍^{1,2}, 赵建国^{1,2}, 杨利娟^{1,2}, 付名利^{1,2}, 吴军良^{1,2}, 黄碧纯^{1,2}, 叶代启^{1,2,*}¹华南理工大学环境科学与工程学院, 广东广州 510006²华南理工大学工业聚集区污染控制与生态修复教育部重点实验室, 广东广州 510006

摘要: 采用浸渍法制备了 Al_2O_3 负载的 5 种过渡金属氧化物催化剂, 考察了它们在常温下催化臭氧氧化甲苯的性能, 并运用程序升温还原、程序升温氧化、 N_2 吸附-脱附和 X 射线光电子能谱对催化剂进行了表征。结果表明, $\text{NiO}/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$ 和 $\text{MnO}_2/\text{Al}_2\text{O}_3$ 催化剂上活性氧中心数量较少, 臭氧与甲苯转化率较高; 而 $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ 和 $\text{CuO}/\text{Al}_2\text{O}_3$ 催化剂上则相反。催化降解臭氧效率较高的催化剂上甲苯转化率也较高, 在本文实验条件下, CO_2 产率低于 30%。当甲苯浓度为 666 mg/m^3 , O_3 浓度从 193 mg/m^3 提高至 965 mg/m^3 时, 甲苯转化率从 15.2% 提高至 46.7%, 并且使反应后催化剂表面产物和晶格氧含量增加。原位漫反射红外光谱研究发现, 反应过程中生成了含 COO^- , C=O 和 C-O 官能团的物质, O_3 浓度的提高加速了 COO^- 向 C=O 与 C-O 的转化, 前者在 573 K O_2 气氛下几乎不发生反应, 而后者在 373 K 开始分解。基于此, 提出了常温下臭氧催化氧化甲苯的反应机理。

关键词: 三氧化二铝; 过渡金属氧化物; 甲苯; 臭氧; 室温; 原位漫反射红外光谱

中图分类号: O643 **文献标识码:** A

收稿日期: 2010-11-19. 接受日期: 2011-01-23.

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基金来源: 国家自然科学基金 (50978103); 高等学校博士学科点专项科研基金 (20070561042); 国家高技术研究发展计划 (863 计划, 2006AA06A310).

本文的英文电子版(国际版)由 Elsevier 出版社在 ScienceDirect 上出版(<http://www.sciencedirect.com/science/journal/18722067>).

Room Temperature Catalytic Ozonation of Toluene over $\text{MnO}_2/\text{Al}_2\text{O}_3$ LONG Liping¹, ZHAO Jianguo^{1,2}, YANG Lixian^{1,2}, FU Mingli^{1,2}, WU Junliang^{1,2},
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Abstract: Five kinds of transition metal oxides supported on alumina and prepared by wetness impregnation were evaluated for the catalytic ozonation of toluene at room temperature and characterized by temperature-programmed reduction, temperature-programmed oxidation, N_2 adsorption-desorption, and X-ray photoelectron spectroscopy. The catalysts with a lower reduction temperature and less H_2 consumption showed a higher efficiency for ozone and toluene decomposition, such as $\text{NiO}/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$, and $\text{MnO}_2/\text{Al}_2\text{O}_3$, while lower efficiency were observed on $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{CuO}/\text{Al}_2\text{O}_3$. Toluene decomposition efficiency was obviously dependent on ozone. Because of the low ozone to toluene concentration ratio, a CO_2 yield of less than 30% was obtained. At a toluene concentration of 666 mg/m^3 and an ozone concentration between 193 and 965 mg/m^3 , toluene conversion was found to vary from 15.2% to 46.7%. Additionally, we observed an increase in oxidation products and lattice oxygen on the catalyst surface. A preliminary investigation into the reaction pathway was undertaken by in situ diffuse reflectance Fourier transform infrared spectroscopy. With regards to the formation of COO^- , C=O , and C-O groups the high ozone concentration accelerated the transformation from COO^- to C=O and C-O . The substance containing COO^- remained unchanged at 573 K , while the substances containing C=O and C-O underwent oxidation at higher than 373 K . A possible reaction pathway is proposed based on these findings.

Key words: alumina; transition metal oxide; toluene; ozone; room temperature; in situ diffuse reflectance Fourier transform infrared spectroscopy

Received 19 November 2010. Accepted 23 January 2011.

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This work was supported by the National Natural Science Foundation of China (0978103), the Specialized Research Fund for the Doctoral Program of Higher Education (20070561042), and the National High Technology Research and Development Program of China (863 Program, 2006AA06A310).

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

等离子体催化因其较快的起燃速度以及较高的能量效率而被广泛认为是一项有前景的废气处理技术^[1,2],但在消除污染物的同时,也产生二次污染物,如 O_3 等. 人们发现,在等离子体催化降解有机废气的过程中,有机污染物降解率与尾气中 O_3 浓度有关^[3~6]. 近年来,关于催化臭氧氧化气体污染物的研究得到了广泛的开展.

在苯^[7]和乙醇^[8]的催化氧化过程中,当 O_3 代替 O_2 时,反应活化能急剧减小,从而降低了反应温度^[9],提高了氧化效率^[10~13]. 另外,在光催化降解污染物的过程中, O_3 同样起到了重要的作用^[14,15]. 过渡金属氧化物广泛用于挥发性有机化合物 (VOCs) 的催化氧化反应中^[16],其中 Mn 氧化物催化 O_3 氧化活性优于 Co, Ni, Ag, Cu, Ce, Fe, V 和 Mo 氧化物,因而备受关注^[17]. 近年来也有将 Mn 基改性催化剂^[18],以及活性炭 (AC) 负载的贵金属催化剂^[19,20]用于低温降解臭氧. 人们广泛研究了催化剂活性组分的负载量^[21]、表面酸性^[22~24]、晶体结构^[25]、比表面积^[26]和亲水性^[27]等性质对催化剂性能的影响. 部分氧化产物的形成是研究催化臭氧氧化 VOCs 反应的重要内容,它不仅是催化剂失活的原因,也是研究反应机理的途径. 在一些反应过程中检测到了醇、醛以及有机酸等产物的生成^[24,27~30]. 可通过热处理或通入过量的 O_3 使催化剂再生.

本文考察了室温下 5 种负载于 Al_2O_3 上的过渡金属氧化物催化剂催化臭氧氧化甲苯性能,采用程序升温还原 (TPR)、 N_2 吸附-脱附和 X 射线光电子能谱 (XPS) 对催化剂结构进行了表征,并运用原位漫反射红外光谱 (DRIFTS) 和程序升温氧化 (TPO) 技术对反应路径和催化剂表面残留物质的转化进行了研究.

