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金属卟啉衍生物催化降解污染物研究进展*

赵晓娜^{1,2#} 张 鹏^{1,2#} 赵义斐^{1,2} 张文豪^{1,2} 孟令鲲^{1,2}
 侯慧杰^{1,2} 刘冰川^{1,2} 杨家宽^{1,2} 胡敬平^{1,2**}

(1. 华中科技大学环境科学与工程学院, 武汉, 430074; 2. 固废处理处置与资源化技术湖北省工程实验室, 武汉, 430074)

摘 要 由于工业化和城市化的快速发展而带来的环境问题已经引起了人们的广泛关注. 土壤和地下水中不断排放的持久性污染物, 对人们的健康造成了极大的威胁, 因此需要更加有效的策略来解决. 卟啉类物质由于具有特殊的氧化还原性质和光敏性, 已经被广泛用于有机污染物的去除. 本文总结了金属卟啉的最新研究进展, 对其在类芬顿和光催化领域的应用进行了详细的介绍, 并且讨论了高价铁氧卟啉物种, 单重态氧和超氧自由基的产生机理. 最后, 指出了现有研究的不足以及未来的发展方向.

关键词 铁卟啉, 类芬顿, 光催化, 高价铁, 活性氧, 异裂, 反应机理.

The degradation of pollutants catalyzed by metalloporphyrin derivatives

ZHAO Xiaona^{1,2#} ZHANG Peng^{1,2#} ZHAO Yifei^{1,2} ZHANG Wenhao^{1,2}
 MENG Lingkun^{1,2} HOU Huijie^{1,2} LIU Bingchuan^{1,2} YANG Jiakuan^{1,2} HU Jingping^{1,2**}

(1. School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan, 430074, China;
2. Hubei Provincial Engineering Laboratory for Solid Waste Treatment, Disposal and Recycling Technology, Wuhan, 430074, China)

Abstract: The recent growing threat of environment and energy crisis have aroused increasing concern due to the rapid development of industrialization and urbanization. The aggravating release of recalcitrant pollutants in water and soil poses great threat to human health, demanding for more efficient strategies to address the environmental issue. Considering the photosensitiveness and redox properties of metalloporphyrins in nature, porphyrin-based chemistry has reached an unprecedented period of rapid development for the application of pollution abatement. This review summarized recent advances of porphyrins chemistry, highlighted Fenton-like redox chemistry and photo-excitability of porphyrins. The generation of high-valent iron oxo porphyrin species, $^1\text{O}_2$ and O_2^- were also discussed. Finally, challenges in current research were identified and perspectives for future development in this area were presented.

Keywords: iron porphyrin, Fenton-like reaction, photocatalysis, high-valent iron, reactive oxygen

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** 通讯联系人, Tel: 027-87793948, E-mail: hujp@hust.edu.cn

Corresponding author, Tel: 027-87793948, E-mail: hujp@hust.edu.cn

赵晓娜、张鹏对本论文有同等贡献

Zhao Xiaona and Zhang Peng contribute equally to this article

species, heterolysis, reaction mechanism.

天然卟啉在自然界中广泛存在,对生物体的生命活动起着十分重要的作用,如叶绿素、细胞色素 P450、血红素和维生素 B12 等.通过对金属卟啉的化学结构、光电特性、电化学性质等的研究,发现金属卟啉具有良好的催化活性^[1],独特的光电化学性质^[2],故在酶仿生催化^[3]、烷烃选择性催化氧化^[4]、光催化^[5]等领域有着广泛的应用.天然卟啉一般难溶于水,通过酸性条件下中心金属离子的置换,以及在卟啉大环上引入磺酸基、羧基、氨基、吡啶基等亲水性基团,可以制备得到各种水溶性的金属卟啉化合物.

随着工业化的不断发展,各种污染物的排放日趋增加,对人类的健康和生态环境造成了极大的威胁.传统的生物处理技术虽然成本低廉,但对一些难降解的有毒物质的处理效果不佳.高级氧化技术由于其反应迅速、适用范围广、降解彻底、无二次污染等特点,在难生物降解污染物的处理方面具有独特的优势^[6].

基于芬顿反应的高级氧化技术由于其操作简单,反应迅速,成本相对较低,已经有一些工业化的应用.但传统的芬顿反应只能在酸性条件下发生,在中性和碱性条件下会产生大量铁泥^[7],且受到 Fe(Ⅲ)/Fe(Ⅱ)循环速率慢的限制^[8].为了解决这一问题,研究者们开始采用类芬顿技术代替传统的芬顿反应.一方面,一些非均相的过渡金属氧化物如铝、铈、铬、钴、铜、锰等,可以取代传统芬顿反应中的亚铁离子,在中性甚至碱性 pH 下催化 H₂O₂ 分解产生强氧化性自由基来氧化目标污染物,但大多存在催化效率较低的问题^[8],并存在重金属离子浸出的风险.另一方面,可以使用有机配体与铁、铜、锰等过渡金属离子形成均相的配位化合物,如乙二胺四乙酸(EDTA)^[9]、氨三乙酸(NTA)^[7]、柠檬酸^[10]、乙二胺二琥珀酸(EDDS)^[11],以及近年来发现的一些新型配体,如糖酸^[12]、原儿茶酸^[13]等.然而这些配位化合物作用的 pH 范围有限,EDTA 只能在中性或碱性条件下发挥作用^[7],而原儿茶酸的最适 pH 为酸性^[13].有机配体能防止铁离子在中性和碱性 pH 下沉淀^[7],同时因其自身的还原性,加速 Fe(Ⅲ)/Fe(Ⅱ)循环^[11-12],从而提高 H₂O₂ 的利用率,促进污染物降解.

近些年来,卟啉类物质作为一种环境友好的仿生配体,能与铁、钴、锰等过渡金属形成一系列的配位化合物,在偶氮染料、芳香烃类污染物的降解过程中均表现出了良好的催化性能^[14-16],因此逐渐进入广大研究者的视野.

