

净水技术前沿与热点综述

王筱月, 李亮, 张思濡, 等. 催化臭氧氧化工艺中催化剂应用的研究进展[J]. 净水技术, 2023, 42(12): 8-16, 43.

WANG X Y, LI L, ZHANG S R, et al. Research progress of catalysts application in catalytic ozone process[J]. Water Purification Technology, 2023, 42(12): 8-16, 43.

催化臭氧氧化工艺中催化剂应用的研究进展

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摘要 催化臭氧氧化法作为一种高级氧化技术, 在难生物降解有机废水的深度处理领域具有良好的应用前景。催化剂可以促进臭氧分解并生成活性自由基, 增强有机污染物的降解速率和矿化程度, 是影响催化臭氧氧化法效能的关键因素。文章阐述了均相和非均相催化臭氧法的反应机理, 在此基础上梳理了近年来催化臭氧氧化工艺中常用催化剂的分类和研究进展, 包括金属离子、金属氧化物、碳基材料、矿物质材料等, 并对其在工业废水深度处理上的应用进行总结, 探讨了该技术目前存在的问题, 并展望了未来研究方向及应用前景, 包括新型高效催化剂的制备、复杂难降解废水臭氧化预处理、二级生化处理出水的深度处理等。

关键词 催化臭氧法 负载型催化剂 金属型催化剂 催化机理 难生物降解废水

中图分类号: X703 **文献标识码:** A **文章编号:** 1009-0177(2023)12-0008-10

DOI: 10.15890/j.cnki.jsjs.2023.12.002

Research Progress of Catalysts Application in Catalytic Ozone Process

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Abstract As an advanced oxidation technology, catalytic ozonation has a good application prospect in the field of advanced treatment of non-biodegradable organic wastewater. The catalyst can promote the decomposition of ozone and generate active free radicals, enhance the degradation rate and mineralization degree of organic pollutants, and is a key factor affecting the efficiency of catalytic ozonation. In this paper, the reaction mechanism of homogeneous and heterogeneous catalytic ozonation is described. In recent years the classification and research progress of commonly used catalysts in the catalytic process are summarized, including metal ions, metal oxides, carbon-based materials, mineral materials, etc. and their applications in advanced treatment of industrial wastewater are summarized. The existing problems of this technology are discussed, and the future research direction and application prospect have been prospected, which includes the preparation of new efficient catalyst, ozonation pretreatment of complex and refractory wastewater, and advanced treatment of secondary biochemical treatment effluent.

Keywords catalytic ozonation supported catalyst metal catalyst catalytic mechanism non-biodegradable wastewater

[收稿日期] 2022-10-11

[基金项目] 国家自然科学基金(21876111)

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随着医药、化学、印染等相关工业的蓬勃发展, 全球每年有超过 4 200 亿 t 有机废水排放到河流、湖泊和海洋中^[1], 其中含有染料、洗涤剂、药品、个人护理产品、农药、羧酸和芳香族化合物等有机污染物^[2]。如果这些污染物在水环境中长期滞留, 不仅会破坏水体生态, 消耗水体溶解氧, 还可通过生物沉积和食物链的富集作用最终威胁人体健康^[3]。传统

的城市生活污水处理厂一般采用物理法(格栅、沉淀)、生物法(活性污泥法、生物膜法)、化学法(氯消毒、紫外线消毒)等工艺^[4],然而这些方法通常具有明显的局限性,不能有效去除污水中复杂有机物^[5]。高级氧化技术(AOPs)作为高效的新型水处理技术,可高效矿化二级生化出水中残存的难降解有机物,受到水处理行业研究者和工程师的广泛关注。

AOPs 的去除效果与工艺中生成的活性自由基有着直接关联,其中最主要的是羟基自由基($\cdot\text{OH}$),还有超氧化氢自由基($\text{HO}_2\cdot$)、硫酸根自由基($\text{SO}_4\cdot^-$)和超氧阴离子自由基($\text{O}_2\cdot^-$)^[6]。AOPs 涵盖 6 种工艺,包括辐射、光解和光催化、超声波分解、电化学氧化技术、基于芬顿的反应和基于臭氧的工艺^[7]。臭氧氧化作为 AOPs 的一种,在难降解工业废水处理中有良好的表现。臭氧是一种高效氧化剂,能直接氧化污染物,或通过间接方式由臭氧分解过程中产生的 $\cdot\text{OH}$ 与污染物发生反应^[8]。然而,单独臭氧氧化的局限性较多,如臭氧利用率低、能耗高、污染物矿化度较低、pH 影响大且某些有机副产物可能会对水体造成更为严重的污染^[9]。催化臭氧氧化法能弥补单独臭氧氧化的不足,催化剂可以促进臭氧分解并生成活性自由基,从而提高有机污染物的矿化程度,达到更好的污染物去除效果^[10]。近年来,研究者们研发了许多性质稳定、效果良好的催化剂,本文对近年来催化臭氧氧化法中常用催化剂进行了总结。