1 实验部分

1.1 催化剂的制备

将 Al_2O_3 (凤凰精密陶瓷有限公司, $A_{\text{BET}} = 106$

m^2/g) 分别浸渍于一定浓度的 $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 和 $\text{Cu}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$ 溶液中,磁力搅拌 12 h 后,于 373 K 水浴干燥. 干燥的样品经研磨后在空气中于 773 K 焙烧 4 h. 活性组分理论负载量 (以质量计) 为 20%. 由于催化剂活性组分的化合价较复杂,为了表达简便,制备好的催化剂分别表示为 $\text{MnO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$, $\text{NiO}/\text{Al}_2\text{O}_3$ 和 $\text{CuO}/\text{Al}_2\text{O}_3$.

1.2 催化剂的表征

TPR 测试在美国麦克公司 Autochem II 2920 型多功能化学吸附仪上进行. 100 mg 样品首先在 573 K 用 50 ml/min Ar 吹扫 30 min,以去除表面杂质,随后在 5% H_2 -95% Ar 中以 10 K/min 升至 1073 或 1273 K, TCD 检测耗氢量. 在 TPO 测试前,样品在 He (30 ml/min) 中于 323 K 吹扫 30 min,然后在 5% O_2 -95% He 中以 10 K/min 升温至 673 K, TCD 检测耗氧量.

催化剂比表面积在美国麦克公司 ASAP 2000 型全自动比表面分析仪上测量,测试前样品于 573 K 脱气 4 h,然后进行 N_2 吸附-脱附实验.

采用德国 VG Multilab 2000 型 XPS 仪对催化剂成分进行分析. Al K_α ($h\nu = 1253.6 \text{ eV}$) 射线, C 1s (284.6 eV) 校准结合能. 测试结果通过 XPSPEAK 4.1 软件进行分析.

原位 DRIFTS 实验在 Nicolet 6700 型红外光谱仪 (美国 Thermo Fisher Scientific) 上进行,样品置于带有 ZnSe 窗片的反应池中,仪器分辨率为 4 cm^{-1} ,扫描范围 $4000 \sim 600 \text{ cm}^{-1}$. 测试前,样品在纯 O_2 气氛中加热至 673 K 并保持 1 h,温度降至室温后在不同条件下反应.

1.3 催化剂的评价

气态甲苯通过 N_2 鼓泡 (273 K) 产生,臭氧发生器将纯 O_2 转化为 O_3 , N_2 为平衡气体,此三路气通入缓冲瓶进行混合. 气体中甲苯和 O_3 浓度分别采用气相色谱 (GC-7890) 和臭氧分析仪 (DCS-1) 进行分析. 催化反应器为直径 10 mm、长度 40 mm 的石英管.

2 结果与讨论

2.1 甲苯的臭氧催化氧化反应活性

甲苯与 O_3 的均相反应分别在两个浓度比例下进行, 结果见图 1. 可以看出, 随着时间的延长, 混合气体中甲苯与 O_3 的浓度几乎不变. 可以认为在不加催化剂时, 甲苯与 O_3 几乎不发生反应, 可忽略其对催化臭氧氧化反应的影响.

图 1 气相中甲苯与 O_3 的反应

Fig. 1. Homogeneous reaction of toluene and ozone in gas phase. Reaction conditions: flow rate 100 ml/min, N_2 balance, room temperature.

当甲苯在催化剂表面吸附平衡后开始催化臭氧氧化甲苯反应. 图 2 为 Al_2O_3 负载的 5 种过渡金属氧化物催化剂上甲苯臭氧氧化反应结果. 可以看出, Fe_2O_3/Al_2O_3 与 CuO/Al_2O_3 上甲苯转化率较低, 而 MnO_2/Al_2O_3 , CoO/Al_2O_3 与 NiO/Al_2O_3 上的则较高, 但仍不超过 40%, 低于文献值^[10]. 这与实验中采用较高的甲苯初始浓度和较低的 O_3 与甲苯浓度比有关. 对于臭氧降解率而言, NiO/Al_2O_3 显示出最高的活性, 其它依次为 MnO_2/Al_2O_3 , CoO/Al_2O_3 , CuO/Al_2O_3 和 Fe_2O_3/Al_2O_3 , 且所有催化剂上臭氧转化率都随反应时间的延长而下降. 另外, NiO/Al_2O_3 催化剂上高的臭氧转化率对应于高的甲苯转化率; 而类似地, CuO/Al_2O_3 与 Fe_2O_3/Al_2O_3 催化剂上臭氧与甲苯的转化率都较低. 还可以看出, NiO/Al_2O_3 上 CO_2 产率最高, 其次为 CoO/Al_2O_3 和 MnO_2/Al_2O_3 , 而 CuO/Al_2O_3 的 CO_2 产率随着甲苯转化率的降低而最终降为 0. 所有催化剂上 CO_2 产量均低于 30%, 表明 70% 以上的甲苯转化为了其它物质.

图 3 为各催化剂上无甲苯存在时臭氧转化率随反应时间的变化. 与图 2 比较后可知, 甲苯存在时的

图 2 MnO_2/Al_2O_3 , Fe_2O_3/Al_2O_3 , CoO/Al_2O_3 , NiO/Al_2O_3 与 CuO/Al_2O_3 催化剂催化臭氧氧化甲苯反应

Fig. 2. Time profiles for toluene conversion (a), ozone decomposition (b) and CO_2 yield (c) over MnO_2/Al_2O_3 , Fe_2O_3/Al_2O_3 , CoO/Al_2O_3 , NiO/Al_2O_3 , and CuO/Al_2O_3 catalyst. Reaction conditions: catalyst 100 mg, toluene 666 mg/m^3 , ozone 193 mg/m^3 , flow rate 100 ml/min, N_2 balance, room temperature.

臭氧转化率低于无甲苯时. 其原因可能有两种: (1) 甲苯与 O_3 在催化剂表面活性位上的吸附存在竞争, 甲苯的存在限制了臭氧与活性位的接触; (2) 反应产物覆盖在催化剂表面, 占据了活性位, 减小了 O_3 与活性位结合的几率.

Einaga 等^[28,31]发现, 在 O_3 体积浓度为 VOCs 物质 10 倍的条件下, 以 MnO_2/Al_2O_3 为催化剂, VOCs 转

图3 无甲苯存在时 $\text{MnO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$, $\text{NiO}/\text{Al}_2\text{O}_3$ 和 $\text{CuO}/\text{Al}_2\text{O}_3$ 催化剂上的臭氧催化反应

Fig. 3. Ozone decomposition without toluene over $\text{MnO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$, $\text{NiO}/\text{Al}_2\text{O}_3$, and $\text{CuO}/\text{Al}_2\text{O}_3$. Reaction condition: catalyst 100 mg, ozone 193 mg/m^3 , flow rate 100 ml/min , N_2 balance, room temperature.

