



# Enhanced Fenton-like catalysis by iron-based metal organic frameworks for degradation of organic pollutants



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## ABSTRACT

The Fenton reaction is an efficient technology for degrading refractory organic pollutants in water. Heterogeneous Fenton-like catalysts have been demonstrated to be promising alternatives to homogeneous catalysts because of their reusability and lack of sludge production. These catalysts, however, generally show low activity for generating  $\cdot\text{OH}$  due to their limited exposed active sites and difficulty in the reduction of Fe(III) to Fe(II). Here, enhanced catalytic performance was achieved by using an iron-based metal organic framework (MIL-88B-Fe) as a heterogeneous Fenton-like catalyst over a wide pH range (4–6). The catalytic activity of MIL-88B-Fe was about 1–3 orders of magnitude higher than that of three other conventional catalysts ( $\text{Fe}_2\text{O}_3$ ,  $\alpha\text{-FeOOH}$ , and  $\text{Fe}_3\text{O}_4$ ) and two other iron-based MOFs (MIL-53-Fe and MIL-101-Fe). The superior activity of MIL-88B-Fe could originate from the abundance of active sites, the flexible structure, and facilitated reduction of Fe(III) to Fe(II). Hydroxyl radicals generated from reaction between MIL-88B-Fe and  $\text{H}_2\text{O}_2$  were the main reactive oxidative species for phenol degradation.

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## 1. Introduction

The Fenton reaction is an efficient advanced oxidation process for refractory organic wastewater treatment because of its ability to produce highly reactive hydroxyl radicals ( $\cdot\text{OH}$ ,  $E_0 = 2.80\text{ V}$ ), which are able to degrade most organic compounds without selectivity. Nevertheless, the traditional homogeneous catalysts,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions, are difficult to recover and are restricted to acidic conditions ( $\text{pH} \leq 3$ ) [1]. In the past decades, various iron oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{FeOOH}$ ) and supported iron catalysts have been applied in heterogeneous Fenton-like reactions to replace dissolved  $\text{Fe}^{2+}/\text{Fe}^{3+}$  catalysts, since they can be recycled and the processes can be carried out over a wide pH range [2–4]. These catalysts, however, generally show low activity for generating  $\cdot\text{OH}$ . For heterogeneous Fenton-like reactions, catalytic decomposition of  $\text{H}_2\text{O}_2$  into  $\cdot\text{OH}$  mainly contains two steps: initially, the interaction of  $\text{H}_2\text{O}_2$  with the active sites; second, reversible electron transfer between  $\text{H}_2\text{O}_2$  and active sites ( $\text{Fe(II)/Fe(III)}$ ). In the overall reaction, the reaction rate is strongly dependent on the number of exposed active sites and the reduction of Fe(III) to Fe(II) by  $\text{H}_2\text{O}_2$  ( $0.001\text{--}0.02\text{ M}^{-1}\text{ s}^{-1}$ ), which has been demonstrated to be the rate-limiting step in homogeneous and heterogeneous Fenton-like reactions [4].

In the past decades, porous solid matrices such as activated carbon, zeolites, silica, and clays have been used for immobilizing active iron species to enhance their catalytic activity [5–8]. However, the active species are generally unevenly distributed and the surface area decreases, attributable to pore blockage. The photo-Fenton or electro-Fenton process has been found to accelerate the reduction of Fe(III) to Fe(II) and improve the catalytic performance with the assistance of light or electricity [9,10]. However, the need for specific equipment and energy consumption will increase the cost of these processes. Thus, exploring highly effective heterogeneous Fenton-like catalysts with large numbers of exposed active sites and effective reduction from Fe(III) to Fe(II) is of considerable significance.

