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烟气中氯代芳构化合物催化氧化的研究进展*

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摘要 焚烧是固体废物处理的重要方式, 但由此产生的烟气中含有氯代芳构化合物 (chlorinated aromatic hydrocarbons, CAHs), 对环境和健康构成威胁. 催化氧化技术因其高去除率、低能耗、低二次污染等优点被认为是去除烟气中 CAHs 最有效的方法之一. 本文系统介绍了常见的催化剂种类, 包括贵金属催化剂、过渡金属氧化物催化剂和分子筛催化剂, 并比较了它们的优缺点. 同时, 深入探讨了催化氧化反应的机制、催化剂失活原因和再生方法, 并强调了催化剂的组分、载体、结构和制备方法对催化剂活性的重要影响. 最后, 根据文献研究, 对 CAHs 的催化氧化进行了展望. 未来研究应进一步优化催化剂设计, 提高反应效率, 并将其应用于实际焚烧烟气治理.

关键词 催化氧化, 氯代芳构化合物 (CAHs), 催化剂, 催化氧化机制, 催化失活.

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Research progress on the catalytic oxidation of chlorinated aromatic hydrocarbons in flue gas

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Abstract Incineration is an important method for solid waste treatment, but the resulting flue gas contains Chlorinated aromatic hydrocarbons (CAHs), which pose a threat to both the environment and human health. Catalytic oxidation technology is recognized as one of the most effective methods for removing CAHs due to its high removal rate, low energy consumption, and minimal secondary pollution. This paper systematically introduces common catalyst types, including noble metal catalysts, transition metal oxide catalysts, and molecular sieve catalysts, and compares their respective advantages and drawbacks. Furthermore, the mechanism of catalytic oxidation reactions, causes of catalyst deactivation, and regeneration methods are discussed, with an emphasis on the significant impact of catalyst components, structures, supports, and preparation methods on catalyst activity. Finally, based on existing research, the prospects of catalytic oxidation of CAHs are examined. Future research should focus on optimizing catalyst design, enhancing reaction efficiency,

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and applying the technique to the practical treatment of incineration flue gas.

Keywords catalytic oxidation, chlorinated aromatic hydrocarbons (CAHs), catalyst, catalytic oxidation mechanism, catalyst deactivation.

氯代芳构化合物(chlorinated aromatic hydrocarbons, CAHs)是一类芳香族化合物,其特征在于苯环上的一个或多个氢原子被氯原子所取代.它们在药物生产、汽车尾气以及工业热过程中产生或释放,是一类众所周知的有毒物质.大部分的CAHs因其高毒性、生物累积性、远距离迁移性和难降解而被认定为持久性有机污染物(persistent organic pollutants, POPs),包括多氯联苯(polychlorinated biphenyls, PCBs),多氯萘(polychlorinated naphthalenes, PCNs)和二恶英(polychlorinated dibenzo-*p*-dioxins and dibenzofurans, PCDD/Fs),六氯苯(hexachlorobenzene, HCB)和五氯苯(pentachlorobenzene, PeCB)等.含有三个或更多稠环芳香环的氯代多环芳烃(chlorinated polycyclic aromatic hydrocarbons, Cl-PAHs)也被证实具有强烈的毒性和致癌突变特性,因此被认为是潜在 POPs^[1].许多研究表明,焚烧过程中产生的烟气中含有大量CAHs,是空气中的CAHs的主要来源^[2].其中,多氯联苯的生成量与二恶英相当,多氯萘和氯代多环芳烃的生成量总和至少比二恶英高2—3个数量级,氯苯、氯酚类的含量通常比二恶英高3—6个数量级^[3].

焚烧过程包括垃圾焚烧、工业固体废弃物焚烧、医疗废物焚烧、燃煤、燃气等人类生产工艺.在焚烧过程中,烟气环境的特性会显著影响CAHs的生成和去除.这些特性主要由焚烧过程中的各项参数,如温度、氧浓度以及原料的化学组成,特别是氯和有机物的含量等决定.当处于高温并有氯源存在时,原始材料(例如废弃物)中的有机物通过热解和氯化反应能生成大量的CAHs^[4].目前,人们开发了多种破坏CAHs的方法,如电化学法^[5]、生物降解法^[6-7]、光催化法^[8]、吸附法^[9]、超临界水氧化法^[10]、热解法^[11]及催化氧化法等.其中,催化氧化技术备受关注,并取得了一定的研究成果.催化氧化技术具有反应条件温和、能耗低、效率高、无二次污染、适用范围广等优点^[12-14].本文综述了近年来在焚烧源中氯代芳构化合物催化氧化领域取得的研究成果,主要涵盖催化剂、催化氧化机制、催化剂失活与再生等方面的内容.