化率可达到50%或更高,根据反应物的不同,CO与 CO_2 组成的碳平衡为26%~37%或50%左右.可见高浓度 O_3 对甲苯转化率与碳平衡的提高具有重要作用.图4为 $\text{MnO}_2/\text{Al}_2\text{O}_3$ 催化剂上 O_3 浓度不同时甲苯和臭氧的转化率.可见,随着 O_3 浓度从0升至965 mg/m^3 ,甲苯转化率逐渐增加,而臭氧转化率缓慢下降.有人假设^[28],如果 O_3 在分解过程中释放出来的活性氧(O^*)是唯一可以氧化甲苯的物种,则在甲苯完全氧化的前提下, O_3 与甲苯的反应遵循以下化学计量关系: $\text{C}_7\text{H}_8 + 18\text{O}_3 = 7\text{CO}_2 + 4\text{H}_2\text{O} + 18\text{O}_2$.图4中 O_3 与甲苯的摩尔比为0~2.8,在此范围内,甲苯转化

图4 $\text{MnO}_2/\text{Al}_2\text{O}_3$ 催化剂上甲苯与臭氧转化率随臭氧浓度的变化

Fig. 4. Dependences of toluene and ozone conversion on inlet ozone concentration over $\text{MnO}_2/\text{Al}_2\text{O}_3$. Reaction conditions: catalyst 100 mg, toluene 666 mg/m^3 , flow rate 100 ml/min , N_2 balance, room temperature.

率随着 O_3 浓度的增加而提高.

金属氧化物催化剂上 O_3 的催化降解机理如下所示(*表示催化剂表面的活性位)^[32]:

在降解过程中检测到了 O^* , O_2^* 与 O_3^{2-} 氧物种. O_3^{2-} 通过库仑力稳定在催化剂表面被认为是产生高臭氧催化活性的原因^[33].由此可见,氧物种与催化剂之间的相互作用是形成较高臭氧与甲苯转化率的重要因素.

2.2 催化剂的表征结果

图5给出了各催化剂的TPR谱.由图可见, $\text{MnO}_2/\text{Al}_2\text{O}_3$ 分别在323~523和523~723 K处出现还原峰,分别归属于非化学计量的 MnO_x ($1.5 < x < 2$)与 Mn_2O_3 物种的还原^[34]. $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ 在620和865 K处出现还原峰,依次对应于 $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$ 的过程,其中865 K处还原峰面积比620 K处的大3~4倍,1076 K处的还原峰对应于 $\text{FeO} \rightarrow \text{Fe}$ 的过程^[35].与之相类似, $\text{CoO}/\text{Al}_2\text{O}_3$ 的还原出现在较宽的温度范围,539 K处还原峰可归为大颗粒 Co_3O_4 的还原,这部分 Co_3O_4 由于颗粒较大,位于载体表面,与载体之间的相互作用较弱,因此在较低温度下即可被还原^[36];887 K处的还原峰可归属于与载体之间相互作用较强的 Co_3O_4 的还原;1124 K附近的还原峰可归属于

图5 $\text{MnO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$, $\text{NiO}/\text{Al}_2\text{O}_3$ 与 $\text{CuO}/\text{Al}_2\text{O}_3$ 催化剂的TPR谱

Fig. 5. TPR profiles of $\text{MnO}_2/\text{Al}_2\text{O}_3$ (1), $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ (2), $\text{CoO}/\text{Al}_2\text{O}_3$ (3), $\text{NiO}/\text{Al}_2\text{O}_3$ (4), and $\text{CuO}/\text{Al}_2\text{O}_3$ (5) samples. Reaction conditions: catalyst 100 mg, temperature ramp 10 K/min.

CoO 的还原, 高的还原温度可归结于 CoO 与载体 Al_2O_3 之间较强的相互作用^[37]. 而 $\text{NiO}/\text{Al}_2\text{O}_3$ 则在 764 K 处出现一个宽峰, 对应 NiO 的还原^[38]. $\text{CuO}/\text{Al}_2\text{O}_3$ 在 323~500 K 出现还原峰, 对应于 $\text{CuO} \rightarrow \text{Cu}$ 的还原^[39], 位于 391 与 451 K 处的还原峰归属于与载体相互作用程度不同的 CuO 的还原.

表 1 列出了各催化剂的耗氢量. 由表可见, 各催化剂的耗氢量大小顺序为 $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3 > \text{CoO}/\text{Al}_2\text{O}_3 > \text{NiO}/\text{Al}_2\text{O}_3 > \text{CuO}/\text{Al}_2\text{O}_3 > \text{MnO}_2/\text{Al}_2\text{O}_3$, 而其比表面积的大小顺序为 $\text{CoO}/\text{Al}_2\text{O}_3 > \text{NiO}/\text{Al}_2\text{O}_3 > \text{CuO}/\text{Al}_2\text{O}_3 > \text{MnO}_2/\text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$. 可见, 催化剂比表面积对其催化活性的影响不明显. 催化剂的还原峰位置与氧中心的活性以及活性组分与载体的相互作用强弱有关, 耗氢量则代表催化剂氧中心的数量. 结合催化剂活性可知, 氧中心活性低、数量少、活性组分与载体间相互作用强的催化剂上臭氧与甲苯催化效率高.

表 1 各催化剂耗氢量与比表面积

Table 1 The amount of H_2 consumption and specific surface area of catalysts

Catalyst	H_2 consumption (mmol/g)	$A_{\text{BET}}/(\text{m}^2/\text{g})$
$\text{MnO}_2/\text{Al}_2\text{O}_3$	0.70	90.42
$\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$	2.30	87.31
$\text{CoO}/\text{Al}_2\text{O}_3$	1.94	100.93
$\text{NiO}/\text{Al}_2\text{O}_3$	1.73	100.46
$\text{CuO}/\text{Al}_2\text{O}_3$	1.71	94.17

图 6 为新鲜和经不同条件反应后 $\text{MnO}_2/\text{Al}_2\text{O}_3$ 催化剂中 O 元素的 XPS 谱, 结果汇总于表 2. 由表可见, 经臭氧催化分解反应后, $\text{MnO}_2/\text{Al}_2\text{O}_3$ 样品的 Mn/Al 值略低于新鲜催化剂, 并且 O 含量明显增加, 化学吸附氧与晶格氧所占比例基本保持不变. 在对 Au/AC 催化剂上臭氧分解的研究中同样发现, 由于载体 AC 被 O_3 氧化, 催化剂表面的氧含量增加^[20]. 可推测在反应过程中, O_3 分解生成的氧化物首先作为吸附氧停留在催化剂表面, 其中活性吸附氧通过与表面相互作用并不断得到电子, 成为晶格氧 O^{2-} , 即 $\text{O}_3 \rightarrow \text{O}^*/\text{O}_2^* \leftrightarrow \text{O}(\text{ads})^- \leftrightarrow \text{O}^{2-}$. Radhakrishnan 等^[40]深入研究了 O_3 在 $\text{MnO}_x/\text{Al}_2\text{O}_3$ 催化剂上的分解机理, 认为 O_3 在分解的过程中, 电子从 Mn 转移到 O_3 , 当氧化物从催化剂表面脱附时, Mn 被还原为原来的价态, 该过程可表示如下:

图 6 经不同条件反应后 $\text{MnO}_2/\text{Al}_2\text{O}_3$ 催化剂表面 O 元素 XPS 谱

Fig. 6. XPS spectra of O element on the surface of fresh and used $\text{MnO}_2/\text{Al}_2\text{O}_3$ catalyst. (1) Fresh catalyst; (2) Used catalyst for ozone decomposition (ozone 193 mg/m^3); (3) Used catalyst for catalytic ozonation of toluene (toluene 666 mg/m^3 , ozone 193 mg/m^3); (4) Used catalyst for catalytic ozonation of toluene (toluene 666 mg/m^3 , ozone 965 mg/m^3).

表 2 $\text{MnO}_2/\text{Al}_2\text{O}_3$ 催化剂的 XPS 测试结果

Table 2 Summary of the results of XPS on $\text{MnO}_2/\text{Al}_2\text{O}_3$ catalyst

Sample	Mn:Al mass ratio (%)	Mass concentration of O (%)	O content (%)	
			Chemically adsorbed O	Lattice O
(1)	9.38	25.08	34.15	65.85
(2)	9.18	33.78	32.79	67.21
(3)	8.51	25.89	15.67	84.33
(4)	8.54	30.69	15.03	84.97

用于甲苯臭氧催化氧化反应后的两个 $\text{MnO}_2/\text{Al}_2\text{O}_3$ 样品的 Mn/Al 值则有更大幅度的减小, 这是由于 MnO_2 发生团聚所致^[41]. 在较低 O_3 浓度下反应的催化剂中 O 含量几乎不变, 但化学吸附氧比例减小至 15% 左右, 其中可能包括 O_2 , CO_2 以及不完全氧化产物中的 O, 晶格氧比例增至 85% 左右, 较新鲜催化剂的增加量可能是由臭氧分解过程中产生的活性氧进入催化剂晶格所致. 在较高 O_3 浓度下反应的催化剂中 O 元素含量有所增加, 但催化剂中化学吸附氧与晶格氧的比例仍为 15% 与 85% 左右, 可以认为, O_3 浓度的提高同时增加了吸附在催化剂表面 O_2 、催化氧化产物, 以及进入催化剂晶格活性氧的量.

2.3 原位 DRIFTS 结果

研究表明^[42,43], 423 K 下甲苯在 V₂O₅/TiO₂ 上吸附的 DRIFTS 谱中于 1700~1400 和 3000~2800 cm⁻¹ 区域出现归属于甲苯的特征吸收峰. 然而本文在常温下只观察到水的特征峰, 无明显甲苯特征峰. 这可能是由于甲苯与催化剂之间较弱的相互作用, 以及室温下较低的甲苯浓度所致.

当甲苯在 MnO₂/Al₂O₃ 催化剂表面吸附 30 min 后, 向反应池中通入 O₃, 采集甲苯与 O₃ 反应的 DRIFTS 谱, 结果见图 7. 随着反应的进行, 在

图 7 MnO₂/Al₂O₃ 催化 O₃ 氧化甲苯反应的原位 DRIFTS 谱
Fig. 7. In situ DRIFTS spectra of ozone reacting with toluene on MnO₂/Al₂O₃ catalyst. (a) Ozone 193 mg/m³; (b) Ozone 965 mg/m³. Reaction conditions: catalyst 50 mg, toluene 666 mg/m³, flow rate 100 ml/min, N₂ balance, room temperature.

3100~2900 和 1800~1200 cm⁻¹ 处出现了一系列特征峰, 其归属详见表 3^[44~46]. 由图 7(a) 可见, 催化剂表面生成了 COO⁻, C=O 和 C-O 官能团, 其中 COO⁻ 特征峰强度大大超过了 C=O 与 C-O. 当臭氧浓度较高时, C=O 与 C-O 特征峰强度增加, COO⁻ 特征峰的强度增加缓慢. 这是由于 (1) 高浓度 O₃ 提高了 C=O 与 C-O 相关物质的选择性, 抑制了 COO⁻ 的生成; (2) 较高的 O₃ 浓度加速了 COO⁻ 向 C=O 与 C-O 的转化.

值得注意的是, 1700~1400 cm⁻¹ 区域是众多有机官能团特征峰的所在区域, 如苯环的碳骨架伸缩振动和甲基伸缩振动等, 因此要对某一种物质进行准确性难度较大.

当甲苯臭氧催化氧化反应进行了一定时间后, 停止通入甲苯与 O₃, 将 N₂ 通入反应池, 直至气相色谱检测不到甲苯时, 再次通入 O₃. 图 8 为 O₃ 与催化剂表面残留物质反应的原位 DRIFTS 谱. 可以看出, 随着 O₃ 的不断通入, COO⁻ 特征峰缓慢减弱, 而 C=O 和 C-O 特征峰强度增大. 可以认为, O₃ 将含 COO⁻ 的

图 8 O₃ 与催化剂表面残留物质反应的原位 DRIFTS 谱
Fig. 8. In situ DRIFTS spectra of ozone reacting with the residual adspecies on the MnO₂/Al₂O₃ catalyst surface. Reaction conditions: catalyst 50 mg, ozone 193 mg/m³, flow rate 100 ml/min, N₂ balance, room temperature.

表 3 MnO₂/Al₂O₃ 催化剂上甲苯臭氧催化氧化反应中 DRIFTS 特征峰的归属

Table 3 Assignment of DRIFTS bands appearing during the catalytic ozonation of toluene on MnO₂/Al₂O₃ catalyst

Position (cm ⁻¹)	Assignment	Characteristic
3069, 3033	phenylic C-H stretching vibration	aromatic ring
2938	symmetric C-H stretching vibration of CH ₃ group	benzyl species
1712	C=O stretching vibration	aldehyde, esters or carboxylic acid
1600, 1555	asymmetric COO ⁻ stretching vibration	benzoate
1450, 1417	symmetric COO ⁻ stretching vibration	benzoate
1286	asymmetric C-O stretching vibration	esters
1179	symmetric C-O stretching vibration	esters

物质氧化为含 C=O 与 C–O 的相关物质。

2.4 反应后催化剂表面吸附物质分析

用 O₂ 代替 O₃ 通入反应池, 在 O₂ 气氛下加热反应后的催化剂, 相应的原位 DRIFTS 谱见图 9。由图可见, 随着温度的升高, C=O 和 C–O 的特征峰逐渐减弱, 与此同时, COO[−] 特征峰在 303~573 K 范围变化很小, 可以认为, 高温使 C=O 与 C–O 的相关物质发生转化或分解, 从而离开催化剂表面, 但很难使 COO[−] 发生转化, 说明此羧酸盐物质有较高的热稳定性。

图 9 催化臭氧氧化甲苯反应后在 O₂ 气氛中加热 MnO₂/Al₂O₃ 催化剂的原位 DRIFTS 谱

Fig. 9. Evolution of in situ DRIFTS spectra by heating the MnO₂/Al₂O₃ catalyst after the reaction between toluene and ozone in O₂ flow. Reaction conditions: catalyst 50 mg, O₂ flow rate 30 ml/min.