1 催化臭氧氧化法

根据催化剂在溶液中存在状态的差异性,可将催化臭氧氧化法分为均相催化臭氧氧化法和非均相催化臭氧氧化法。

1.1 均相催化臭氧氧化法

均相催化臭氧氧化法中的催化剂以溶解态形式存在,一般为过渡金属离子,如 Mn^{2+} 、 Fe^{2+} 、 Cu^{2+} 、 Co^{2+} 、 Ni^{2+} 、 Zn^{2+} 、 Pb^{2+} 等,能够均匀分散在水溶液中,反应效率较高。一般来说,均相催化臭氧氧化有两个机理,一是臭氧在过渡金属离子的作用下,分解产生高活性、高氧化性的 $\cdot\text{OH}$ 来降解有机物;二是金属离子与有机物分子反应形成络合物,更容易失电子而被臭氧氧化分解^[11]。均相催化臭氧氧化法能有效提高水中有机物的去除率,但反应物质和催化剂在同一个物相体系中,难以将催化剂从体系中分

离,从而容易造成二次污染、催化剂流失、重复利用率低等诸多不利影响^[12],发展前景有限。

1.2 非均相催化臭氧氧化法

非均相催化臭氧氧化法的催化剂为固体,种类也更加丰富。其降解机理主要有:(1)自由基理论,固体催化剂能促使臭氧在其表面分解,产生活性更高的 $\cdot\text{OH}$;(2)氧空位理论,金属氧化物催化剂表面的晶格缺陷能够捕捉臭氧分子,从而引发臭氧分解产生自由基;(3)表面配位络合理论,有机分子被吸附在催化剂表面形成螯合物,再被臭氧或 $\cdot\text{OH}$ 氧化降解;(4)协同反应理论,催化剂、臭氧、有机物和水分子之间有相互协同作用,在催化剂表面和液相主体中均能发生反应。研究者们已制备出许多效果优良、性能稳定、原料易得的催化剂,如 $\text{Cu-O-Mn}/\gamma\text{-Al}_2\text{O}_3$ ^[13]、 $\text{MgO}/\text{Co}_3\text{O}_4/\text{CeO}_2$ ^[4] 等,将这些催化剂应用于催化臭氧氧化难降解有机废水试验,均能明显提高废水的处理效果。相较于均相催化剂,非均相催化剂得到越来越广泛的研究和应用。

2 催化剂的分类及其性能

催化剂的分类如图 1 所示。

2.1 负载型催化剂

负载型催化剂通过共沉淀、浸渍、水热、离子交换、焙烧等方法将具有催化活性的金属以及金属氧化物均匀分散负载在载体表面制备而成。载体通常有较大的比表面积,能够提高催化剂的活性强度以及稳定性,增大催化剂与污染物的接触面积,提高反应效率。常用的催化剂载体种类有金属氧化物、碳材料、天然矿物、人工合成无机材料等。

2.1.1 氧化物载体催化剂

Al_2O_3 是一种常见的金属氧化物载体,孔隙结构多,力学性能稳定,有利于承载 Fe 、 Cu 、 Mo 、 Mn 和 Co 等过渡金属,能为反应物提供更多的活性位点^[14]。Kruanak 等^[15]采用浸渍法制备了 $\text{NiO}/\text{Al}_2\text{O}_3$,提高了 2,4,6-三氯苯酚(TCP)去除率。Chen 等^[16]合成了以具有分层结构和大表面积的介孔 Al_2O_3 微球为载体的 CuO 催化剂,相比于浸渍法,这种方法得到的 CuO_x 催化剂尺寸更小,在降解苯酚废水中表现出显著的催化性能,且循环稳定性高。除了 Al_2O_3 外, MnO_2 、 CeO_2 、 Co_3O_4 等金属氧化物均可作为载体,如以 MnO_2 空心微球为载体的催化剂 $\text{Ag}/\text{R-MnO}_2$ ^[17]、 PdO/CeO_2 ^[18]、 $\text{Fe}_3\text{O}_4/\text{Co}_3\text{O}_4$ ^[19],此