1 催化剂(Catalyst)

催化氧化技术的关键在于筛选和制备具有高活性、高稳定性和高选择性的催化剂.催化剂的活性受到催化剂结构和反应底物特性的影响.同时,催化剂需要高稳定性以防止反应产物、特别是副产物毒化催化中心.对于脱氯反应,催化剂的高选择性可以避免产生大量非目标产物或毒性更大的化合物.催化氧化技术中,常用的催化剂包括贵金属催化剂、过渡金属催化剂、分子筛催化剂.然而,单一催化剂在应用中常面临效率低下和易中毒失活等问题.为了优化这些局限性,研究人员通常会通过掺杂其他金属元素或利用分子筛来提升催化剂的反应活性.总之,催化剂的开发和改进在催化氧化技术中持续扮演着关键角色,同时也面临着诸多挑战.

1.1 贵金属催化剂

贵金属催化剂,如铂(Pt)、钌(Ru)、钯(Pd)等,广泛应用于各类化学反应中,以其高活性、长使用寿命、高选择性和优异的抗毒性能著称.表1对比了近年来贵金属催化剂在催化氧化CAHs中的应用研究.值得注意的是,Ru作为最经济实惠的贵金属催化剂,其催化活性超过了其他贵金属,并且作为迪肯反应的高效催化剂,能有效去除催化剂表面的反应性氯离子物种^[15].

为了进一步提高催化效率和稳定性,研究者尝试将贵金属掺杂于过渡金属氧化物中或负载在分子筛上.例如,Wang等^[16]将Ru负载在介孔Fe-Mn氧化物上,成功提高了其催化活性,并发现Ru-O-Mn和Ru-O-Fe分别增加了还原性、表面吸附氧和氧空位的产生,提供了更多的催化活性位点以及更好的反应物扩散条件.Cano等^[17]利用分子筛作为载体,制备了Pd/Co-HMOR和Pd/Co-SZ催化剂,研究其对1,2-二氯苯(*o*-DCB)的催化降解活性.实验结果显示,Pd/Co-HMOR和Pd/Co-SZ在500℃和550℃表现出最高活性,而在250—400℃的温度范围内,Pd/Co-SZ的催化活性更为突出.XAFS进一步揭示了Pd和Co可在HMOR上形成的高度分散的催化剂活性中心.这些研究结果均验证了选择合适的载体能显著提高催化剂的活性和稳定性.

表 1 贵金属催化剂用于催化氧化 CAHs 的研究

Table 1 Research on noble metal catalysts for catalytic oxidation of CAHs

催化剂 Catalysts	CAHs 污染物 CAHs pollutants	转化温度/°C Conversion temperature	转化率/% Conversion efficiency	参考文献 References
Ru/TiO ₂		287	90	[15]
Ru/Fe1Mn2		197	90	[16]
钌基催化剂	Ru-CeO ₂ , Ru/CeO ₂ -r	250—280	90	[21—22]
	0.4Ru-1.0Ce/TiO ₂ , Ru/Ti-CeO ₂	180—250	90—95	[18, 23]
	Ru/TiCeO _x	305	90	[20]
铂基催化剂	Pt/γ-Al ₂ O ₃	210—225	50	[24—25]
	2Pt- Al-PILC	321	50	[26]
	PtHFAU(5)	350	95	[27]
	Pt/CeO-ZrO ₂	350	97	[28]
	Pt-110Mn	290	90	[19]
钯基催化剂	Pd/Co-HMOR	500	100	[17]

催化剂性能的优化也与助催化剂的选择有着密切关系. 例如, 向 Ru/TiO₂ 催化剂中添加 CeO₂, 不仅可以提高贵金属的活性和分散性, 还可以提高 CO_x 的产率和无机氯的选择性, 同时降低有毒二恶英的生成^[18]. 此外, 催化剂的晶面选择对催化活性同样有重要影响. 例如, Pt/Mo 负载于 3 种晶面的 MnO₂ 纳米棒中, 不同 MnO₂ 晶面催化活性不同, 而 Pt 和 Mo 的负载和修饰也有利于活性、多功能性及耐久性的提高^[19]. 除此之外, 催化剂抗水性也会影响其催化活性. Wu 等^[20] 发现具有疏水性的 Ru/TiCeO_x 催化剂对 *o*-DCB 具有良好降解效果, 因为水分子占据催化剂表面氧空位从而降低了活性中心利用率. 总之, 催化剂载体、助催化剂、晶面的选择以及抗水性都是影响催化性能的关键因素, 综合利用这些策略可以显著提升贵金属的活性和稳定性.