金属卟啉以卟吩作为母体结构,其中的 18 个 π 电子形成平面的连续循环,这种大的共轭体系使得金属卟啉具有一些特殊的氧化还原性质,并且在特定的波长范围内表现出强烈的吸收,因此在类芬顿和光催化领域都有广泛的应用^[17-20].当金属卟啉与过氧化氢、过硫酸盐或过氧酸等氧化剂反应时,氧化剂的 O—O 键能通过均裂或异裂的方式形成具有强氧化性的高价金属卟啉或高价金属卟啉阳离子自由基^[21],能快速去除多种有机污染物,表现出了良好的类芬顿反应催化活性;在紫外或可见光的照射下,金属卟啉及其衍生物还能吸收光能,将能量或激发态的电子转移给氧气,形成单重态氧(¹O₂)或超氧自由基(O₂⁻)^[22],引发光催化反应.

近年来,许多研究者利用金属卟啉及其衍生物类芬顿或光催化活性,已经实现了羟基苯甲醛、亚甲基蓝(MB)、环氧乙烷等难降解有机污染物的快速去除^[23,125],并且对金属卟啉催化氧化的反应机理、活性中间体的产生也有了一定的研究^[26-29].此外,传统的均相催化剂由于自身氧化和低聚作用容易失活,因此对于负载型卟啉催化剂也有一定的研究^[30-31].在此基础上,结合近年来的一些最新研究进展,我们分别对金属卟啉在类芬顿反应和光催化反应中的应用以及相关的反应机理进行了系统的总结.

1 金属卟啉在类芬顿反应中的应用(Application of metalloporphyrins in Fenton like reactions)

1.1 均相类芬顿降解污染物

作为一种高活性的类芬顿反应催化剂,金属卟啉可以催化 H₂O₂ 等氧化剂的分解,产生活性氧物种来降解各种目标污染物,常用的氧化剂有 H₂O₂、Na₂S₂O₈ 等.

早在 1981 年, Groves 等^[32]在研究细胞色素 P450 单加氧酶的人工模拟反应时,合成了一种新的高价铁-卟啉配合物,对其进行了表征,并将其用于有机物的降解.之后,学者们围绕金属卟啉的催化氧化

开展了多方面的研究.Sorokin 等^[33]通过检测四磺酸铁酞菁(FePcS)催化 H₂O₂氧化三氯苯酚(TCP)的产物分布,发现 FePcS/H₂O₂体系能促进 TCP 分子释放两个氯离子,从而完成 TCP 矿化的关键步骤,具有良好的催化活性和脱氯效果.随后,Sorokin 等^[34]采用¹⁴C 同位素标记法发现 FePcS/H₂O₂体系可以进一步将 TCP 的脱氯产物转化为 CO₂和其他无机物.通过使用环境友好的氧化剂,FePcS/H₂O₂体系可以实现污染物的彻底矿化,具有可观的应用潜力.一些金属卟啉及其衍生物的化学结构式如图 1 所示.

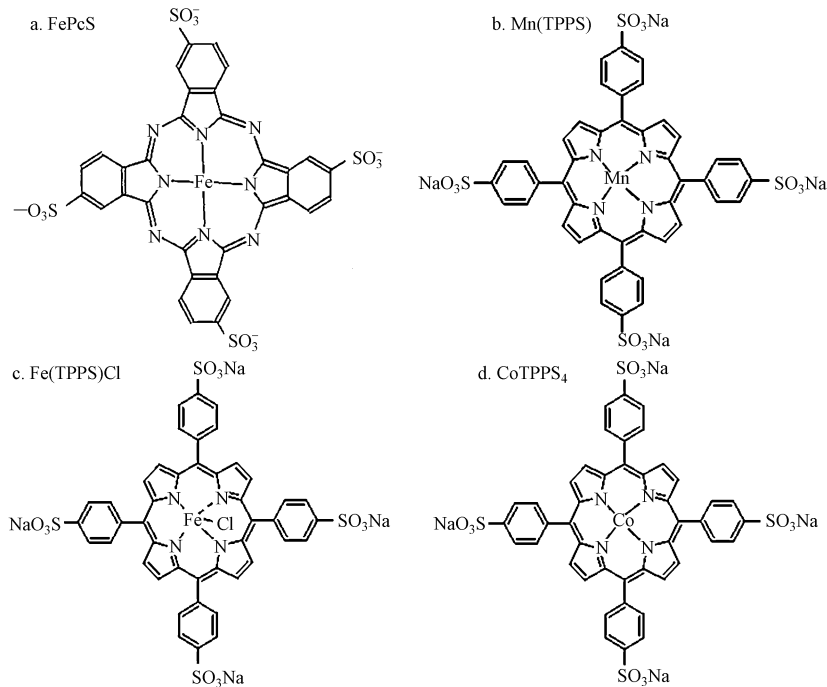


图 1 部分金属卟啉的化学结构式^[33, 35-36]

(a) FePcS: 2,9,16,23-四磺基铁酞菁;(b) Mn(TPPS): 四(对-磺酸基苯基)锰卟啉;
(c) Fe(TPPS)Cl: 四磺酸基苯基铁卟啉;(d) CoTPPS₄: meso-四-(4-磺基苯基)钴卟啉

Fig.1 Chemical structure of some typical metalloporphyrins^[33, 35-36]

(a) FePcS: 2,9,16,23-tetrasulfonyl iron phthalocyanine;(b) Mn(TPPS): Tetra (p-sulfonylphenyl) manganese porphyrin;
(c) Fe(TPPS)Cl: Tetrasulfonyl phenyl iron porphyrin;(d) CoTPPS₄: Meso-tetra-(4-sulfophenyl) cobalt porphyrin

表 1 总结了金属卟啉在均相类芬顿反应中对不同有机污染物的降解效果.Sorokin 等^[37]发现,以 KHSO₅做氧化剂时,即使催化剂与 TCP 比值为 0.1%,在几分钟内也可以观察到底物被完全转化.此外,以 H₂O₂等绿色氧化剂代替 KHSO₅时也可以获得较高的转化率.Crestini 等^[36]的研究结果表明,在 H₂O₂存在时,阴离子和阳离子水溶性锰卟啉比铁卟啉可以更有效地降解木质素与木质素模型化合物.Colomban 等^[38]对比了四磺基酞菁铁(FePcS)及相应的 μ -nitrido 二聚体[(FePcS)₂N]的催化性能,在反应 3 h 后,以 0.5 mol%的(FePcS)₂N 和 FePcS 作为催化剂降解二氯苯酚(DCP),可分别获得 92%的转化率、0.91 的脱氯度、33%的总有机碳去除率和 81%的转化率、0.81 的脱氯度、27%的总有机碳去除率.Fukushima 等^[16]发现含有一定浓度的四磺酸基苯基卟啉(TPPS)和 Fe(Ⅱ)的水溶液在 pH 6 的条件下可以氧化 O₂产生 H₂O₂降解五氯苯酚(PCP),添加抗坏血酸(ASC)会促进 PCP 的降解.

