

Review

Metal-organic frameworks for highly efficient heterogeneous Fenton-like catalysis

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ABSTRACT

The heterogeneous Fenton-like reaction is an advanced oxidation process which has gained wide spread acceptance for high removal efficiency of recalcitrant organic contaminants. Recently, the use of metal-organic frameworks (MOFs) or MOF composites as catalysts for Fenton-like catalysis has received increasing attention due to their permanent porosity and tunable open metal centers. In this article, we present an overview of the development and progress in the synthesis of different types of MOF-based catalysts and their applications for Fenton-like oxidation of organic pollutants. Special attention has been paid to the catalytic mechanism, namely the production of reactive species on the surface of the catalysts. Representative studies in this area were comprehensively reviewed. Overall, it is concluded that several classes of MOF materials with fixed metal centers are able to catalytically degrade organic pollutants over a wide pH range. Meanwhile, research in this field is still at an early stage, many improvements are required before the technology can be efficiently scaled-up and put into practice.

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1. Introduction

Water pollution is one of the most important environmental problems in the world. Large amounts of synthetic organic contaminants, such as pharmaceuticals and personal care products (PPCPs), pesticides and dyes are released daily into different types

of wastewaters and ultimately enter into natural water bodies [1–6]. It is well known the vast majority of these compounds are persistent organic pollutants (POPs), owing to their high stability to sunlight irradiation and resistance to microbial attack [7–10]. Many POPs are able to cause damage to living organisms, including human beings [11–14]. Thus, it is imperative to develop an effective method for eliminating these compounds from the environment. Advanced oxidation processes (AOPs) have been demonstrated to achieve good results for the elimination of organic pollutants from wastewater with very short treatment times [15–17]. AOPs are environmentally friendly chemical, electrochem-

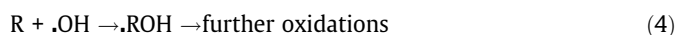
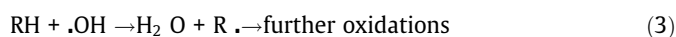
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ical or photochemical methods sharing the common feature of the in-situ production of the highly active hydroxyl radical ($\cdot\text{OH}$) as their main oxidizing agent [7].

The Fenton process has attracted considerable attention in the field of environmental remediation [18–21]. In the classical Fenton reaction (Eq. (1)), the ferrous ions (Fe^{2+}) catalyze the decomposition of hydrogen peroxide (H_2O_2), resulting in the generation of $\cdot\text{OH}$ radicals [22]. The formed ferric ions (Fe^{3+}) can be reduced through Eq. (2), which is known as a Fenton-like reaction [23,24]. The $\cdot\text{OH}$ radicals generated from the Fenton reaction are the second most reactive chemical species, they can initiate the decomposition of organic pollutants by hydrogen abstraction (Eq. (3)) or hydroxyl addition (Eq. (4)) [19].



Following the pioneering practical use of the Fenton reaction for the degradation of organic compounds in the 1930s [22], the Fenton reaction and its derivative technologies, such as electro-Fenton [25–28] and photo-Fenton [29–31], have been extensively studied for the decomposition of numerous organic pollutants. Since mass transfer limitations are negligible in homogeneous Fenton oxidation systems, the reaction can work very effectively during the degradation process [32]. However, the traditional Fenton process suffers from some drawbacks, such as the need for strict pH regulation (pH 2.8–3.5) [33], sludge generation [34] and the loss of the catalyst in the effluent [35]. In order to overcome these drawbacks, heterogeneous Fenton-like processes using solid catalysts have been developed. In heterogeneous Fenton-like catalysis, iron (or other transition metals) is stabilized on/in the catalyst's structure and thus can reduce hydroxide precipitation over a wider pH range [36–39]. Several reviews have summarized a wide range of materials that have been used as catalysts or metal supports in heterogeneous Fenton-like processes [40–44]. These reviews highlight that the development of new types of heterogeneous catalysts with low cost, high activity, good stability and environmental benignity is important, yet challenging.

Metal-organic frameworks (MOFs), also called porous coordination networks (PCNs) [45,46], or porous coordination polymers (PCPs) [47,48], are crystalline inorganic-organic hybrids assembled from organic ligands and metal ions (or clusters) [49]. MOFs not only combine the respective beneficial characteristics of inorganic and organic components, but also often exhibit unique properties that exceed the expectations for a simple mixture of the components [50,51]. Besides, MOF materials can be designed with dimensions, textural characteristics and specific structures to meet the need of a specific application [52]. Early efforts in this research area were mainly focused on the synthesis of new MOF materials [53–55]; however, in recent years the search for potential applications has been a topic of much interest. [52,56–58]. Since their discovery in the late 1990s [59], MOFs have influenced many fields, such as separation [60], energy storage [61], sensing [61] and catalysis [62].