1.2 过渡金属氧化物催化剂

过渡金属氧化物催化剂因其成本低、资源丰富和良好活性的特性, 被视为贵金属催化剂的理想替代品. 常见的过渡金属氧化物催化剂包括铈(Ce)、钛(Ti)、钒(V)、铬(Cr)、锰(Mn)、铜(Cu)等金属氧化物及其复合氧化物. 表 2 比较了近年来过渡金属氧化物催化剂用于催化氧化 CAHs 的研究. 研究人员通过引入不同的过渡金属以优化催化剂结构以提高其活性. 例如, 将 Mn 与 Co₃O₄ 尖晶石结构相结合, 可以提高 *o*-DCB 和 CHCl₃ 的降解率, 这是由于 Mn 增加了尖晶石的分散度和 Co²⁺ 浓度, 提高表面活性氧的氧迁移率^[29]. Ce-Zr 共改性的锰基氧化物催化剂的活性明显高于单一锰基催化剂, 这归因于比表面积的增加、Mn⁴⁺ 阳离子和表面氧化物数量的增加, 以及由 Ce-Zr 改性引起的氧迁移率和锰还原性的增强^[30]. WO_x/CeO₂ 催化剂在 CB 和 *o*-DCB 催化活性测试中表现出色, 这取决于 W 含量, WO_x 和 CeO₂ 之间的相互作用形成的 W-O-Ce 增加了氧空位, 从而促进了催化剂的还原性和酸性, 在 350 °C 下, 两种污染物的降解率均超过 90%^[31]. 以 Co 基氧化物为基底制备了 Co/M = 3 (M = Al、Fe、Cr) 的催化剂, 添加第二种金属能增强了催化剂的酸性和碱性位点的活性, Cr 或 Fe 的添加还提高了原始 Co₃O₄ 在低温下的表观活性, 并有效抑制了多氯代副产物的形成^[32].

表 2 过渡金属氧化物催化剂用于催化氧化 CAHs 的研究

Table 2 Research on transition metal catalysts for catalytic oxidation of CAHs

催化剂 Catalysts	CAHs 污染物 CAHs pollutants	转化温度/°C Conversion temperature	转化率/% Conversion efficiency	参考文献 References
VO _x /CeO ₂		307—325	90	[36, 38]
HSiW/CeO ₂		283	90	[39]
铈基催化剂	MnOx-CeO ₂ , CuO-MnO _x -CeO ₂	236—336	90—100	[40—45]
	ACeO _x (A = Co, Cu, Fe, Mn, Zr)	328	99	[46]
	2.4W/CeO ₂	CB/ <i>o</i> -DCB	339	90

续表 2

	催化剂 Catalysts	CAHs污染物 CAHs pollutants	转化温度/°C Conversion temperature	转化率/% Conversion efficiency	参考文献 References
铈基催化剂	Co ₃ O ₄ -CeO ₂	1,2,4-TCB	300	96	[47]
	Fe _x O _y -CeO ₂	HCB	300	100	[48]
钛基催化剂	V ₂ O ₅ /TiO ₂ , TiV10, TiV10Mo, TiV10W, V ₂ O ₅ -WO _x /TiO ₂		247—300	50—100	[49—53]
	CeMn/Ti-400, Ce _{0.5} Ti _{0.5}	CB	198—375	90	[54—55]
	MnO _x /TiO ₂		150—296	90—95	[56—57]
	V ₂ O ₅ /TiO ₂ , V ₂ O ₅ /TiO ₂ -SiO ₂		200—400	80—100	[58—65]
	Cr _{0.1} Ti _{0.9}	DCB	304	95	[66]
	MnCe/Ti		275	100	[67]
钛基催化剂	V ₂ O ₅ /TiO ₂	1,3,5-TCB, 1,2,3,4- TeCB, PeCB, HCB, 2,3-DCDD, 2-MCDD	300—400	25—85	[49, 58]
	V ₂ O ₅ -TiO ₂ , V ₂ O ₅ -WO ₃ /TiO ₂ , Ce-V _x O _y /TiO ₂ , V ₂ O ₅ -CeO ₂ /TiO ₂	PCDD/Fs	180—280	73—98	[68—74]
	V ₂ O ₅ -WO ₃ /TiO ₂	PCBs	300	98	[75]
	Fe1Mn1		197	90	[34]
锰基催化剂	CM-R		388	90	[37]
	LaMnO ₃ , La _{0.8} Sr _{0.2} MnO ₃ , La _{0.8} MnO ₃	CB	291—410	90	[76]
	30Cu/MnO _x		290	90	[77]
	Co9Mn1	o-DCB	347	90	[29]
	CuO/Mn _x O _y		230	80	[78]
	Mn-Ce-Mg/Al ₂ O ₃	HCB	315	90	[79]
	Mn _x Ce _y /Al ₂ O ₃		338	100	[80]
	LaMn _{0.8} Fe _{0.2} O ₃	CB	500	90	[76]
铁基催化剂	Mn-Ce-Fe		350	98	[81]
	CaCO ₃ /α-Fe ₂ O ₃	DCB	450	100	[82]
	CaO/α-Fe ₂ O ₃		300	99	[83—84]
	Fe _x O _y	HCB	300	100	[85]
	MgFe ₂ O ₄ /Fe ₃ O ₄		300	100	[86]
	NiFe ₂ O ₄	PCBs	300	96	[87]
	Mn-Ce-Zr		326	90	[30]
其他催化剂	CoCr		242	90	[32]
	LaMn _{0.8} Al _{0.2} O ₃		380	90	[76]
	Mn(x)-CeLa		229—279	90	[35, 88]
	CrCe/Ti-PILC, CrCe(5:1)/AlFe-PILC, MnCe(9:1) /AlZr-PILC	CB	250—290	100	[89—91]
	Mn-Co-Ce-cordierite		325	90	[92]
	WO ₃ -Nb ₂ O ₅		350	90	[93]
	Co ₃ O ₄ -A		310	90	[94]
	V ₂ O ₅ /TiO ₂ -CNTs, MnO _x /TiO ₂ -CNTs, CuO _x /CNTs	CB, DCB, PCDD/Fs	150—320	78—95	[95—98]
	CeSn/Ti ₆ Zr ₄ O _x		343	90	[33]
	15CM/Ts-1.5	o-DCB	360	100	[99]
	Fe/AC	PCBs	350	100	[100]
CuAl ₂ O ₄ , Cu _x Mg _{1-x} Al ₂ O ₄	HCB, OCDD	300—350	85—99	[101—102]	
γ-Al ₂ O ₃ , La ₂ O ₃ (MgO, CaO, BaO, La ₂ O ₃ , CeO ₂ , MnO ₂ , Fe ₂ O ₃ , Co ₃ O ₄)/Al ₂ O ₃	HCB	300	30—100	[103—104]	