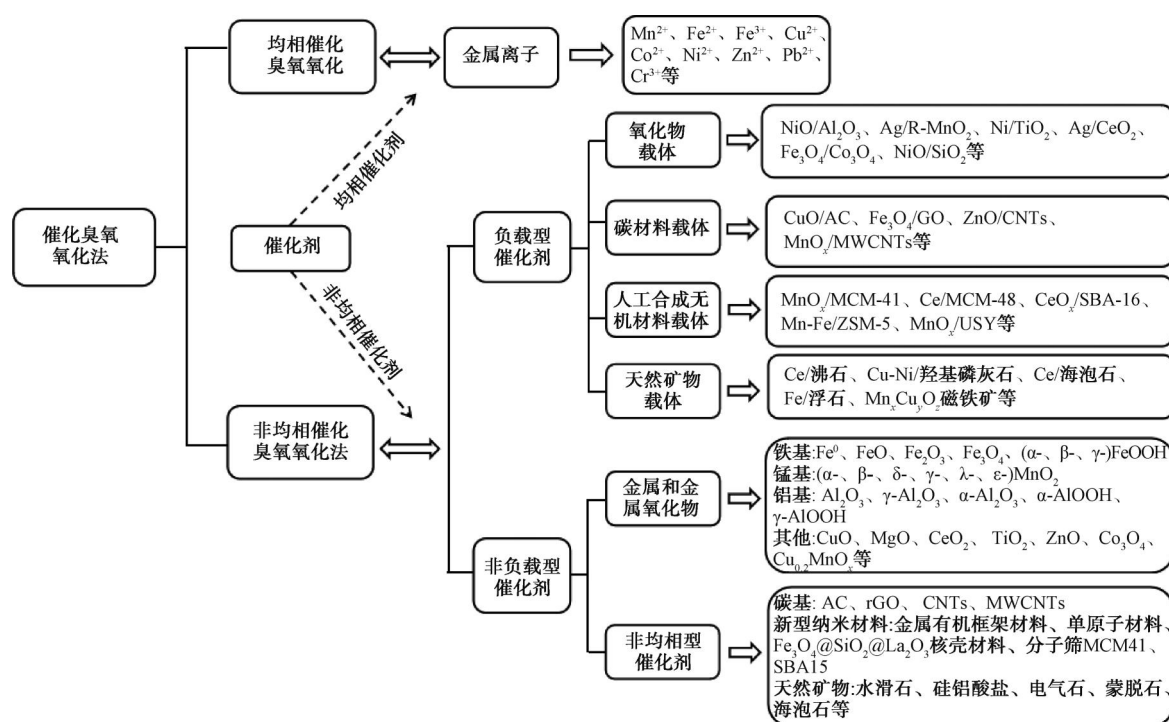


图 1 催化臭氧氧化法中的均相和非均相催化剂

Fig. 1 Homogeneous and Heterogeneous Catalysts in Catalytic Ozonation

外还有以 SiO_2 作为载体的 NiO/SiO_2 ^[20] 等。

2.1.2 碳材料载体催化剂

碳材料孔径丰富、比表面积大,是常见的催化剂载体。Liu 等^[21]用共沉淀法制备了锰铁氧化物/活性炭 ($\text{Mn}_x\text{Fe}_y\text{O}_z/\text{AC}$), 最优条件下对磺胺嘧啶 (SMZ) 的降解率为 90.5%, 比单独臭氧氧化提高 25.7%。Fahadi 等^[22]用共沉淀法制备介孔 Fe_3O_4 /氧化石墨烯 ($\text{Fe}_3\text{O}_4/\text{GO}$) 纳米杂化材料降解酸性红染料, COD_{Cr} 去除率从 25% 提高到 69%。Sui 等^[23]通过浸渍法制备了碳纳米管负载的锰氧化物 ($\text{MnO}_x/\text{MWCNT}$), 将环丙沙星的矿化率从 4.5% 提高至 38.5%。