在反应过程中,O—O 键存在均裂和异裂两种断键方式.均裂过程指 O—O 键直接断裂;异裂过程指 O—H 键先断裂,然后 O—O 键再断裂.不同的断裂方式对污染物的降解效果不同.Kudrik 等^[21]对 (FePc^tBu₄)₂N/H₂O₂体系和 (FePc^tBu₄)₂N/^tBuOOH 体系的氧化产物进行分析,发现 (FePc^tBu₄)₂N/H₂O₂体系和 (FePc^tBu₄)₂N/^tBuOOH 体系会产生不同类型的活性氧化物,其生成途径如图 2 所示.使用 H₂O₂做氧化剂时,过氧加合物 PcFe(Ⅳ)μNFe(Ⅳ)-OOH(Pc)通过 O—O 键异裂产生了两电子氧化的产物 PcFe(Ⅳ)μNFe(Ⅳ)=O(Pc⁺);而使用过氧化叔丁醇(^tBuOOH)做氧化剂时,PcFe(Ⅳ)μNFe(Ⅳ)-OO^tBu(Pc)通过 O—O 键均裂产生两个一电子氧化的产物 ^tBuO·和 PcFe(Ⅳ)μNFe(Ⅳ)=O(Pc).两电

子氧化的产物具有更强的氧化性,甚至可以使甲烷中化学性质稳定的 C—H 键断裂.此外,李继斌等^[41]发现 pH 对 H₂O₂ 的 O—O 键的断裂方式有很大影响,在中性环境下均裂倾向大于异裂倾向.

表 1 金属卟啉均相催化氧化对有机污染物的降解效果

Table 1 Degradation of organic pollutants by homogeneous catalytic oxidation of metalloporphyrin							
催化剂 Catalyst	氧化剂 Oxidant	污染物 Substrate	Cat./sub * /(mol) %	温度 Temperature/℃	pH	反应时间 Reaction time/min	转化率 Conversion rate/%
TpyMePMnAc ₅ ^[36]	H ₂ O ₂	木质素	—	50	3	6	72.9
Fe(PcS) ^[37]	KHSO ₅	TCP	0.1	20	7	1	97
Fe(PcS) ^[37]	H ₂ O ₂	TCP	3.7	20	7	5	100
(FePcS) ₂ N ^[38]	H ₂ O ₂	DCP	1	60	—	120	94
FePcS ^[38]	H ₂ O ₂	DCP	1	60	—	120	61
Mn(TPPS) ^[39]	H ₂ O ₂	MB	100	60	—	240	97
CoTSPc ^[40]	H ₂ O ₂	酸性红	—	25	7	240	60

注：* Cat./sub 表示催化剂浓度和污染物初始浓度的比值。* Cat./sub represents the ratio of the catalyst concentration to the initial concentration of the contaminant.

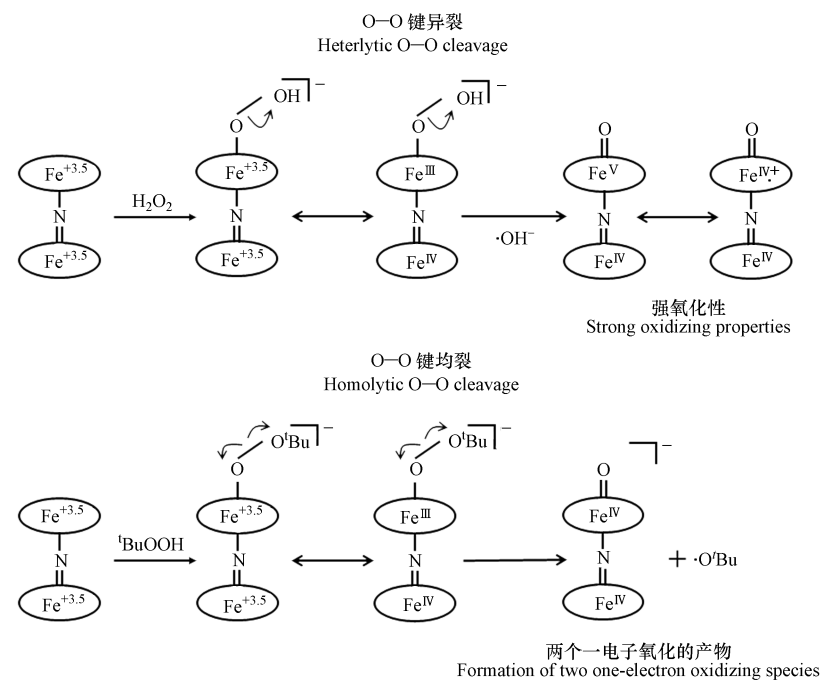


图 2 KUDRIK 等^[21]提出的活性中间体形成过程

Fig.2 Formation process of active intermediates by Kudrik et al.^[21]

在金属卟啉主导的类芬顿催化反应中,起主要氧化作用的物质为高价铁氧物种和 ·OH,其中,高价铁氧物种主要包括高价铁氧卟啉和高价铁氧卟啉 π 阳离子自由基.一般情况下,金属卟啉催化 H₂O₂ 氧化底物时,先生成金属卟啉-过氧化氢加合物,该加合物的 O—O 键的断裂有均裂异裂两种方式,不同的断裂方式决定了产生的不同活性中间体,即高价铁氧物种的类型.Bruice 等^[42-46]认为在水溶液中,加合物的 O—O 键均裂生成 ·OH 和一电子氧化产物高价铁氧卟啉,之后又发现一电子氧化产物可转化为两电子氧化产物,即高价铁氧卟啉 π 阳离子自由基.结合 T aylor^[47-50]、Meunier^[51]、Nam 等^[52]的研究可以发现,加合物 O—O 键的断裂方式与溶剂、卟啉配体电子属性、溶液 pH 等有关.Stephenson 等^[29]对金属卟啉催化 H₂O₂ 烯烃环氧化过程中影响活性中间体的各种因素进行了详细的研究,绘制了由铁卟啉催化 H₂O₂ 氧化烯烃的完整机理图,分析了卟啉的组成、溶剂效应对每一步骤的影响,具体过程如图 3 所示.