催化剂的制备方法和金属元素的配比也会影响催化剂的活性. Wu 等^[33]通过浸渍法调节 Ti/Zr 物质的量比制备了一系列有序介孔催化剂 $\text{CeSn/Ti}_z\text{Zr}_{10-z}\text{O}_x$, 催化性能随 Zr 含量呈现先增后降的趋势, 其中 $\text{CeSn/Ti}_6\text{Zr}_4\text{O}_x$ 催化性能最佳. Wang 等^[34]采用无模板草酸盐法合成多孔 Fe-Mn 氧化物催化剂发现, 当 Fe/Mn 为 1:1 时, 催化剂对 CB 催化活性和选择性也更高, 这归因于 Fe 和 Mn 间的强烈相互作用使催化剂表面富集 Mn^{4+} . Dai 等^[35]通过溶胶-凝胶法制备 $\text{Mn}(x)\text{-CeLa}$ 混合氧化物催化剂, 高 $\text{Mn}/(\text{Mn} + \text{Ce} + \text{La})$ 比率的催化剂表现出高稳定性活性, 其中, $\text{Mn}(0.86)\text{-CeLa}$ 催化剂的活性最高. Huang 等^[36]用湿法浸渍法制备了不同负载量 VO_x 的 VO_x/CeO_2 催化剂, 发现 VO_x 的加入显著提高了催化活性和稳定性.

此外, 催化剂的形貌也被证明对 CAHs 的降解具有重要影响. Wang 等^[37]证实了 3 种形态的 Ce-Mn 催化剂(纳米片、纳米颗粒和纳米棒)对 CB 的氧化活性存在显著差异, 纳米片催化剂活性最高, 可能因其层状结构及高氧空位和 Ce^{3+} 含量增强了含氯物种的吸附. 另外, Shi 等^[38]制备了多种纳米结构的 VO_x/CeO_2 催化剂, 发现纳米棒催化剂活性最强, 可能源于其结构和表面特性变化增加了 S_{BET} 和 O_{β}/O_{α} 比率, 以及通过形成新相 CeVO_4 和增加 Ce^{3+} 来增加氧空位, 从而提高氧迁移率和活性表面氧.

这些研究表明, 优化催化剂的性能涉及多方面的调整, 包括组成、结构设计、制备方法、元素配比及形态调整. 这些改变能提高催化剂的适应性以及应对多样的环境问题, 并在处理 CAHs 污染物方面表现出更高的效率和效果.

1.3 分子筛催化剂

分子筛, 一种由无机氧化物构成的多孔晶体, 具有特定的微孔结构和化学成分, 能够在化学反应中充当催化剂. 除了优秀的热稳定性外, 分子筛具有较大比表面积并含有大量的酸性位点. 然而, 研究发现, 分子筛在应用于催化氧化 CAHs 反应时, 相较于贵金属和过渡金属氧化物催化剂并无明显优势. 因此, 研究人员通常采用分子筛作为载体, 制备金属型复合催化剂以降解 CAHs. 这一过程中, 分子筛与活性组分之间的协同作用能够提升催化效率和稳定性. 其中, 分子筛载体上丰富的酸性位点有助于吸附和脱氯 CAHs, 活性中心则通常具有出色的氧化能力, 可以促进 CAHs 及其副产物的氧化. 表 3 列出了近年分子筛催化剂用于催化氧化 CAHs 的研究.