2.1.3 人工合成无机材料载体催化剂

人工合成无机材料 (例如分子筛) 拥有稳定的结构和良好的吸附能力, 规整的介孔结构和较大的比表面积能够使负载的活性组分分布良好, 从而达到理想的催化效果。Li 等^[24]用 $\text{Mn-Fe}/\text{ZSM-5}$ 作为旋转填料床 (RPB) 填料, 优化条件下硝基苯和 TOC 的去除率分别达到 99.9% 和 72.0%。除此之外, Sui 等^[25]制备了不同 Si、Mn 比例的 $\text{MnO}_x/\text{MCM-41}$, Mu 等^[26]制备了 $\text{CeO}_x/\text{SBA-16}$, Li 等^[27]制备了 $\text{Ce}/\text{MCM-48}$, 他们发现中孔结构材料表面积大、孔分布均匀, 金属氧化

物簇随机分布在载体的孔通道内, 有利于反应副产物的吸附和传质, 同时提高了臭氧的利用效率。

2.1.4 天然矿物载体催化剂

天然矿物材料相对于金属及金属氧化物而言, 来源广泛易得、无污染、化学性质稳定、具有较高的机械强度。Yuan 等^[28]制备的 $\text{Fe}/\text{浮石}$ 催化剂与 Qu 等^[29]合成的负载 Ce 的海泡石 (Ce/SEP) 催化剂具有中孔结构、较大的表面积和丰富的强酸位点, 有利于臭氧分子在催化剂表面的吸附, 吸附的臭氧分子可以与催化剂表面的羟基反应生成 $\cdot\text{OH}$, 进而促进污染物的去除。此外, 在催化臭氧氧化体系中加入负载 Ce 的天然沸石 (CZ), 15 min 内对污水中的青霉素 G 去除率达到 99.5%^[30]; 加入锰铜氧化物/磁赤铁矿复合材料 ($\text{Mn}_x\text{Cu}_y\text{O}_z/\gamma\text{-Fe}_2\text{O}_3$), 能完全降解氯霉素 (CAP), 证实了过渡金属的掺杂有利于促进臭氧的催化分解^[31]。表 1 列举了几种典型的负载型金属氧化物类催化剂及其性能^[15, 18-19, 21, 26, 31-33]。

2.2 非负载型催化剂

2.2.1 金属和金属氧化物型催化剂

(1) 铁基催化剂

铁基材料有零价铁 (Fe^0) 和氧化铁, 如 Fe_2O_3 、 Fe_3O_4 和 FeOOH 等, 研究^[34]表明 FeOOH 可能是铁

表 1 典型的负载型金属氧化物催化剂的性能

Tab. 1 Performance of Typical Metal Supported Oxide Catalysts

催化剂	污染物	试验条件	催化性能	参考文献
NiO/Al ₂ O ₃	TCP	[TCP] ₀ = 75 mg/L, pH 值 = 4.0, t = 40 min, [NiO/Al ₂ O ₃] = 5 g/L	去除率为 94.4%, 反应速率可达单独臭氧的 1.76 倍; 重复使用 3 次后去除率略有下降, 仍优于单独臭氧氧化	[15]
PdO/CeO ₂	丙酮酸(PA)	[PA] ₀ = 5 mg/L, pH 值 = 4.7, t = 5 min, Pd 负载量为 4%	PA 被完全降解; 催化剂表现出高结构稳定性	[18]
Co/Al ₂ O ₃	PA	[PA] ₀ = 88 mg/L, pH 值 = 2.5, [臭氧] = 40 mg/L, t = 120 min, 40 g 的催化剂床	PA 去除率为 98.9%, DOC 去除率为 90.2%; Co 的浸出百分比很低, 催化剂性能稳定	[32]
Fe ₃ O ₄ /Co ₃ O ₄	磺胺甲恶唑(SMX)	[SMX] ₀ = 20 mg/L, pH 值 = 5.1, 臭氧流速 = 0.30 L/min, t = 60 min, [Fe ₃ O ₄ /Co ₃ O ₄] = 0.10 g/L	TOC 去除率为 60.0%, 较单独臭氧提高 44.0%, 臭氧利用率提高	[19]
CeO ₂ /MWCNT、CeO ₂ /AC	SMX	[SMX] ₀ = 50 mg/L, [催化剂] = 0.14 g/L, pH 值 = 4.8, t = 180 min, [臭氧] = 50 mg/L	TOC 去除率: CeO ₂ /MWCNT 为 56.0%; CeO ₂ /AC 为 73.0%	[33]
Mn _x Fe _y O _z /AC	SMZ	Fe : Mn = 1 : 11.2, [SMZ] ₀ = 10 mg/L, 臭氧流速 = 0.05 L/min, [Mn _x Fe _y O _z /AC] = 0.05 g/L, pH 值 = 6.1, t = 8 min	TOC 去除率为 90.5%, 降解速率显著提高; 使用 5 次后 TOC 去除率降低至 77.5%	[21]
CeO _x /SBA-16	双酚 A(BPA)	[BPA] ₀ = 0.01 mg/L, pH 值 = 6.2, [CeO _x /SBA-16] = 0.20 g/L, t = 90 min, Ce 负载量为 3%	TOC 去除率为 69.0%, 较单独臭氧提高 2 倍	[26]
Mn _x Cu _y O _z /γ-Fe ₂ O ₃	CAP	[CAP] ₀ = 10 mg/L, [Mn _x Cu _y O _z /γ-Fe ₂ O ₃] = 0.20 g/L, [臭氧] = 10 mg/L, pH 值 = 7.0, t = 30 min	CAP 被完全降解, 约为单独臭氧处理的 2.22 倍; 可通过外部磁体将催化剂从溶液中分离, 循环利用后催化性能稳定	[31]