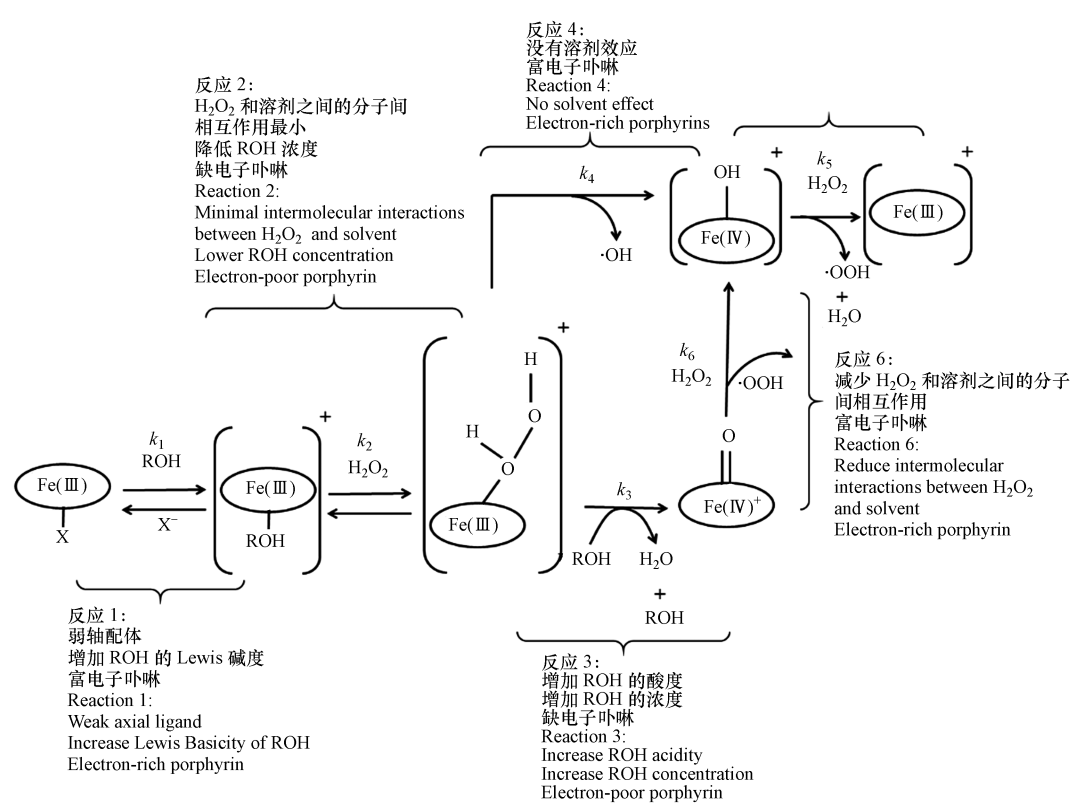


图 3 卟啉的组成和溶剂效应对铁卟啉氧化反应的影响^[29]

图中所列反应条件利于各阶段反应的进行

Fig.3 Effect of composition of porphyrin and solvent effect on oxidation reaction of iron porphyrin^[29]

The reaction conditions listed in the figure facilitate the progress of the reaction at each stage.

1.2 负载非均相类芬顿降解污染物

虽然金属卟啉在均相的类芬顿反应中表现出良好的催化活性,但溶解态的金属卟啉不利于反应后的回收和再利用.因此,一些与载体结合而形成的非均相类芬顿反应催化剂也引起了研究者的广泛关注.

活性碳纤维(ACF)、碳纳米管、聚乙二醇等具有较大的比表面积、丰富的空间结构,已经作为催化剂的载体而被广泛使用.实验证明,高分子聚合物会影响金属配合物的稳定性、活性氧化物的种类,从而对催化剂的催化性能产生积极的影响^[53].表 2 总结了负载于高分子聚合物上的金属卟啉在非均相类芬顿反应中对不同有机污染物的降解效果.Sorokin 等^[37]分别将铁磺化酞菁 Fe(PcS)、锰磺化酞菁负载到 Amberlite 离子交换树脂上,获得了能利用 H₂O₂ 高效氧化 TCP 的催化剂,且多次循环使用后催化活性保持稳定.Ren 等^[54]发现铁卟啉(FeTPPS)和聚酰胺树枝状大分子(dendrimer)非共价结合的 FeTPPS/dendrimer 可以多次催化 H₂O₂ 氧化水中的 TCP,他们认为 FeTPPS 与 dendrimer 之间的相互作用降低了 FeTPPS 的氧化降解,并防止了非反应性 μ-oxo 二聚体的形成和卟啉的光解.Zhu 等^[55]的研究结果表明,FePc/PAN 纳米纤维/H₂O₂ 系统在进行了 8 次循环降解后,对卡马西平(CBZ)的去除率仍保持在 99% 左右.此外,Lu 等^[56]发现被固定在活性碳纤维(ACF)上的钴酞菁(Co-TDTAPc-ACF)在宽 pH(3—11)范围内也具有良好的催化活性和再生能力.

负载型金属卟啉催化剂的稳定性和选用的载体有关.Shen 等^[40]将钴(Ⅱ)四磺基酞菁(CoTSPc)固定在壳聚糖微球上,获得了具有低浸出率、高稳定性、高催化活性、可回收的催化剂 CoTSPc@chitosan,与未固定的 CoTSPc 相比,C.I.酸性红 73(AR173)的去除率增加了 35% 左右.但是,在 CoTSPc@chitosan 上仍然可以观察到不利于催化反应的二聚体 CoTSPc.这表明,虽然 CoTSPc 通过共价键固定在壳聚糖微球的表面上,但这不能防止无活性的 CoTSPc 二聚体的形成.为了改善了 CoTSPc 的稳定性,Shen 等^[58]依次

选用介孔二氧化硅 (MCM-41、MCM-48 和 SBA-15)、微孔硅铝酸盐 (ZSM-5) 和不同孔径的氧化铝 ($\gamma\text{-Al}_2\text{O}_3$) 固定 CoTSPc, 并比较不同催化剂对多种染料的降解效果. 结果表明, 在 pH 12 的条件下, 固定在 MCM-41 二氧化硅上的催化剂 CoTSPc@ MCM-41 稳定性最好. 由此推测高稳定性 CoTSPc 催化剂的制备应满足两方面的要求, 如图 4 所示: 1) 调节 pH 值至 12 左右, 减少 CoTSPc 二聚体的生成, 确保足够浓度的 CoTSPc 单体; 2) 选择孔径与 CoTSPc 单体的大小相匹配的多孔载体, 通过有限的密闭空间避免 CoTSPc 单体聚集.