图 10 为新鲜和反应后 MnO₂/Al₂O₃ 催化剂的 TPO 谱。可以看出, 各条件下反应后催化剂都于 570 K 处出现氧化峰, 且随着反应时 O₃ 浓度的提高, 于 500 K 处出现新的氧化峰, 并且强度逐渐增加。结合原位 DRIFTS 结果可知, 在 570 K 被氧化的为含有 COO[−] 基团的物质, 而在 500 K 被氧化的为含有 C=O 与 C–O 的物质。

2.5 常温下催化臭氧氧化甲苯反应机理

综上所述, 甲苯的降解效率和 CO₂ 产率受臭氧降解效率的影响较大, 目前也有人认为臭氧催化分解时产生的活性吸附氧是氧化相关有机物的主要物种, 因此本文认为 O₃ 的催化分解是甲苯催化氧化以及 CO₂ 生成的关键。催化臭氧氧化环己烷的研究表明^[30], 反应物首先被氧化为环己醇、环己酮、己酸等部分氧化产物, 后者进一步氧化生成 CO_x。在本文中也同时观察到了部分氧化产物和完全氧化产物的生

图 10 新鲜与反应后 MnO₂/Al₂O₃ 催化剂的 TPO 谱

Fig. 10. TPO profiles of the fresh (1) and used MnO₂/Al₂O₃ catalysts with ozone concentration of 193 mg/m³ (2), 463 mg/m³ (3), 618 mg/m³ (4), 849 mg/m³ (5), and 965 mg/m³ (6). Other conditions: catalyst 100 mg, toluene 666 mg/m³, temperature ramp 10 K/min.

成。由于甲苯中 C₆H₅CH₂–H 与 C₆H₅–CH₃ 键能分别为 317 和 414 eV, 而苯环中的 C–H 和 C–C 的键能分别为 419 和 510~513 eV^[6], 可见, C₆H₅CH₂–H 是最易被氧化的键, 可能生成苯甲醇、苯甲醛和苯甲酸; 而反应中 CO₂ 的生成则最可能来自于苯环上所连接碳原子的氧化。基于现有结果, 难以分辨部分氧化产物究竟是中间产物还是反应旁观者, 要明确部分氧化产物与 CO₂ 的生成之间的关系, 需要更深入的研究。另外, 对于其他部分氧化产物以及含有 COO[−], C=O 与 C–O 官能团产物各种结构的识别, 也有待进一步确证。甲苯的臭氧催化氧化过程可表示如下, 其中用苯甲酸、苯甲醛与苯甲醇分别指代含 COO[−], C=O 与 C–O 官能团的产物:

本文认为提高臭氧催化氧化效率的主要途径有: (1) 开发高活性的催化剂, 研究表明, 具有较高耐还原性的物质有较高的催化活性; (2) 适当地提高反应温度, 从而有利于有机物分子的活化, 使得臭氧催化氧化反应更易进行, 但反应温度过高, 则 O₃ 在气相中自行分解, 催化剂的作用效果减弱, 不利于有机物的催化氧化; (3) 降低有机物的初始浓度, 提高 O₃ 与有机物的浓度比, 有利于有机物的转化与 CO₂ 产率的提

高,但这可能导致尾气中的 O_3 浓度增加,造成污染.

3 结论

考察了负载于 Al_2O_3 上的 5 种过渡金属氧化物催化剂 $\text{MnO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$, $\text{NiO}/\text{Al}_2\text{O}_3$ 和 $\text{CuO}/\text{Al}_2\text{O}_3$ 在常温下对催化臭氧氧化甲苯性能,发现氧中心活性低、数量少、活性成分与载体间相互作用强的催化剂有较高的臭氧与甲苯催化效率,反之亦然. 低 O_3 /甲苯浓度比导致低 CO_2 产率,较高的 O_3 浓度可提高甲苯转化率,并使反应后催化剂表面产物以及晶格氧含量增加. 反应中生成了含 COO^- , $\text{C}=\text{O}$ 与 $\text{C}-\text{O}$ 官能团的物质,并且高 O_3 浓度可以促进 COO^- 向 $\text{C}=\text{O}$, $\text{C}-\text{O}$ 的转化,含 COO^- 的物质具有较高的热稳定性. 针对不完全氧化产物与完全氧化产物 CO_2 之间的关系,以及对所有产物具体结构与种类的确证有待进一步研究.

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英 译 文

English Text

Plasma driven catalysis is widely accepted as a promising technology for gaseous pollutant treatment and it is characterized by fast ignition and high energy efficiency [1,2]. In this process, waste gas molecules decompose and secondary pollutants such as ozone etc. are generated, which causes severe pollution. Several researchers have found a connection between toluene removal efficiency and ozone concentration in the effluent [3–6]. Therefore, recent research work has been directed toward the catalytic ozonation of gaseous pollutants.

It has been confirmed that the activation energy is dramatically reduced in volatile organic compounds (VOCs) catalytic oxidation with the use of ozone instead of oxygen, for example, in the oxidation of benzene [7] and ethanol [8]. The reduced activation energy results in a lower reaction temperature [9] and a higher oxidation efficiency [10–13]. Moreover, it has been found that ozone plays a crucial role in the photocatalytic decomposition of gaseous pollutants [14,15]. Transition metal oxides were widely used as catalysts for VOCs oxidation [16]. Manganese oxide has a higher ozone decomposition efficiency than Co, Ni, Ag, Cu, Ce, Fe, V, and Mo oxides, and it has attracted much attention for the catalytic ozonation of VOCs [17]. Recently, a modified Mn catalyst [18] and novel metal catalysts supported on active carbon [19,20] have been developed for ozone decomposition. The effects of catalyst structures have been investigated by many researchers, and important factors are the loading of the active component onto the support [21], acidity [22–24], crystal structure [25], surface area [26], and hydrophilicity [27]. The build-up of a partial oxidation species is an important issue for the catalytic oxidation of VOCs with ozone, and this is considered to be responsible for the deactivation of the catalysts. Alcohols, aldehydes, and organic acids have been identified as intermediates in these reaction processes [24,27–30]. Heat treatment and excessive ozone feeding favor catalyst regeneration.