基材料主要的有效成分。Wang 等^[35]发现通过溶解的铁离子沉淀形成的 γ-FeOOH 是催化剂的主要成分, 且 Fe⁰ 在低 pH 下可以活化氧生成 H₂O₂, 随着 Fe²⁺ 的离子释放发生内芬顿反应。Li 等^[36]使用改性铁屑为催化剂, 将焦化废水的 TOC 去除率提升至 78.0%, 并发现催化臭氧氧化中小分子有机酸的积累仅为单独臭氧氧化的一半。同样地, Wang 等^[37]使用铁屑基催化剂将苯甲酸的 TOC 去除率提高到 90% 以上。Lin 等^[38]通过引 Cr³⁺ 以促进铁屑上致密的 α-Fe(Cr³⁺)OOH 膜形成, 达到出色的稳定性和高催化性能。Yan 等^[39]和 Lü 等^[40]分别制备了 Si 掺杂的 α-Fe₂O₃ 及 Co、Mn 掺杂的 γ-Fe₂O₃, 发现掺杂后的催化剂表面存在较多的路易斯酸位点, 能促进臭氧吸附-解吸, 产生更多的表面羟基从而提高污染物去除率。Zhu 等^[41]采用纳米铸造工艺制备有序介孔材料(om-Fe₃O₄), 对阿特拉津去除率可达 82.0%, om-Fe₃O₄ 的总孔容远高于纳米 Fe₃O₄, 利于污染物的吸附和传质, Fe²⁺/Fe³⁺ 的氧化还原循环是产生 ·OH 的原因。Wang 等^[42]采用不同的前驱体

(硝酸铁、氯化铁、硫酸铁) 制备 FeOOH 催化臭氧氧化降解布洛芬(ibu), 发现 FeOOH 的粒径越小, 表面羟基的浓度越大, 催化效率越高。

(2) 锰基催化剂

MnO₂ 是气相臭氧分解最有效的催化剂^[43], 近年来也在多相催化中应用广泛。例如, Zhang 等^[44]制备的无定形介孔锰氧化物 MnO_x-Cl 与 Li 等^[45]用含锰尖晶石通过选择性酸蚀制备的 α-MnO₂, 都证实催化剂表面含有丰富的氧空位能促进臭氧的吸附和活化, 产生更多活性物种, 如 ·OH、O₂⁻、单线态氧(¹O₂)、表面氧原子等, 可促进污染物降解。Nawaz 等^[46]合成了六相(α-、β-、δ-、γ-、λ-和 ε-) MnO₂ 降解 4-硝基苯酚(4-NP), 其中 α-MnO₂ 展现出最佳效果, 研究发现具有低平均氧化态的 MnO₂ 晶体上具有更强的氧化/还原峰, 利于臭氧催化分解产生活性物质。