表 3 分子筛催化剂用于催化氧化 CAHs 的研究

Table 3 Research on molecular sieve metal catalysts for catalytic oxidation of CAHs

催化剂 Catalysts	CAHs 污染物 CAHs pollutants	转化温度/ $^{\circ}\text{C}$ Conversion temperature	转化率/% Conversion efficiency	参考文献 References
CuCe(6:1)/MCM-41		262	100	[105]
MnCo(6:1)/MCM-41		270	90	[106]
Mn3/KIT-6		211	90	[107]
Ce3-Co6/HMS	CB	440	90	[108]
$\text{Pt}_{0.5}\text{Ru}_{0.5}/\text{m-HZ}$		234	50	[110]
$\text{Mn}_x\text{Ce}_{1-x}\text{O}_2/\text{HZSM-5}$, $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{HZSM-5}$		230	90	[14, 111]
CNH		222	90	[112]
Pd/ZSM-5(25)	<i>o</i> -DCB	474	90	[109]

复合型分子筛催化剂的催化活性依赖于金属的种类、结构、分散程度及制备方法. Zheng 等^[105]制备的 10% CuCe(6:1)/MCM-41 纳米级催化剂展示了高催化活性和耐久性, 其性能得益于 MCM-41 载体的大孔径和大比表面积, 以及 CeO_2 对 CuO 分散的增强. Cheng 等^[106]研究表明, 物质的量比及负载组分的相互作用影响催化活性, 其制备的 10% MnCo(6:1)/MCM-41 催化剂展现出优异活性. He 等^[107]研究制备多种负载金属的介孔分子筛催化剂, 结果显示分散性、比表面积和还原性是影响催化活性的主要因素. Zhao 等^[108]通过后修饰和直接合成两种途径制备了镧系元素修饰的 Co/HMS 催化剂, 证实了 CeO_2 形成有利于获得精细的 Co_3O_4 晶簇, 外骨架 Ce 修饰催化剂表现出比骨架修饰催化剂更好的催化性能.

另外, 分子筛具有大量酸性位点, 包括 Lewis 和 Brønsted 酸位. 这两种酸位的协同作用有助于提高 CAHs 的降解活性和稳定性^[109-110]. 其中, Lewis 酸位点可以促进晶格氧的活化, 增强氧化还原能力, 有利于有机物的氧化和氯的氧化去除. Brønsted 酸位则能改变 CB 的降解路径, 促使 Cl 离子以 HCl 的形

式释放,从根本上抑制了 Cl_2 的生成,降低了含氯副产物和 Cl_2 的选择性. 在金属复合型分子筛催化剂中,还可以通过分子筛中的 H⁺ 与金属离子交换,调节 Brønsted/Lewis(B/L)比,从而优化催化效果. 值得注意的是, H_2O 与分子筛的相互作用也能显著增加 Lewis 酸度^[14, 111].

总体而言,上述研究强调了分子筛催化剂在降解 CAHs 方面的重要应用潜力. 虽然在某些情况下,分子筛可能无法与贵金属和过渡金属氧化物催化剂竞争,但其与活性组分的协同作用和丰富的酸性位点赋予了它在这个领域的独特优势.

1.4 催化剂载体

催化剂载体在催化反应过程中的作用至关重要,其功能包括支撑和稳定活性组分、提升催化反应效率和选择性,以及降低催化剂成本等. 载体的性能直接影响到催化反应的效率和经济性,通常需要具备高比表面积、优异的化学稳定性、适当的孔径和孔隙度、良好的可控性等特性.

除分子筛外,常见催化剂载体材料还包括氧化铝、硅胶、 TiO_2 、 MgO 等. 载体种类、制备方法以及晶体结构,均能影响载体的性质以及与活性组分之间的相互作用. 因此,深入研究载体材料的性能和结构特征至关重要. Zhao 等^[103]通过调控前体溶液的 $\text{HCl}/(\text{Ti}+\text{Si})$ 物质的量比,制备出具有不同性质的 $\text{CeMn}/\text{TiO}_2\text{-SiO}_2$ 催化剂,相较于纳米 $\text{TiO}_2\text{-SiO}_2$ 为载体的 $\text{CeMn}/\text{TiO}_2\text{-SiO}_2$,其具有更大的比表面积. 载体形态也会影响催化氧化反应效率. Deng 等^[55]发现, Ti 的引入和煅烧温度的差异会影响晶体结构,进而影响催化活性. 特别地,萤石型 $\text{Ce}_{0.9}\text{Ti}_{0.1}$ 显示出基于 Ti 归一化的每平方米速率的最高 TOF. 再如 He 等^[54]研究发现,煅烧温度显著影响 $\text{CeO}_x\text{-MnO}_x/\text{TiO}_2$ 催化剂的活性,低温下煅烧的催化剂表现出较高的活性,这主要是由于 MnCeO_x 固溶体的形成以及氧原子迁移率的提高.

催化剂的载体不仅影响催化反应效率,同时也会影响催化降解副产物的生成. Van 等^[113]对 Pt 在不同载体上对 CB 的催化氧化反应进行了研究,发现载体种类会导致多氯副产物的生成水平和分布有所变化. 研究显示, Pt/ZrO_2 分散度较高(47%),其生成的多氯苯副产物水平较高,而 Pt/SiO_2 的分散度较低(4%),生成的 PhCl_x 较少. 不同的载体可能对 Pt 上发生的反应产生不同的影响,可能是由于其充当吸附在 Pt 颗粒边缘的芳香环的氯源. 另外,载体上的二次反应也可能导致异构体和同系物模式的变化.