Iron-based metal organic frameworks (MOFs) are hybrid solids with periodic network structures constructed from metal ions/clusters and organic ligands. The specific textural properties of MOFs, such as wide distribution of single iron sites, porous structures, and large surface areas, endow them with abundant exposed active sites and favorable access of reactants to active sites, making them promising alternatives to traditional heterogeneous catalysts. Recently, MIL-53-Fe and FeII@MIL-100(Fe) have been applied in the Fenton-like reaction for dye degradation [11,12], yet the catalytic efficiency of MOFs still needs to be improved and the reaction mechanism is unclear. Generally,  $\cdot\text{OH}$  is generated from electron transfer between the complex of  $\text{H}_2\text{O}_2$  and iron sites. Thus, the formation of the  $\text{H}_2\text{O}_2$ –iron complex on the surfaces of

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catalysts is the key step in the generation of  $\cdot\text{OH}$ . As a Lewis base,  $\text{H}_2\text{O}_2$  tends to adsorb onto the Lewis acid sites. Therefore, it is deduced that the iron, coordinatively unsaturated or occupied by some replaceable ligands such as water, is the active site on the surfaces of heterogeneous Fenton-like catalysts.

Recently, open iron sites, which are accessible and coordinatively unsaturated, were found in MIL-88B-Fe [13]. MIL-88B-Fe, a 3D porous MOF, is constructed from 1,4-benzenedicarboxylic acid (BDC) and trimeric Fe octahedral ( $\text{Fe}_3\text{-}\mu_3\text{-oxo}$ ) clusters. Within the trimeric ( $\text{Fe}_3\text{-}\mu_3\text{-oxo}$ ) clusters, Fe atoms exhibit an octahedral environment with open iron sites, which are terminated by some non-bridging ligands such as water or halogen/hydroxide anionic ligands [13]. Previous studies revealed that the nonbridging ligands could be replaced by Lewis bases [14,15]. Thus,  $\text{H}_2\text{O}_2$  can be adsorbed onto the iron sites of MIL-88B-Fe by displacing these ligands, which is the essential step in the Fenton-like reaction. The electron-rich organic ligands (BDC) could donate electrons to the center Fe ions [16], which may increase the redox potential of  $\text{Fe(II)/Fe(III)}$  and thus enhance reduction of  $\text{Fe(III)}$  to  $\text{Fe(II)}$  [17]. Moreover, MIL-88B-Fe undergoes a very large swelling (85% increase of its cell volume) upon exposure to polar solvents such as water and can maintain its open-framework topology [18]. This property is favorable for reactant transfer in MIL-88B-Fe. From these advantages, MIL-88B-Fe is expected to be a promising Fenton-like catalyst.

In this work, MIL-88B-Fe with chemical composition  $\text{Fe}_3\text{O}[\text{C}_6\text{H}_4(\text{CO}_2)_2]_3\text{X}\cdot n\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}^-$  or  $\text{OH}^-$ ) was employed as a heterogeneous Fenton-like catalyst. The influence of reaction parameters (e.g., pH and catalyst and  $\text{H}_2\text{O}_2$  concentration) on the catalytic activity of MIL-88B-Fe and the  $\text{H}_2\text{O}_2$  catalytic decomposition mechanism was investigated. Moreover, the catalytic activity of MIL-53-Fe and MIL-101-Fe, which contain the same organic ligand but different structures from MIL-88B-Fe, was tested to explore the relationship between the catalytic activity of iron-based MOFs and their structures.

## 2. Materials and methods

### 2.1. Chemicals and materials

1,4-Benzenedicarboxylic acid (BDC), benzoic acid,  $\text{Fe}_2\text{O}_3$ ,  $\alpha\text{-FeOOH}$ , and  $\text{Fe}_3\text{O}_4$  were obtained from the Aladdin Industrial Corporation (China).  $\text{H}_2\text{O}_2$  (30%),  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ ,  $\text{N,N}$ -dimethyl formamide, methanol, isopropyl alcohol,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaOH}$ , and  $\text{H}_2\text{SO}_4$  were purchased from the Damao Chemical Reagent Factory (Tianjin, China) and the Fuyu Chemical Co., Ltd. (Tianjin, China).  $\text{T-Butyl}$  alcohol (TBA) was bought from the Bodi Chemical Co., Ltd. (Tianjin, China). All chemicals were analytical grade and used without further purification. Ultrapure water (18.2 M $\Omega$ ) was used throughout the experiments.