(3) 铝基催化剂

铝基材料包含了 γ-AlOOH、γ-Al₂O₃ 和 α-Al₂O₃ 等。Keykavoos 等^[47]发现较小粒径或较高剂量的氧

化铝催化剂可以提高 BPA 的矿化速率。Qi 等^[48]以 γ -AlOOH (HAO)、 γ -Al₂O₃ (RAO) 为催化剂催化臭氧氧化降解 2-甲基异茨醇 (2-MIB), RAO 存在下 2-MIB 的去除率为 98.4%, HAO 仅为 27.5%, 认为 RAO 催化臭氧法以 \cdot OH 反应为主, HAO 则以固体表面反应为主, 两者都可以增强臭氧分解, 但 HAO 表面羟基覆盖率较高, 对 2-MIB 的吸附更强, 从而抑制了 \cdot OH 的生成。然而 Qi 等^[49]在降解 2,4,6-三氯苯甲醚 (TCA) 时发现, HAO 的活性优于 RAO, 认为氧化铝上的表面羟基是催化臭氧氧化的活性位点, HAO 的表面羟基密度高, 催化效果更好。

(4) 其他金属氧化物

其他金属氧化物包含 CuO、MgO、CeO₂、TiO₂、ZnO、Co₃O₄ 等和双/多金属复合氧化物。Turkay 等^[50]用 CuO 催化臭氧氧化降解腐植酸 (HA), 证实催

化臭氧氧化的机理是臭氧与催化剂之间的表面反应。Zhang 等^[51]合成了介孔 CeO₂, 将苯酚的去除率从 51.6% (仅臭氧) 提高至 91.7%, 此外, 催化臭氧氧化降解苯酚的活化能 (20.7 kJ/mol) 远低于单臭氧氧化 (54.7 kJ/mol)。Yang 等^[52]采用溶胶-凝胶法制备了纳米 TiO₂, 结果表明, TiO₂ 的存在会加速 \cdot OH 的产生, 能显著提高硝基苯 (NB) 的去除效率。Chokshi 等^[53]用共沉淀法制备了 Ag-La-Co 纳米复合金属氧化物, 对活性黑 5 (RB5) 染料的 TOC 去除率为 95%, 较单独臭氧氧化提高了 62%, 且有良好的稳定性。Wang 等^[54]制备了双金属氧化物 Cu_{0.2}MnO_x, 在最佳条件下甲苯去除率可达到 85%, 研究发现 Cu 在催化臭氧氧化中起吸附和氧化短链产物的作用, Mn 起开键作用。表 2 列举了几种典型的金属氧化物催化剂及其催化性能。

表 2 典型的金属氧化物催化剂的性能
Tab. 2 Performance of Typical Metal Oxide Catalysts

催化剂	污染物	试验条件	催化性能	参考文献
改性铁屑	焦化废水	[铁基催化剂] = 200 g/L, pH 值 = 6.8, t = 180 min	TOC 去除率为 78.7%, 较单独臭氧氧化提高 47.1%; 重复利用 50 次仍效果良好, 稳定性和可重复使用性优异	[55]
γ -Fe ₂ O ₃	2,4-二氯苯氧乙酸 (2,4-D)	[2,4-D] ₀ = 20 mg/L, [γ -Fe ₂ O ₃] = 1.0 g/L, [臭氧] = 30 mg/L, pH 值 = 6.0, t = 40 min	TOC 去除率为 93.0%	[40]
α -MnO ₂	4-NP	[4-NP] ₀ = 50 mg/L, [α -MnO ₂] = 0.10 g/L, pH 值 = 7.0, t = 45 min	4-NP 去除率为 99.3%, TOC 去除率为 82.4%; 重复利用 4 次后去除率下降, 试验后水溶液中 Mn ²⁺ 质量浓度为 0.1 mg/L	[46]
CeO ₂	对硝基苯酚 (PNP)	[PNP] ₀ = 25 mg/L, [CeO ₂] = 0.40 g/L, pH 值 = 5.7, t = 70 min	TOC 去除率为 86.0%	[56]
Al ₂ O ₃	BPA	[BPA] ₀ = 0.01 mg/L, [臭氧] = 0.004 5 mg/L, [Al ₂ O ₃] = 1.0 g/L, pH 值 = 5.0, t = 60 min	TOC 去除率为 90.0%; 重复使用 3 次, 催化剂仍保持活性	[47]
Fe ₃ O ₄ -MnO ₂ 磁性复合材料	BPA	[BPA] ₀ = 0.05 mg/L, [催化剂] = 0.10 g/L, 臭氧流速 = 0.10 L/min, pH 值 = 7.0, t = 30 min	TOC 去除率为 97.0%; 催化性能稳定, Mn 与 Fe 仅有很少量的浸出	[57]
MgO	喹啉	[喹啉] ₀ = 20 mg/L, [臭氧] = 2.0 mg/L, [MgO] = 0.20 g/L, pH 值 = 6.8, t = 15 min	TOC 去除率为 90.7%	[58]
MgO	4-氯苯酚 (4-CP)	[4-CP] ₀ = 100 mg/L, [MgO] = 1.0 g/L, pH 值 = 6.2, t = 30 min	4-CP 去除率为 95.1%, TOC 去除率为 94.8%; 催化剂稳定性良好, 5 次重复利用后催化活性没有明显影响	[59]
Ag-La-Co 复合金属氧化物	RB5	[RB5] ₀ = 100 mg/L, pH 值 = 7.0, [催化剂] = 0.50 g/L, 臭氧流速 = 0.5 L/min, t = 80 min	TOC 去除率为 95%; 重复利用后催化活性保持不变, 稳定性良好	[53]