2 催化氧化途径和机制(Catalytic oxidation pathway and mechanism)

2.1 反应途径

CAHs 的催化氧化过程可以分为 4 个步骤: 吸附、活化、键断裂($\text{C}-\text{Cl}$ 和 $\text{C}-\text{C}$)、脱附. 即目标有机分子吸附在催化剂的活性位点上,经催化剂表面的氧原子活化发生键断裂,产生一系列降解产物,最后这些产物从催化剂表面脱附并进入反应体系中. 以氯苯和二氯苯在金属氧化物上的催化氧化反应为例^[59, 114],如图 1 所示: 首先,污染物分子通过吸附在活性位点上形成 π -络合物. 然后,氯被亲核氧 [O] 捕获, $\text{C}-\text{Cl}$ 键断裂, [O] 发生亲核取代,形成表面酚盐. 其次,对吸附的部分脱氯物种进行亲电取代,产生邻苯醌(D) (通过表面儿茶酚酸酯(C)形成)或对苯醌(E). 这些物质可以在随后的步骤中进一步反应,形成表面马来酸盐(F)和醋酸盐(G). 亲电取代也可能导致芳香环的键断裂,得到非芳香中间体(B),该中间体快速反应形成表面马来酸盐(F)、醋酸盐(G)和醛(H). 最后,在表面上形成的一些部分氧化产物发生完全氧化反应,生成最终产物 CO 、 CO_2 、 HCl 和 H_2O . 在这过程中, $\text{C}-\text{Cl}$ 键断裂后 Cl 会吸附在氧空位或酸性位,然后在羟基存在下通过生成 HCl 被脱除;同时, HCl 也可通过 Deacon 反应生成作为 Cl_2 . 因此,增加催化剂中羟基的数量将有助于 HCl 的快速脱除. 当大量 Cl 沉积在催化剂表面时,一部分 Cl 会与催化剂形成金属氯化物影响活性,另一部分 Cl 会与 CB 或新生成的中间体结合生成多氯副产物^[107, 115-117].

2.2 反应机制

目前主要由 3 种模型来解释 CAHs 催化氧化机制,即 Langmuir-Hinshelwood(L-H)模型、Eley-Rideal(E-R)模型以及 Mars-van Krevelen(MVK)模型(如图 2). 其中, L-H 模型是基于吸附和脱附原理,如,在贵金属催化剂反应过程中, CAHs 通常被吸附在贵金属位点或酸性位点上,然后与吸附的氧物种发生反应,产生 CO_2 、 H_2O 、 HCl 和其他副产物^[117],在 L-H 机制中,反应速率与吸附能力、表面上反应物之间的相互作用、反应物和产物的解吸能力等因素密切相关,这些因素会影响反应物在催化剂表面上的停留时间和反应的发生速率. E-R 模型类似于 L-H 模型, E-R 机制认为 CAHs 直接与吸附在催化剂

表面的氧物种反应,涉及两个不同的分子反应,一种反应物被吸附在某种物质上,生成一种类似配合物的结构,另一种分子与配合物发生反应,进而得到产物^[118]. E-R 模型中的反应速率取决于吸附的反应物分子的浓度、催化剂表面上的反应活性位点数、反应物分子的解吸速率等因素. MVK 模型,也被称为氧化还原模型,该模型认为氧分子在催化剂表面上与反应物分子发生反应,形成氧化产物. 催化剂表面上的氧空位是反应的活性位点,它们可以吸附反应物分子并与其反应. MVK 模型包含两个步骤:第一步是氧吸附,氧分子通过表面的空位被吸附到催化剂表面上,并与表面上的反应物分子发生反应;第二步是氧解离,已经被吸附的氧分子通过吸收能量而解离,并释放出氧原子,氧原子与表面上的反应物分子发生反应,生成氧化产物. 催化剂表面上的空位会被反应产物占据,因此需要再次吸附氧分子以维持反应的进行. 当催化剂中的氧被不断消耗后,气氛中的氧会不断进入催化剂,对其进行补充,使催化反应得以持续进行. 然而,氧气对晶格氧的补充能力同时又受到催化剂自身被氧化能力的限制. 当气氛中不存在氧时,催化剂表面依然具有一定活性的晶格氧参与催化反应. 一般来说,贵金属的催化氧化更常用两种经典机制来解释,即 L-H 机制和 E-R 机制,分别对应于催化剂表面上两个相邻吸附颗粒之间以及表面吸附颗粒与气体分子之间的反应. 在氧化过程中,贵金属作为界面反应的活性氧化还原中心被认为以其还原态发挥作用^[119]. 贵金属活性位点上的 L-H 机制(见图 2a)经过 3 个步骤: O_2 在贵金属位点上发生解离, CAHs 在没有离解的情况下被吸附在贵金属位点上,解离的 O 物种攻击吸附的 CAH 以形成 CO_2 、 H_2O 和其他副产物等,这些副产物在形成后通常遵循 E-R 机制进入下一个循环^[120],或者, CAHs 不吸附在催化剂表面上,气态 CAHs 与吸附在催化剂上的氧直接反应,遵循 E-R 机制(见图 2b)^[121]. 大多数过渡金属氧化物催化剂在催化氧化 CAHs 时,遵循 MVK 机制(见图 2c). 这是因为过渡金属氧化物在表面上具有更多的氧空位. 在此机制中,催化剂的晶格氧物种参与氧化还原过程,当晶格氧被消耗后,催化剂将被部分还原以形成一个氧空位. 随后,空气中的氧会首先吸附在催化剂表面上,形成表面吸附氧. 然后,表面吸附氧进一步填充催化剂中的氧空位,如此往复循环,从而达到催化效果^[122].