### 2.2. Synthesis of catalyst

MIL-88B-Fe was prepared by a solvothermal method according to the procedure in the literature [19]: briefly, hydrothermal treatment of  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  (270 mg) and 1,4-benzenedicarboxylic acid (116 mg) in  $\text{N,N}$ -dimethyl formamide (5 mL) with  $\text{NaOH}$  (2 M, 0.4 mL) at 100 °C for 12 h. After solvothermal treatment, the as-synthesized MIL-88B-Fe was collected by filtration and washed with DMF, methanol, and water at 50 °C until the supernatant became colorless. Finally, it was activated overnight at 110 °C. The obtained catalysts were stored in a glass desiccator.

### 2.3. Characterization of catalyst

Powder X-ray diffraction (XRD) of catalysts was performed on an EMDPREAN diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) over a  $2\theta$  range of 5°–40°. Scanning electron microscopy (SEM) images were obtained on an S-4800 type SEM (Hitachi, Japan) and transmission electron microscopy (TEM) images were obtained on a Tecnai G2 F30 S-Twin type TEM (FEI Company, USA). The Brunauer–Emmett–Teller (BET) specific surface area was determined by nitrogen adsorption in Quantachrome SI (USA) at 77 K. The thermal stability was measured on a TG-DTG 6300 thermogravimetric analyzer (EXSTAR, Japan) by heating samples to 600 °C at a rate of 5 °C/min in 60 mL/min air flow. The organic groups on the surfaces of catalysts were investigated by infrared spectroscopy (IR), which was recorded on a Bruker VERTEX 70 FTIR spectrometer in the wavenumber range from 4000 to 500  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  at room temperature. The coordinatively unsaturated irons in catalysts were tested by CO adsorption infrared spectra [20]. Elemental analysis of catalysts and the concentrations of leached irons during Fenton reaction were tested by inductively coupled plasma optical emission spectroscopy (ICP, Perkin Elmer Optima 2000, USA). The elemental valence state of catalysts was investigated by X-ray photoelectron spectroscopy, which was performed on an ESCALAB 250XI (Thermo Fisher Scientific, USA). The C1s peak at 284.6 eV was used to calibrate peak positions.

### 2.4. Catalytic activity test

Phenol was selected as a target pollutant to evaluate the catalytic activity of MIL-88B-Fe, as it is a ubiquitous pollutant and an important intermediate in industrial processes. The degradation experiments were carried out in a batch mode using a three-necked flask (250 mL) at room temperature. The pH was adjusted with  $\text{NaOH}$  (0.1 M) or  $\text{H}_2\text{SO}_4$  (0.1 M). In a typical experiment, MIL-88B-Fe was dispersed in phenol solution (50 mg/L, 150 mL) at a specific pH by sonication for 2 min. Then the degradation reaction was initiated by adding  $\text{H}_2\text{O}_2$  under magnetic stirring. At predetermined time intervals, samples were withdrawn and filtered through 0.22  $\mu\text{m}$  membrane filters to remove suspended MOFs. Meanwhile, an aliquot of 1 M isopropyl alcohol was immediately added to quench the reaction, and then the concentration of phenol was analyzed. After reaction, MIL-88B-Fe was separated by filtration, washed with water and methanol, and then reused in a new reaction after being dried at 110 °C. This process was repeated several times to test the reusability of MIL-88B-Fe. The performance of  $\text{H}_2\text{O}_2$  oxidation without MIL-88B-Fe and the amount of phenol adsorbed by MIL-88B-Fe were tested as control experiments. Each degradation experiment was run in triplicate. The reported data are arithmetic means of three measured values.

### 2.5. Analytical methods

The concentration of phenol was analyzed on a high-performance liquid chromatograph (Agilent 1200) equipped with a diode array detector (DAD) and a C18 reversed-phase column (5  $\mu\text{m}$ , 4.6 mm  $\times$  150 mm). The mobile phase was a mixture of methanol and water (55:45, v/v) at a flow rate of 1.0 mL/min with a column temperature of 30 °C, and the analytical wavelength was 270 nm. The total organic carbon (TOC) was measured using a multi N/C 2100S (Analytikjena, Germany). The main reactive oxidative species generated in the systems were tested by electron paramagnetic resonance (EPR) and radical quencher experiments. For the EPR test, 20  $\mu\text{L}$  of 0.1 M DMPO was added rapidly into a 1 mL sample after filtration to form a DMPO–radicals adduct. The EPR spectra were obtained on a Bruker 300E spectrometer

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