表 2 负载型金属卟啉/ H_2O_2 非均相反应体系对有机污染物的降解效果

Table 2 Degradation effect of supported metalloporphyrin/ H_2O_2 heterogeneous reaction system on organic pollutants

催化剂 Catalyst	载体 Carrier	污染物 Substrate	催化剂浓度 Catalyst concentration/ ($\text{g}\cdot\text{L}^{-1}$)	污染物浓度 Substrate concentration	(Cat./sub)/ %	pH	温度 Temperature/ $^{\circ}\text{C}$	反应时间 Reaction time/min	转化率 Conversion rate/%
[Fe(PcS)]-Amb ^[37]	Amberlite	TCP	—	—	1	7	20	5	80
CoTSPc@ chitosan ^[40]	壳聚糖	AR73	10	$50\text{ mg}\cdot\text{L}^{-1}$	—	7	25	240	95
FeTPPS/0.5G2 ^[54]	Dendrimer	TCP	—	—	0.01	—	20	100	35.8
FePC/PAN ^[55]	PAN nanofibers	CBZ	—	—	—	3	70	90	99
Co-TDTAPc-ACF ^[56]	活性碳纤维	4-NP	2	$0.5\text{ mmol}\cdot\text{L}^{-1}$	—	6.84	25	300	97
CoTAPc-MWCNTs ^[57]	MWCNTs	Rh6G	0.5	$0.05\text{ mmol}\cdot\text{L}^{-1}$	—	7	25	200	90
CoTSPc@ MCM-41 ^[58]	SiO_2 (MCM-41)	AR73	3	$10\text{ mg}\cdot\text{L}^{-1}$	—	10	25	180	82
Co-TDTAPc-F ^[59]	纤维素纤维	AR1	20	$0.05\text{ mmol}\cdot\text{L}^{-1}$	—	2	50	60	98

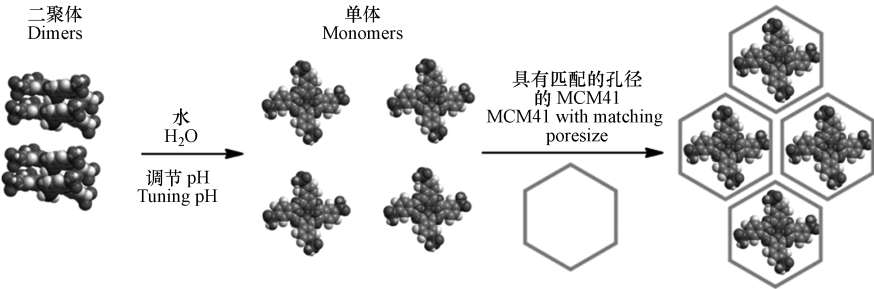


图 4 CoTSPc@ MCM-41 获得更高催化活性的可能机制^[58]
Fig.4 Possible mechanism for higher catalytic activity of CoTSPc@ MCM-41^[58]

某些载体除了有固定卟啉分子的作用外, 还可作为反应的电子库, 参与电子转移. Yao 等^[60] 发现将血红素 (hemin) 结合到活性碳纤维 (ACF) 上, 可以显著增强 hemin 对活性红染料 (RR195) 的分解, 并且 hemin 的 pH 耐受性和稳定性明显改善. 这一现象可以从两个方面来解释, 如图 5 所示: (1) ACF 的另一个重要作用是防止 hemin 在反应过程中形成二聚体, 提高了卟啉的稳定性, 拓宽了催化剂的 pH 适用范围; (2) H_2O_2 作为氧化剂时, hemin 中的 $\text{Fe}(\text{III})$ 转化为 $\text{Fe}^{\text{III}}\text{-OOH}$, $\text{Fe}^{\text{III}}\text{-OOH}$ 进一步转化为活性氧物种 $\text{Fe}^{\text{IV}}=\text{O}$ 和 $\cdot\text{OH}$, 由于 ACF 富含自由电子, 自由电子从 ACF 转移至 hemin 加速了 $\text{Fe}^{\text{IV}}=\text{O}$ 向 $\text{Fe}(\text{III})$ 的转化, 促进了 hemin- Fe^{III} , hemin- $\text{Fe}^{\text{III}}\text{OOH}$ 和 hemin- $\text{Fe}^{\text{IV}}=\text{O}$ 三者之间的循环, 可以产生更多的 $\cdot\text{OH}$. 此外, 在 hemin-ACF/ H_2O_2 体系中加入抗坏血酸 (AA), 可以促进 RR195 降解, 在该过程中, ACF 作为电子库, 抗坏血酸作为电子供体, 将电子传递给 hemin- Fe^{III} , 加速 hemin 的催化循环, 产生更多的 $\cdot\text{OH}$ 和 $\text{Fe}(\text{IV})$ ^[61].

在电子转移的过程中, 某些载体可能会产生空穴, 空穴具有强氧化性, 可以使有机污染物迅速降解, 加快反应进程. Lu 等^[57] 将钴酞菁 (CoTAPc) 固定得多壁碳纳米管 (MWCNTs) 上, 在探究复合催化剂 CoTAPc-MWCNTs 的反应机理时发现 $\cdot\text{OH}$ 和 $\cdot\text{OOH}$ 不会主导催化反应, 并结合电化学实验推断 MWCNTs 会直接参与反应中的电子转移, 在催化氧化过程中产生大量空穴, 使活性位点产生高电位, 从而将吸附在催化剂上的罗丹明 6G (Rh6G) 氧化.