In this work, the catalytic ozonation of toluene was investigated using five transition metal oxides supported on

alumina at room temperature. Catalyst structure was investigated using temperature-programmed reduction (TPR), N_2 adsorption-desorption, and X-ray photoelectron spectroscopy (XPS). In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and temperature-programmed oxidation (TPO) techniques were used to study the reaction pathways and the transformation of residual adspecies on the catalyst surface.

1 Experimental

1.1 Catalyst preparation

The catalysts were prepared using wetness impregnation. Al_2O_3 (Phoenix Fine Ceramics Limited, China, $A_{BET} = 106 \text{ m}^2/\text{g}$) was impregnated in an aqueous solution containing an appropriate amount of $Mn(CH_3COO)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, or $Cu(NO_3)_2 \cdot 8H_2O$. The mixtures were stirred for 12 h and then dried in a water bath at 373 K. The dried samples were ground and calcined in air at 773 K for 4 h. Nominally, all the mass ratios of the corresponding oxides to the support was 20%. For simplicity, the prepared alumina-supported catalysts are denoted MnO_2/Al_2O_3 , Fe_2O_3/Al_2O_3 , CoO/Al_2O_3 , NiO/Al_2O_3 , and CuO/Al_2O_3 , even though the oxidation states could be complex.

1.2 Catalyst characterization

TPR measurements were performed on the five catalysts using an Autochem II 2920 (Micromeritics, USA). 100 mg of the samples were preheated in argon at 573 K for 30 min at 50 ml/min to remove impurities. The TPR measurements were started in 5% H_2 -95% Ar from 323 K to 1073 or 1273 K with a temperature ramp of 10 K/min. A signal was recorded every 0.5 s using a thermal conductivity detector (TCD). Before the TPO test, He (30 ml/min) was used to purge the catalyst sample to remove the remaining adsorbed species at 323 K for 30 min, and then the sample was heated to 673 K in 5% O_2 -95% He at the temperature ramp of 10 K/min.

The specific surface area of each catalyst sample was obtained by N_2 adsorption-desorption with an automated volumetric adsorption apparatus (Micromeritics, ASAP 2000, USA). The samples were degassed at 573 K for 4 h before the measurements.

XPS studies were carried out using a VG Multilab 2000 photoelectron spectrometer (Germany) using $Al K_{\alpha}$ radiation with an energy of 1253.6 eV. The binding energy values were referenced to the C 1s line at 284.6 eV. The results were analyzed with the software package XPS PEAK 4.1.

In situ DRIFTS experiments were performed in a reaction cell containing a ZnSe window on a Nicolet 6700 (Thermo

Fisher Scientific, USA) at a resolution of 4 cm^{-1} from $4000\text{--}600\text{ cm}^{-1}$. Before the measurement, the catalyst was heated at 673 K for 1 h in pure O_2 to remove surface impurities. The reactions under different conditions started when the sample was cooled to room temperature.

1.3 Catalytic activity measurements

Gaseous toluene was produced by N_2 -bubbling in liquid toluene, and it was kept in a water bath (273 K). A silent discharge ozone generator transformed pure O_2 into O_3 while N_2 was used for the balance. The three gas streams passed into a buffering bottle for complete mixing. The effluent was sampled and analyzed using gas chromatography (GC-7890, Techcomp Limited, China) and an ozone analyzer (DSC-1, Lida Instrument Factory, China). The catalytic reaction took place in a quartz tube with a diameter of 10 mm and a length of 400 mm .

2 Results and discussion

2.1 Catalytic decomposition of toluene and ozone

The homogenous reaction between toluene and ozone was carried out under two toluene/ozone concentration ratios (Fig. 1). The toluene and ozone concentrations in the effluent remained almost unchanged with $C:C_0 = (1\pm 3)\%$, and this is within the accepted tolerance of experimental error. We considered that the effect of a homogeneous reaction between toluene and ozone could be eliminated, as has been reported by other researchers [30].

The catalytic ozonation of toluene was initiated after the adsorption-desorption equilibrium was established for toluene between the gas phase and the catalyst surface. Figure 2 shows time courses for toluene and ozone decomposition, as well as the CO_2 yield over the $\text{MnO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$, $\text{NiO}/\text{Al}_2\text{O}_3$, and $\text{CuO}/\text{Al}_2\text{O}_3$ catalysts, respectively. Different decomposition behavior was observed among these five Al_2O_3 supported oxide catalysts with comparably low toluene conversion for $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{CuO}/\text{Al}_2\text{O}_3$ and a higher toluene conversion for $\text{MnO}_2/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$, and $\text{NiO}/\text{Al}_2\text{O}_3$. The toluene conversions found in this study (no more than 40%) are lower than those reported in Ref. [10], because of the higher initial concentration of toluene and the low concentration ratio of ozone to toluene (this will be discussed later). As far as ozone decomposition is concerned, $\text{NiO}/\text{Al}_2\text{O}_3$ shows the highest activity, followed by $\text{MnO}_2/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$, $\text{CuO}/\text{Al}_2\text{O}_3$, and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, and for all these catalysts the ozone conversion decreased with time on stream, as shown in Fig. 2(b). By combining the catalytic decomposition of ozone and toluene and using the reaction on $\text{NiO}/\text{Al}_2\text{O}_3$ as an example,

it is clear that a higher ozone conversion indicates a higher toluene conversion. Similar trends were observed for $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{CuO}/\text{Al}_2\text{O}_3$, but both the ozone and toluene conversions are low.

The approximate activity sequence is apparent for ozone decomposition over these five catalysts in the absence of toluene. As shown in Fig. 2(c), the CO_2 yields obtained over these five catalysts are less than 30% , indicating that more than 70% of the decomposed toluene converted to other compounds, such as partial oxidation compounds. The highest CO_2 yield was obtained on $\text{NiO}/\text{Al}_2\text{O}_3$, followed by $\text{CoO}/\text{Al}_2\text{O}_3$ and $\text{MnO}_2/\text{Al}_2\text{O}_3$. The yield from $\text{CuO}/\text{Al}_2\text{O}_3$ decreased to zero along with the toluene conversion.

As shown in Fig. 3., it is obvious that ozone conversion without toluene is higher than that in the presence of toluene. Two reasons may be responsible for this phenomenon. Firstly, toluene competes with ozone for active sites on the catalyst surface. Secondly, partial oxidation products are generated in the reaction and then occupy active sites. The presence of either toluene or partial oxidation products inhibits the combination of ozone and active sites leading to lower ozone conversion.