2.2.2 非金属型催化剂

非金属催化剂主要有碳基材料、新型纳米材料和天然矿物材料。常见的碳材料载体有 AC、GO 和

碳纳米管 (CNTs) 等。Wang 等^[60]合成了具有低缺陷/无序水平的还原氧化石墨烯 (rGO), 发现无金属 rGO 材料在活化臭氧以催化氧化有机酚类物质方面

表现出优异的活性,表面的羰基是主要活性位点。Song 等^[61]制备了磁核壳 $Fe_3O_4@SiO_2@La_2O_3$ 纳米催化剂,该催化剂呈现以 Fe_3O_4 为核、 SiO_2 为中间层、 La_2O_3 为外层的核壳结构,能极大地促进 $\cdot OH$ 的生成,对肉桂醇的去除和有机物矿化方面有明显改善。Zhang 等^[62]采用浸渍法制备 Cu 改性 SEP (Cu-

SEP), Cu 元素取代了 SEP 晶格中的 Mg 形成 Cu-SEP,最佳条件下对草酸的去除率可达 95.8%。Qi 等^[63]用原铝土矿(主要成分为 $\gamma-AlOOH$)作为催化剂结合臭氧氧化降解 TCA,去除率可达 86.0%,高于单独臭氧氧化(34.6%)。表 3 列举了几种典型的碳材料催化剂催化臭氧氧化水中有机物的效果。

表 3 典型的碳材料催化剂及其性能

Tab. 3 Performance of Typical Carbon Material Catalysts

催化剂	污染物	试验条件	催化性能	参考文献
AC	二甲酯(DMP)	[DMP] ₀ = 20 mg/L, [臭氧] = 30 mg/L, [AC] = 5.0 g/L, pH 值 = 7.0, T = 25 °C, t = 100 min	DMP 去除率为 61.2%	[64]
rGO	对羟基苯甲酸 (PHBA)	[PHBA] ₀ = 20 mg/L, [臭氧] = 20 mg/L, [催化剂] = 0.05 g/L, pH 值 = 3.5, t = 30 min	PHBA 被完全去除, TOC 去除率从 25.0% 提高到 95.0%; 循环使用催化剂失活, 原因为比表面积的损失和表面化学的变化	[60]
rGO、杂原子 (N、P) 掺杂的氧化石墨烯 (NGO、PGO)	SMX	[SMX] ₀ = 50 mg/L, [催化剂] = 1.0 g/L, T = 25 °C, pH 值 = 9.0, t = 5 min	SMX 的降解率分别为 83%、95%、99%; 稳定性良好, 可在热退火处理后长期重复使用	[65]
CNT	4-硝基苯甲醛 (4-NBA)	[4-NBA] ₀ = 0.08 mg/L, [催化剂] = 0.50 g/L, [臭氧] = 50 mg/L, t = 180 min	TOC 去除率为 60.0%, 提高了 4-NBA 降解速率; 循环利用 5 次后, TOC 的去除率下降 15.0%	[66]

3 催化剂在催化臭氧工艺中工程中的应用——与反应器相结合

催化剂与反应器结合可以显著提高催化臭氧氧化的效率,反应时间更短,且能降低运营和维护成本^[67]。Qu 等^[68]将活性炭纤维 (ACF) 与流化床反应器相结合,发现 30 min 内苯酚几乎被完全去除。同样地, Moussavi 等^[69]证实了流化床反应器能增强