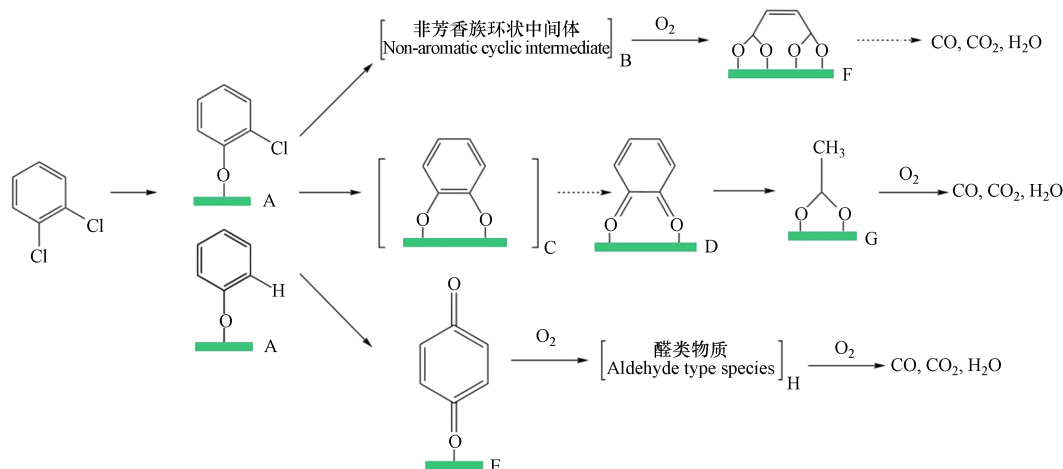


图 1 氯苯类化合物在 V_2O_5/TiO_2 催化剂上的催化氧化反应机制^[59]

Fig.1 Reaction mechanism for the oxidation of chlorinated benzenes over V_2O_5/TiO_2 catalysts^[59]

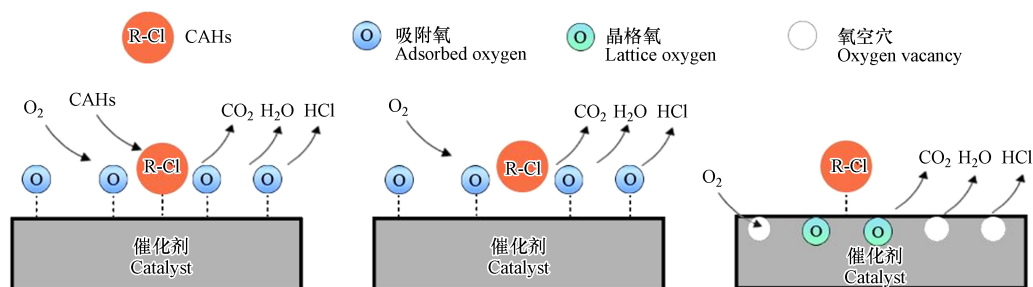


图 2 催化 CAHs 氧化的动力学模型

(a) L-H 模型, (b) E-R 模型, (c) MVK 模型^[123]

Fig.2 Kinetic models of catalytic CAHs oxidations^[123]

(a) L-H model, (b) E-R model, (c) MVK model

3 催化剂失活与再生方法(Catalyst deactivation and regeneration methods)

3.1 催化剂失活

催化剂失活是指催化剂在反应过程中活性下降或完全失去活性的现象,可能多种因素导致,包括催化剂的化学变化、物理变化或结构变化以及反应条件的变化.失活降低了催化系统的运行能力,增加了未完全氧化物质的产生,包括一系列氯代有机物,甚至可能诱发更危险的化合物如 PCDD/Fs 或 PCBs 的产生,这种情况导致包括 CAHs 在内的多种污染物排放到环境中,从而增加了排放量,并提高了运行成本^[124].因此,研究催化剂失活和可能的再生对于评估催化剂具有重要意义.常见的催化剂失活原因通常分为积碳、烧结和中毒.催化剂积碳是指反应物或反应中间体在催化剂表面吸附和转化时形成碳质物质沉积在催化剂表面的现象.积碳会覆盖催化剂表面活性中心,减少可利用的表面导致催化剂失活.另一方面,积碳容易堵塞催化剂孔道,使孔内金属颗粒不能正常发挥催化作用^[60].催化剂暴露在过高温下导致结构和性能的变化称为催化剂的烧结或热失活.它涉及活性元素分散度的降低,比面积、孔体积和孔径的减少、酸度的降低以及结构的破坏.根据这些结果,很难精确地确定载体或金属在催化剂热失活中的作用^[125].热失活基本上是不可逆的.因此,为了避免烧结,有必要提高催化剂的热稳定性并阻碍催化剂中活性元素的流动性,或者开发在较低温度下已经具有活性的催化剂^[100].