Einaga et al. [28,31] reported that when ozone concentration in terms of volume was 10 times of VOCs, VOCs conversion on $\text{MnO}_2/\text{Al}_2\text{O}_3$ could reach 50% or higher, and carbon balance consisting of CO_2 and CO was $26\%\text{--}37\%$ or around 50% , depending on different reactants. However, the highest toluene conversion that we obtained was around 40% . We suggest that the ozone concentration plays an important role in the studied reaction. As shown in Fig. 4, when ozone concentration varies from $0\text{--}965\text{ mg/m}^3$, toluene conversion increases linearly, while ozone conversion decreases slightly. Many researchers believe that if the active oxygen atom (O^*) that is generated by ozone decomposition was the only species capable of oxidizing toluene, then the reaction should have a stoichiometry as follows when complete oxidation is achieved: $\text{C}_7\text{H}_8 + 18\text{O}_3 = 7\text{CO}_2 + 4\text{H}_2\text{O} + 18\text{O}_2$. In this study, the inlet molar concentration ratio of ozone to toluene varied from $0\text{--}2.8$, which resulted in a linear increase in toluene conversion.

The mechanism for ozone decomposition on the oxide catalyst has been well established as follows [32]:

where * denotes an active site on the catalyst surface.

The oxygen species O^* , O_2^* , and O_3^{2-} were detected. The high catalytic activity of ozone was due to the stability of O_3^{2-} on the catalyst surface through a Coulombic interaction [33]. From [32,33] it is obvious that both the high ozone and toluene conversions result from the stable interaction between the oxygen species and the catalyst surface.

2.2 Characterization of the catalysts

TPR experiments were carried out to investigate the redox properties of the studied transition metal oxides. As shown in Fig. 5, $\text{MnO}_2/\text{Al}_2\text{O}_3$ showed consecutive reduction peaks from 323–723 K indicating a rapid hydrogen consumption rate and a high dispersion of MnO_2 on Al_2O_3 . The peaks from 323–523 K and 523–723 K corresponded to the reduction of MnO_x ($1.5 < x < 2$) and Mn_2O_3 [34]. Reduction peaks at 620, 865, and 1076 K were found for $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$. The intensity of the peak at 865 K was 3–4 times stronger than that at 620 K suggesting that the latter corresponded to the transformation of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ and the former to $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$. Reduction peak at 1076 K was assigned to the process of $\text{FeO} \rightarrow \text{Fe}$ [35]. A similar curve was observed for $\text{CoO}/\text{Al}_2\text{O}_3$ with reduction peaks at 539, 887, and 1124 K. The peak at 539 K is assigned to the reduction of large particle size Co_3O_4 , which settles on the surface and weakly interacts with the support [36]. The peak at 887 K is due to the reduction of Co_3O_4 caused by its stronger interaction with Al_2O_3 , while the peak at 1124 K comes from CoO , which strongly interacts with the support [37]. A single wide reduction peak at 764 K was found for $\text{NiO}/\text{Al}_2\text{O}_3$, and this is assigned to the reduction of NiO [38]. Reduction peaks in the low temperature range were observed for $\text{CuO}/\text{Al}_2\text{O}_3$, which corresponds to the $\text{CuO} \rightarrow \text{Cu}$ reduction process [39]. The peaks at 391 and 451 K resulted from the different interactions of CuO with Al_2O_3 .

As shown in Table 1, the H_2 consumption of the five catalysts decreases in the order $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3 > \text{CoO}/\text{Al}_2\text{O}_3 > \text{NiO}/\text{Al}_2\text{O}_3 > \text{CuO}/\text{Al}_2\text{O}_3 > \text{MnO}_2/\text{Al}_2\text{O}_3$, and the specific area decreases in the sequence $\text{CoO}/\text{Al}_2\text{O}_3 > \text{NiO}/\text{Al}_2\text{O}_3 > \text{CuO}/\text{Al}_2\text{O}_3 > \text{MnO}_2/\text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$. Together with the results of catalytic activity, the catalysts that had a low H_2 consumption ($\text{MnO}_2/\text{Al}_2\text{O}_3$) or a higher reduction temperature ($\text{CoO}/\text{Al}_2\text{O}_3$ and $\text{NiO}/\text{Al}_2\text{O}_3$) gave higher activity. The catalysts that were characterized by more H_2 consumption ($\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$) or a lower reduction temperature ($\text{CuO}/\text{Al}_2\text{O}_3$) were less active. No significant difference in specific surface area was observed for these five catalysts and their relationship with catalytic activity was ambiguous. Furthermore, H_2 consumption indicated that the amount of oxidation sites and the different interactions between the active components and the supports with reduction temperature reflected activity. We conclude that small amounts of oxidation sites with low activity along with weak interactions between the active components and the supports favor an increase in the toluene and ozone catalytic decomposition efficiency.

The XPS results of the fresh and used $\text{MnO}_2/\text{Al}_2\text{O}_3$ catalysts are summarized in Fig. 6 and Table 2. The O mass concentration on the $\text{MnO}_2/\text{Al}_2\text{O}_3$ catalyst increased from 25.08% to 33.78% after ozonation. A similar discovery was

found for ozone decomposition with a Au/AC catalyst as a result of the oxidation of active carbon with ozone [20]. With regard to the composition of the chemically adsorbed and lattice O, no significant difference was found. We predict that the oxygen species was adsorbed on the catalyst surface, and that the electron obtained by the interaction with MnO_2 leads to a transformation from adsorbed oxygen to lattice oxygen. The process could be described as $\text{O}_3 \rightarrow \text{O}^*/\text{O}_2^* \leftrightarrow \text{O}(\text{ads})^- \leftrightarrow \text{O}^{2-}$. Radhakrishnan et al. [40] showed that ozone decomposition over the $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalyst proceeds by electron transfer from the Mn site to ozone, and Mn is reduced when the oxygen species desorb from the catalyst surface.

Regarded to the data, difference was found for the Mn:Al mass ratio values. For sample (2), the Mn:Al ratio was slightly lower than that of the fresh catalyst and the value was even lower for samples (3) and (4). This decrease is attributed to the agglomeration of the loaded MnO_2 [41]. For samples (3) and (4), which were both used for the catalytic ozonation of toluene, the relative concentration of chemically adsorbed O decreased to around 15% and that of lattice O increased to around 85%. The chemically adsorbed oxygen included oxygen species in O_2 , CO_2 and the partial oxidation products that were generated in the reaction process. A higher O mass concentration of sample (4) suggests that with the higher concentration ratio of ozone to toluene both the products adsorbed on the surface, and that the amount of oxygen that transformed from adsorbed oxygen to lattice oxygen increased.