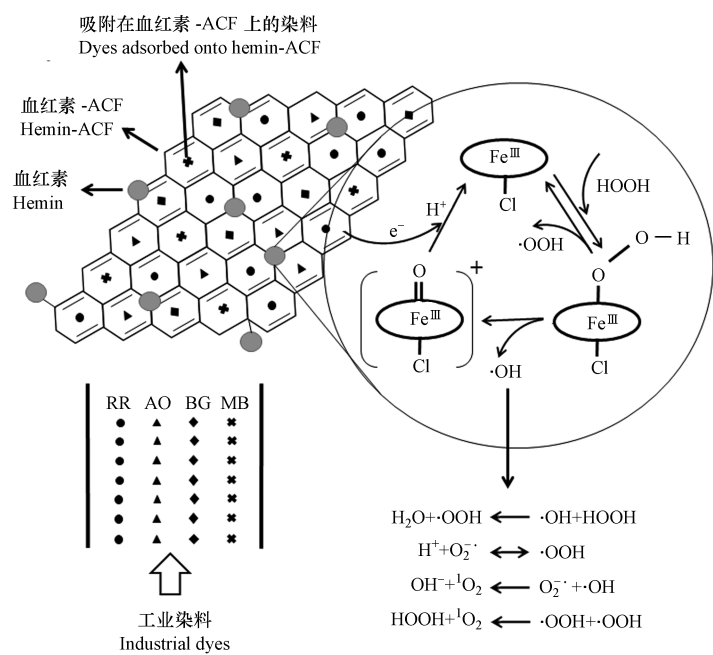


图 5 hemin-ACF/H₂O₂体系的催化循环^[60]
(a) RR:活性红 195;(b) AO: 吖啶橙;(c) BG: 碱性亮绿;(d) MB: 亚甲基蓝
Fig.5 Catalytic cycle of hemin-ACF/H₂O₂ system^[60]
(a) RR: Reactive Red;(b) AO: Acridine Orange;(c) BG: Brilliant Green;(d) MB: Methylene Blue

2 光催化反应 (Photocatalytic reaction)

2.1 均相光催化

近年来,随着环境问题的日益加重,作为一种高级氧化工艺,光催化技术由于具有反应条件温和、能耗低、可以氧气作为氧化剂、二次污染小等优点,受到越来越多的关注,在废水处理方面具有广阔的应用前景.TiO₂在紫外光(10—400 nm)照射下能产生氧化性极强的羟基自由基^[62],可以有效地降解多种污染物,但可见光(380—780 nm)的能量较低,难以直接将半导体激发^[63].由于可见光辐射约占太阳辐射总能量的50%,紫外区只占总量的7%左右,TiO₂的光催化响应范围有限,对太阳光的利用率低.在自然界中,一些金属卟啉类物质,如细胞色素 P-450 和叶绿素,具有特殊的光化学活性,可以在光照的激发下向外界传递电子.受此启发,一些金属卟啉类物质也被应用于光催化反应中,并且表现出一定的光催化活性^[2].表 3 总结了金属卟啉及其衍生物在均相光催化反应中对不同有机污染物的降解效果.Guo 等^[64]研究了一种新型的锌酞菁(ZnPc)分层纳米结构对可见光照射下罗丹明 B(RhB)的催化活性,由于其高结晶度和优异的疏水性能,可以为光催化剂和 RhB 溶液提供更多的接触位点,并提高了太阳光的利用率,与普通 ZnPc 相比光催化活性显著提高.Luo 等^[65]比较了各种天然卟啉在光照条件下对苯并[a]芘(BaP)的光降解效果,发现叶绿素 a 能转化 95.8%的 BaP.此外,叶绿素 a 由于自身不稳定产生的光降解产物也加速了 BaP 的转化.Kim 等^[66]证明了水溶性锡卟啉(s-SnP, [Sn(OH₂)₂(TPy^HP)](NO₃)₆)在可见光下对 4-氯苯酚(4-CP)和酸性橙 7(AO7)均具有良好的降解效果.Tai 等^[67]研究了在可见光照射下多环锌酞菁配合物(ZnPPc)催化降解双酚 A(BPA),观察到溶液中的 BPA 在 20 min 内完全转化为 CO₂和羧酸,40 min 后 BPA 及其中间产物被全部氧化.

作为一种十分优异的光催化剂,卟啉(或酞菁)容易与中心的金属离子形成配位,这使得卟啉(或酞菁)在可见光区域具有良好的吸收性能.此外,卟啉中心的金属离子的种类也会影响金属卟啉的光催化活性.钮金芬等^[24]发现四羟基苯基卟啉(THPP)及其金属配位化合物(MTHPP)与 TiO₂以氢键结合后,具有不同摩尔吸光系数,从而表现出不同的降解效果.Oliveros 等^[69]将 4 种苯基卟啉(TcPPCu、TcPPFe、TcPPZn 和 TcPPH)负载在 TiO₂表面,在 UV 光照射下降解阿特拉津,观察到 TcPPFe、TcPPCu 的降解效

果更好,并指出中心离子有未填充 d 轨道的金属卟啉往往显示出更高的光催化活性.

表 3 金属卟啉在均相光催化反应中对污染物的降解效果*

Table 3 Degradation effect of metalloporphyrins on contaminants in homogeneous photocatalytic reaction							
催化剂 Catalyst	污染物 Substrate	催化剂浓度 Catalyst concentration	污染物浓度 Substrate concentration	pH	温度 Temperature/℃	反应时间 Reaction time/min	转化率 Conversion rate/%
TDCPPS ^[20]	阿特拉津	4.3 μmol·L ⁻¹	4.3 μmol·L ⁻¹	2.1	—	1 (d)	64
TPPS ^[20]	ametryn	4.3 μmol·L ⁻¹	4.3 μmol·L ⁻¹	5.8	—	5 (d)	77
ZnPc ^[64]	RhB	1.0 g·L ⁻¹	10 mg·L ⁻¹	—	—	660	88.5
叶绿素 a ^[65]	BaP	0.001 g·L ⁻¹	1.0 mg·L ⁻¹	—	22	4 (d)	95.8
s-SnP ^[66]	4-CP	0.05 mmol·L ⁻¹	0.1 mmol·L ⁻¹	—	—	50	100
s-SnP ^[66]	AO7	0.05 mmol·L ⁻¹	0.1 mmol·L ⁻¹	—	—	120	100
ZnPPc ^[67]	BPA	0.021 mmol·L ⁻¹	1.0 mmol·L ⁻¹	12	—	20	100
TNCuPc ^[68]	RhB	0.5 g·L ⁻¹	10 mg·L ⁻¹	—	—	240	91

注: * 上述反应中的氧化剂均为 O₂.The oxidant in the above reaction is O₂.