气、液、固三相传质,从而提高污染物的降解速率。Mei 等^[70]采用了一种将陶瓷膜反应器与加压臭氧氧化工艺相结合的新型气升式反应器,采用平均孔径为 5.5 nm 的 TiO_2 超滤膜,与常规气升式反应器相比,该体系对于 HA 的 COD_{Cr} 和 TOC 的去除率均有显著提高。表 4 列举了几种催化剂与反应器相结合

表 4 催化剂与反应器相结合典型体系

Tab. 4 Typical Systems of Combined Catalysts and Reactors

催化臭氧体系	反应器	反应条件	催化性能	参考文献
催化剂: $CuMn_2O_4/g-C_3N$ 污染物: 二苯甲酮-4 (BP-4)	膜反应器	[臭氧] = 20 mg/L, [催化剂] = 0.25 g/L, pH 值 = 6.4, t = 30 min	BP-4 降解反应速率常数是单独臭氧氧化的 3 倍, 一级动力学常数为 0.3878 min^{-1}	[71]
催化剂: Mn^{2+} 、 Fe^{2+} 、 Fe^{3+} 、 Zn^{2+} 、 Co^{2+} 、 Ni^{2+} 污染物: 活性红 2 (RR2)	气泡塔反应器	[RR2] ₀ = 100 mg/L, 臭氧流速 = 0.20 L/min, pH 值 = 2.0, [金属离子] = 0.60 mmol/L, t = 5.38 min	提高了臭氧在 RR2 脱色中的效率, 臭氧/ Mn^{2+} 体系表现出最高的脱色率和 TOC 去除率; 各类催化剂的一级脱色速率常数分别为 3.295、1.299、1.278、1.015、0.843、0.822 min^{-1}	[72]
催化剂: $FeOOH$ 污染物: 咖啡因	浮选槽反应器	[咖啡因] ₀ = 30 mg/L, [FeOOH] = 0.80 g/L, [臭氧] = 10 mg/L, pH 值 = 7.0, t = 20 min	20 min 内可实现 57.0% 的咖啡因完全降解和矿化	[73]
催化剂: 沸石 污染物: IBU	半间歇式反应器	[IBU] ₀ = 10 mg/L, T = 25 °C, t = 240 min, 搅拌速度 = 1 070 r/min	4 h 内实现约 93.0% 的 IBU 降解, 且 IBU 的降解速率显著提高	[74]
催化剂: 改性铁屑 污染物: 印染废水 (BTDW); 造纸废水 (BTPW)	间歇式反应器	[铁基催化剂] = 200 g/L, t = 180 min	TOC 去除率: BTDW 为 39.2%, BTPW 为 63.5%; COD_{Cr} 去除率较单独臭氧氧化提高了 10.7% (BTPW) 和 13.2% (BTDW)	[75]

4 总结与展望

催化臭氧氧化法是一种非常有前景的新型 AOP,非均相催化剂的引入使得臭氧利用率和污染物去除率得到显著提高。随着研究不断深入,许多高效的催化剂被应用在各种难降解废水深度处理工艺中。催化臭氧氧化法的机理国内外已有很多报道,目前受到广泛认可的是自由基理论,对其他机理的研究尚不深入,且未有充分理论证明臭氧分子、污染物分子和水分子如何吸附在催化剂表面,以及水分子与臭氧分子的吸附具有怎样的竞争关系,也未证明不同过渡金属 3d 电子排布与水分子吸附能的强弱关系对有机物降解是否有显著影响。

目前还需要在以下方面进行突破:(1)负载型催化剂比表面积大、活性高、催化效果好,但活性成分与载体结合力较弱,在反应过程中易流失并造成二次污染,值得进一步研究;(2)为了追求较高的催化活性,研究所用的催化剂多为粉末或纳米形态,难以广泛应用在实际废水处理中;(3)研究采用的模拟废水多为配制而成,成分较实际废水简单得多,需加强实际废水中各种成分对于催化臭氧氧化法的影响研究;(4)需开发更稳定、高效、环保的新型催化剂,完善催化剂制备方法,提高催化剂的使用寿命;(5)催化剂与反应器相结合可有效提高臭氧传质效率与污染物去除率并降低处理成本。在传统反应器基础上进行改进,或设计新型高效稳定的反应器以实现大规模推广,是环保和水处理领域今后重要的研究方向。

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