2.3 In situ DRIFTS studies

The in situ DRIFTS spectra were initially collected for the catalysts in the toluene stream without the ozone feed. The characteristic bands assigned to toluene adsorbed on $\text{V}_2\text{O}_5/\text{TiO}_2$ at 423 K were observed in the regions around 3000–2800 and 1700–1400 cm^{-1} [42,43]. However, no bands could be assigned to toluene and only the bands assigned to water could be detected on the catalyst surface in this study. This is due to the weak interaction between toluene and the catalyst surface and the low concentration of the toluene adspecies at room temperature.

Toluene was initially adsorbed on the catalyst for 30 min and then O_3 was fed into the reaction cell. The collected spectra are shown in Fig. 7. As the reaction progressed a series of characteristic transmission bands appeared between 3100–2900 and 1800–1200 cm^{-1} . According to previous work [44–46], the band assignment is summarized in Table 3. As shown in Fig. 7(a), the intensity of the COO^- band

eventually exceeded that of $\text{C}=\text{O}$ and $\text{C}-\text{O}$. Compared to Fig. 7(a), at a higher ozone concentration the intensity of $\text{C}=\text{O}$ and $\text{C}-\text{O}$ grew faster than that of COO^- , as shown in Fig. 7(b). A possible reason for this difference could be the higher O_3 concentration, which improved the selectivity of $\text{C}=\text{O}$ and $\text{C}-\text{O}$, suppresses the formation of COO^- ; secondly, a larger amount of O_3 accelerates the evolution from COO^- to $\text{C}=\text{O}$ and $\text{C}-\text{O}$.

It is worth noting that a variety of bands are present between $1700\text{--}1400\text{ cm}^{-1}$, such as a $\text{C}-\text{C}$ stretching vibration from the aromatic ring skeleton and the methyl group, along with the bands mentioned previously. However, it is difficult to distinguish and accurately assign these bands because of their overlap.

Consequently, toluene and O_3 were both cut off, and N_2 was added to the reaction cell to remove the residual toluene in the gas phase until no toluene was detected by gas chromatography. Ozone was fed into the reaction cell again and the spectra for the reaction of ozone with the residual adspecies on the $\text{MnO}_2/\text{Al}_2\text{O}_3$ catalyst surface were recorded, as shown in Fig. 8. The intensity of COO^- gradually decreased and the $\text{C}=\text{O}$ and $\text{C}-\text{O}$ bands grew stronger. We suggest that COO^- was oxidized to $\text{C}=\text{O}$ and $\text{C}-\text{O}$ by a reaction with O_3 .

2.4 Analysis of the residual adspecies on the catalyst surface

In this experiment, O_3 addition was stopped and O_2 was fed into the reaction cell while the catalyst was heated. As shown in Fig. 9, the $\text{C}=\text{O}$ and $\text{C}-\text{O}$ bands weaken as the temperature increases, while the intensity of COO^- remains almost unchanged. Therefore we conclude that $\text{C}=\text{O}$ and $\text{C}-\text{O}$ probably decompose with heat, while COO^- could not be oxidized at high temperature, which shows its higher thermal stability.

Figure 10 shows TPO profiles of the fresh and used $\text{MnO}_2/\text{Al}_2\text{O}_3$ catalysts. An oxidation peak formed around 570 K on all the used catalysts and as the ozone concentration increased a new peak formed at 500 K and its intensity increased with the ozone concentration. This finding is consistent with the in situ DRIFTS study result, that the intensity of characteristic peak assigned to COO^- was strong under a low ozone concentration, and that those of $\text{C}=\text{O}$ and $\text{C}-\text{O}$ were weak but became stronger at higher ozone concentrations. Therefore, the adspecies that was oxidized at 500 K might correspond to the species containing $\text{C}=\text{O}$ and $\text{C}-\text{O}$, and the species that was oxidized at 570 K may be the ones that contain COO^- . A difference is apparent between the oxidation temperatures determined by TPO and those by in situ DRIFTS. This could be result from the different flow rates and permeability of these two instruments.

2.5 Mechanism of the catalytic ozonation of toluene

Based on the relationship between toluene and ozone decomposition, some researchers presumed that actively adsorbed oxygen was the only species capable of oxidizing corresponding organic compounds, and it has been predicted that the interaction between ozone and the catalyst surface is the most important step in the catalytic ozonation of toluene, which influences toluene decomposition and product formation.

Einaga and Futamura [30] suggested that in the catalytic ozonation of cyclohexane the reactant is initially degraded to partial oxidation products, such as cyclohexanol, cyclohexanone, and hexane diacid, and finally that CO_x is generated as a complete oxidation product. In this study, both partial and complete oxidation products were detected. In the molecular structure of toluene the bond energy of $\text{C}_6\text{H}_5\text{CH}_2-\text{H}$, $\text{C}_6\text{H}_5-\text{CH}_3$, $\text{C}-\text{H}$, and $\text{C}-\text{C}$ are 317, 414, 419, and $510\text{--}513\text{ eV}$, respectively [6]. The methyl group on the benzene ring is more reactive than the other parts of the molecule, which results in its oxidation to benzyl alcohol, benzophenone or benzoic acid. Based on the current results, it is not clear whether the former molecule acts as an intermediate or just as a spectator. Further work is necessary to determine the relationship between the partial oxidation products and CO_2 . In addition, thorough work is required to identify the complete scope and specific structure of products. The proposed reaction pathway is as follows where benzoic acid, benzaldehyde, and benzyl alcohol represent the products containing the COO^- , $\text{C}=\text{O}$, and $\text{C}-\text{O}$ group, respectively. It is possible that one of the products may contain both $\text{C}=\text{O}$ and $\text{C}-\text{O}$. The products may include, but are not limited to, the substances mentioned below.

To improve the efficiency of the catalytic ozonation for the removal of VOCs, it is worth paying attention to: (1) the development of a desirable catalyst. TPR results revealed that the materials that are more resistant to reduction had higher activity; (2) elevating the reaction temperature to an appropriate temperature increases the VOCs conversion; (3) increasing the concentration ratio of ozone/VOCs gives rise to both VOCs conversion and CO_2 selectivity, but it can also lead to a high level of ozone in the effluent.

3 Conclusions

Five kinds of transition metal oxides that were supported on alumina were investigated for the catalytic ozonation of toluene at room temperature. We found that low amounts and

low activity of oxidation site and a strong interaction between the active component and the support gave a higher ozone and toluene decomposition efficiency. The low ozone to toluene concentration ratio led to a low CO_2 yield, while a higher ozone concentration favored toluene conversion and caused the catalytic oxidation products and the lattice oxygen of the catalyst to increase. Substances containing the COO^- , C=O and C-O groups were detected in the reaction process. Moreover, increasing the ozone concentration accelerated the

transformation from COO^- to C=O and C-O . The thermal stability of COO^- was stronger than that of the other two. However, further research is required to determine the relationship between the complete and the partial oxidation products, as well as to identify the complete scope and the specific structure of the products.

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