常见的激发态金属卟啉与基态氧相互作用降解污染物的机制有两种^[22].如图 6 所示,一种是通过机制 I 产生 O₂⁻.另一种是通过机制 II 产生单线态氧(¹O₂),即在吸收光之后,卟啉达到三重态,并且能量转移到基态氧,导致 O₂ 中的一个电子自旋反转形成¹O₂^[65],反应路径如图 7 所示.但是,目前关于金属卟啉在可见光下催化降解水中有机污染物的研究还不够充分,溶液的 pH、催化剂的稳定性等也会影响底物的降解,反应机理有待完善.

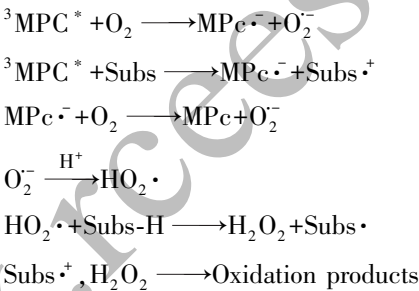


图 6 金属卟啉与基态氧相互作用降解污染物的机制 I^[22]
(a) MPC: 金属卟啉; (b) Subs: 反应底物

Fig.6 Type I mechanism of metal porphyrins interacting with ground state oxygen to degrade pollutants^[22]
(a) MPC: metal porphyrins; (b) Subs: Reaction substrate

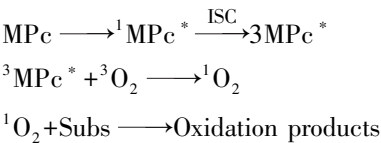


图 7 金属卟啉与基态氧相互作用降解污染物的机制 II^[22]
(a) MPC: 金属卟啉; (b) ISC: 系间窜越; (c) Subs: 反应底物

Fig.7 Type II mechanism of metal porphyrins interacting with ground state oxygen to degrade pollutants^[22]
(a) MPC: Metal porphyrins; (b) ISC: Intersystem crossing; (c) Subs: Reaction substrate

2.2 非均相光催化

与均相类芬顿反应类似,金属卟啉在水溶液中会发生分子聚集导致催化剂活性下降,聚集产物悬浮在溶液中难于回收^[70],研究者们为了获得催化性能优异、稳定性更强,并且可循环使用的光催化剂,近年来做了大量关于负载型金属卟啉的研究.表 4 总结了一些负载型金属卟啉的常见类型及负载方式.

表 5 总结了负载于高分子聚合物上的金属卟啉在非均相光催化反应中对不同有机污染物的降解效果.Wu 等^[80]以聚二乙烯苯负载锌酞菁(PDVB-ZnPc)为催化剂,在可见光照射下进行光辅助芬顿反应,对多种含氯酚类均有很好的降解效果.Alvaro 等^[81]对比了 FePc/SiO₂(将铁酞菁吸附在 SiO₂上)和

FePc@ NaY(铁酞菁被包封在 NaY 沸石内)两种催化剂的催化特性,发现 FePc/SiO₂在水溶液中具有更强的催化活性,FePc@ NaY 在有机溶剂具有更优异的催化活性,且后者具有更高的稳定性,有效的抑制了金属酞菁的溶出.Chen 等^[82]将四羧基铁酞菁(TCFcPc)固定在核壳型磁铁矿二氧化硅纳米粒子(NPs)表面,以罗丹明 B(RhB)和甲基橙(MO)为目标物质测定了催化剂 P-M/SiO₂-NPs 的光催化活性,结果表明,新型催化剂在较宽的 pH 范围内具有良好的催化活性,120 min 内 RhB 和 MO 的降解率可达 90%.Cabir 等^[83]用 TiO₂纳米粉末负载铜酞菁(CuPc),获得的负载型 CuPc-TiO₂光催化剂在实验中表现出优异的抗烧结性能,并在第 5 次重复使用时保留其初始催化活性的 80%.Gorduk 等^[84]制备了不同类型的酞菁-TiO₂纳米复合材料(MPc-TiO₂),发现每种 MPc-TiO₂纳米复合材料的催化速率非常接近,且在 100 min 内至少有 95%的亚甲基蓝(MB)被降解.此外,部分研究表明^[85-87],负载型金属卟啉衍生物还具有一定的杀菌能力.

表 4 负载型金属卟啉常见类型与负载方式
Table 4 Typical types and loading methods of supported metalloporphyrins

	载体 Carrier	负载方式 Way of loading
无机载体	沸石/分子筛载体 ^[71-72]	轴向配位;静电吸引
	蒙脱土载体 ^[73]	阳离子交换法
	介孔分子筛载体 ^[74]	共价键结合
	硅胶载体 ^[75-76]	共价键结合;轴向配位
有机载体	聚苯乙烯树脂载体 ^[77]	共价键结合
	聚硅氧烷载体 ^[78-79]	吸附作用

表 5 负载型金属卟啉非均相光催化对有机污染物的降解效果
Table 5 Degradation of organic pollutants by heterogeneous photocatalysis of supported metalloporphyrins