The occurrence of MOFs opens up new opportunities for the development of catalysts with excellent characteristic features, such as chemical tenability, well-defined structure, large pore volume and high specific area [52,63]. To date, various MOF-derived catalysts have been reported. Moreover, an increasing number of review articles on this topic have appeared in recent years [64–72]. For example, Wen et al. [64] systematically reviewed

the recent progress in the design and architectures of MOF-involved H_2 production systems. In a more recent one, Zhu et al. [71] summarized the synthesis, structures and photocatalytic applications of titanium-based MOFs.

The past few years have witnessed rapid progress in MOF-derived Fenton-like catalysts. To date, various MOF-derived Fenton-like catalysts, including single metal (e.g. Fe, Co, Cu) and multiple metal (e.g. Fe/Co, Fe/Cu) containing MOFs, have been reported. The growing number of publications on this topic suggests that MOF-based Fenton-like catalysis will play a significant role in the elimination of organic pollutants. Several review papers [73–76] have mentioned the performance of MOF-based Fenton-like catalysis. To the best of our knowledge, however, MOFs for Fenton-like catalysis and the related mechanism have never been reviewed to date. Therefore, a review summarizing MOFs-based Fenton-like reactions is highly expected.

This review aims at giving an account of the fundamental aspects of MOF-based Fenton-like catalysis. Sections 2–4 discuss the synthesis of different types of MOF-derived catalysts and their application for the Fenton-like oxidation of organic pollutants. Special attention has been paid to the catalytic mechanism and the effects of structure on the catalytic activity of MOF-based catalysts. Section 5 introduces the effects of the initial pH on the performance of MOF-based Fenton-like catalysis. Afterward, the stability and reusability of MOF-based Fenton-like catalysts are presented in Section 6. Section 7 provides a conclusion of the review and finally, the outlooks of these emerging technologies are given for plausible research directions.

2. Fe-based MOFs for heterogeneous Fenton-like catalysis

Among the various types of reported MOFs, Fe-based MOFs showed great potential as heterogeneous Fenton-like catalysts. This is because Fe is non-toxic, abundant in earth crust minerals and Fe-based MOFs show an intensive absorption in the visible light region due to the existence of iron-oxo (Fe-O) clusters [77,78]. To date, a vast number of Fe-based MOFs have been developed, employing multiple types of organic ligands. Bipyridine is one of the most widely used ligands because of the oxidative resistance of the pyridine ring to $\cdot\text{OH}$ radicals and its strong binding affinity with the Fe^{2+} ion [79,80]. Also, recent progress has shown that the introduction of a carboxyl group to the 2,2'-bipyridine ligand can further stabilize the obtained complex, which is because the carboxyl group could bind with the Fe^{3+} ion formed in the catalytic cycle, avoiding its hydrolyzation. As reported by Li et al. [81], a Fe(II) MOF material (Fe-bpydc) was successfully synthesized with 2,2'-bipyridine-5,5'-dicarboxylate as the ligand and exhibited high catalytic activity for H_2O_2 at near neutral pH conditions. The total turnover number (TON) of a three cycles degradation is 23, revealing its activity and stability are superior to most of the reported MOF catalysts [81]. The ligands can also affect the catalytic performance of Fe-based MOF catalysts by affecting the spatial structure of the MOFs [77,82]. For instance, MIL-100(Fe) (Figs. 1 and 3D, with 1,3,5-benzenetricarboxylic acid as the ligand) showed a much more intensive absorption in the visible light region and higher catalytic ability as compared with MIL-68(Fe) (Figs. 1 and 2D, with 1,4-benzenedicarboxylic acid as the ligand) [77]. This was likely because MIL-100(Fe) contains the Fe_3O cluster in its framework, thus the formed electron in the Fe_3O cluster could be effectively transferred from the metal center to the substrate. Previous studies have demonstrated a $\mu_3\text{-O}$ atom in the catalysts could promote the formation of a pronounced electronic delocalized state in the $\mu_3\text{-O}$ cluster unit, which could help electron transfer from the metal ion to the oxidant to form active species [83,84]. The results highlight the great potential to find more economical and sustainable MOFs

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