催化剂中毒主要是由于活性组分吸附了对其有毒性的物质^[37],在活性位点上生成稳定且催化活性很低的物种.CAHs 催化氧化的研究主要集中在 Cl 中毒上.首先,Cl 元素的强电负性容易绑定在活性位点内,从而覆盖了活性点,阻碍了 CAHs 的吸附和活化,导致催化剂失活.其次,Cl 会与金属表面发生相互作用,引起金属组分和载体的腐蚀,导致不可逆的失活.Cl 的积累也会导致比表面积减小,微晶尺寸增加,活性相团聚等问题,进而降低催化活性^[37, 80, 126-129].贵金属和 Cl 之间的存在强烈相互作用,因此在反应过程中很容易形成氯化物覆盖活性位点,导致催化剂失活^[130-132].然而,不同的过渡金属氧化物在抗 Cl 中毒方面表现不同.例如,在 CB 催化氧化中,VO_x 催化剂表面未检测到氯化物种,表现出良好的抗失活性,而 MnO_x 催化剂则深度失活,形成了氯化锰和氧氯化物,证明了通过化学反应形成(氧)氯化物是更为明显和持久的失活类型^[51].在这种情况下,催化剂的活性可以通过金属氧化物的再氧化,在适当的高温下去除 Cl 物种得以部分恢复^[133].除此之外,还可以通过添加其他金属改善催化剂表面性质.因为引入新的活性组分可以促进沉积在催化剂表面的无机氯物种的解吸,并抑制金属氯化^[21, 77, 79, 134-135].

3.2 催化剂再生方法

催化剂再生能力取决于其失活过程的可逆性.热处理、化学再生、臭氧氧化、汽提或空气处理等手段可以用于恢复失活的催化剂^[123].在大多数情况下,碳质沉积物可以通过氧气、水蒸气、二氧化碳或氢气的气化完全消除.然而,催化剂的烧结通常是不可逆的.此外,挥发性金属氯化物的形成也会导致催化剂不可逆失活.找到有效的再生和再利用方法对于针对 CAHs 的失活催化剂来说是个挑战.因此,研究人员正在探索各种催化剂再生方法.Ji 等^[136]针对 V₂O₅-WO₃/TiO₂ 商业催化剂的再生研究,发现在 O₂ 环境下 50 °C 处理数小时可消除焦炭,使催化剂得到完全再生,并提高了 PCDD/F 的去除率.Zhu 等^[137]尝试用盐酸可以部分恢复与 o-DCB 反应过的 Pd/Fe 催化剂,部分消除了其表面腐蚀.Sun 等^[112]研究指出,Brønsted 位点的损失主要是由含有芳环的焦炭所致.针对此,可采用 400 °C 的等温空气流再生方法,该方法可将芳香环焦炭转化为更饱和的碳氢化合物或 CO₂,进而恢复 Cu-Nb/HZSM-5 催化剂中的大多数 Brønsted 酸位点.此外,研究还发现,水可以促进 HCl 的生成,从而去除表面氯化物并促进碳氧化物形成,有利于焦炭和氯的去除,从而更好地再生催化剂.但水也会与 CAHs 竞争活性位点,减少催化剂酸性位点数量^[121, 138],降低催化效率.

4 总结与展望(Conclusion and perspective)

催化氧化技术作为处理焚烧烟气中 CAHs 的有效手段,已经得到了广泛关注.贵金属催化剂具有高催化活性,但其昂贵的价格、易中毒的特性以及产生大量多氯副产物限制了其实际应用.相对而言,过渡金属复合氧化物的催化活性虽然不及贵金属催化剂,但是通过改性可以提高其催化活性、稳定性和抗失活性.此外,分子筛的催化活性依赖于自身酸性,能够有效地抑制多氯副产物的生成,但易受碳沉积的影响.总体而言,催化氧化技术在处理 CAHs 方面仍面临诸多挑战和问题.首先,催化氧化过程

机制理解尚不深入. 其次, 高反应温度窗口的需求也是一大挑战. 最后, 缓解催化剂的失活并找到有效的再生方法亦是迫切的课题. 因此, 未来的研究应该全面考虑催化剂的构造、反应机制、失活和再生等因素, 以推动高效、经济、环保的催化氧化技术的发展, 并推动其在实际应用中的广泛使用.

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