催化剂 Catalyst	载体 Carrier	氧化剂 Oxidant	污染物 Substrate	催化剂浓度 Catalyst concentration/ (g·L ⁻¹)	污染物浓度 Substrate concentration	pH	反应时间 Reaction time/min	转化率 Conversion rate/%
PDVB-ZnPc ^[80]	聚二乙烯苯	H ₂ O ₂	2,4-DCP	1.0	16.3 mg·L ⁻¹	13	60	82
FePc/SiO ₂ ^[81]	SiO ₂	H ₂ O ₂	苯酚	1.5	40 mg·L ⁻¹	7	180	100
FePc@ NaY ^[81]	NaY 沸石	H ₂ O ₂	苯并噻吩	1.5	40 mg·L ⁻¹	—	120	40
P-M/SiO ₂ -NPs ^[82]	NPs	H ₂ O ₂	RhB	0.5	0.01 mmol·L ⁻¹	5.7	60	90.2
P-M/SiO ₂ -NPs ^[82]	NPs	H ₂ O ₂	MO	0.5	0.01 mmol·L ⁻¹	4.8	60	91.3
CuPc-TiO ₂ ^[83]	TiO ₂	O ₂	MB	0.33	20 mmol·L ⁻¹	—	150	54
MPc-TiO ₂ * ^[84]	TiO ₂	O ₂	MB	1.0	3.0 mg·L ⁻¹	6-7	100	95
CuPc-4/TiO ₂ ^[85]	TiO ₂	O ₂	Cr(VI)	2.0	10 mg·L ⁻¹	2	150	100
TPP-nanofabrics ^[88]	聚氨酯纳米材料	O ₂	2-CP	—	1.0 mmol·L ⁻¹	9	45	81
ZnPcs@ Al-MCM-41 ^[89]	MCM-41	O ₂	苯线磷	0.002	0.1 mmol·L ⁻¹	7	300	80
TiO ₂ /FePc ^[90]	TiO ₂	O ₂	MB	1.0	0.04 mmol·L ⁻¹	—	90	97
TiO ₂ /FePc ^[90]	TiO ₂	O ₂	罗丹明蓝	1.0	0.04 mmol·L ⁻¹	—	90	88
SDS-LDH-PdPcS _{int} ^[91]	SDS-LDH	O ₂	TCP	1.0	0.31 mmol·L ⁻¹	6	60	90
ZnPc-TiO ₂ ^[92]	TiO ₂	O ₂	4-CP	1.0	13.0 mmol·L ⁻¹	7	30	99.51
CoPc-TiO ₂ ^[92]	TiO ₂	O ₂	4-CP	1.0	13.0 mmol·L ⁻¹	7	30	99.99
TNFePc/TiO ₂ ^[93]	TiO ₂	H ₂ O ₂	MO	0.5	10 mg·L ⁻¹	—	180	94
ZnO-CuPc ^[94]	ZnO	O ₂	氰化钾	0.6	30 mg·L ⁻¹	11	300	95
CuPp-ZnO ^[95]	ZnO	O ₂	RhB	0.2	0.01 mmol·L ⁻¹	—	36	94.6
CuTCPP/TiO ₂ ^[96]	TiO ₂	O ₂	MB	50	16 μmmol·L ⁻¹	1	180	99
TCPP/TiO ₂ ^[96]	TiO ₂	O ₂	MB	50	16 μmmol·L ⁻¹	1	90	100

注: * MPc-TiO₂包括 Pc-TiO₂、ZnPc-TiO₂、CoPc-TiO₂、NiPc-TiO₂、CuPc-TiO₂. * MPc-TiO₂ include Pc-TiO₂、ZnPc-TiO₂、CoPc-TiO₂、NiPc-TiO₂、CuPc-TiO₂.

以高聚物为载体负载金属卟啉制备的复合催化剂在光催化过程中一般会产生多种活性氧物种,如

O_2^- 、 $\cdot OH$ 等,有机污染物在多种活性物质的协同作用下被氧化分解.吴景悦等^[70]用负载型锌卟啉仿酶催化剂在氙灯照射下降解对苯二酚,通过在反应体系中加入不同的捕获剂,发现在此光催化过程中的起主要作用的活性氧物种是 $\cdot OH$ 、 O_2^- 、单线态氧(1O_2).操兰等^[97]将含硫氮杂钴卟啉负载在氮掺杂石墨烯/四氧化三铁复合物上,用于光降解有机染料罗丹明 B(RhB),通过淬灭剂投加实验检测到了 $\cdot OH$ 、 O_2^- 和 1O_2 等活性氧物种.刘欣阳等^[98]在研究磁微球负载硝基锌卟啉光催化特性时也发现 $\cdot OH$ 、 O_2^- 、空穴(h^+)等协同作用降解有机污染物的现象.

经过卟啉或金属卟啉光敏化的复合材料的可见光催化活性往往高于 TiO_2 .多项研究表明,金属卟啉负载在 TiO_2 表面后,在紫外光或可见光照射下会被激发,激发态的金属卟啉将光生电子传递到 TiO_2 的导带上,导带上的电子与溶解氧反应生成 O_2^- ^[99-101].一方面 O_2^- 可以直接与污染物发生作用,另一方面, O_2^- 可以通过一系列的反应产生氧化性极强的 $\cdot OH$, $\cdot OH$ 可以氧化难以被 O_2^- 降解的有机污染物,如图 8 所示.

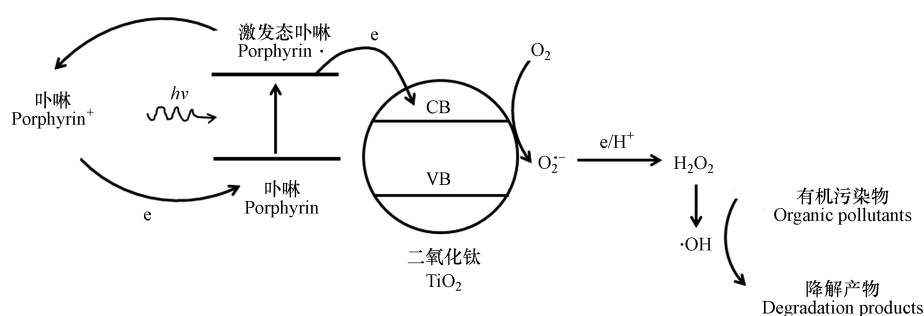


图 8 金属卟啉- TiO_2 光催化剂在可见光下的光催化机理^[62]

(a) CB: 导带; (b) VB: 价带

Fig.8 Photocatalytic mechanism of metalloporphyrin photocatalyst- TiO_2 under visible light^[62]

(a) CB: conduction band; (b) VB: valence band

3 结论与展望 (Conclusions and perspectives)

由于金属卟啉具有良好的催化特性,催化降解产物无二次污染,故其在处理环境中有机污染物方面有着可观的应用前景.目前对其催化机理的研究也取得了很大进展,但要实现大规模的应用还有很多问题需要解决.在今后的发展过程中,以下几个关键问题应该是研究关注的焦点:

(1) 进一步探究轴向配体、中心金属离子、外围取代基等因素对金属卟啉催化性能的影响和作用机理.

(2) 研究在不同外界条件下金属卟啉的催化降解效果,并筛选适合工程应用的金属卟啉催化剂.

(3) 探究反应条件对反应活性物种的影响,以获得更优的降解效果.

(4) 进一步深入探究负载型金属卟啉催化系统,解决金属溶出、催化剂自身氧化等问题,获得可循环使用的高性能催化剂.

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