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Research paper

# Effect of electronic migration of MIL-53(Fe) on the activation of peroxymonosulfate under visible light

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ABSTRACT

In this study, metal-organic framework (MOF) MIL-53(Fe) was synthesized. MIL-53(Fe) is capable of activating peroxymonosulfate to achieve highly efficient rhodamine B (RhB) degradation under visible light, and MIL-53(Fe) shows good photocatalytic activity in a wide pH range. The results of the recycling experiments, X-ray diffraction patterns, and Fourier transform infrared spectra of MIL-53(Fe) before and after the catalytic reaction revealed that MIL-53(Fe) is stable. Electron paramagnetic resonance tests indicated that sulfate radicals are the dominant reactive species in RhB degradation. This study provides some guidance in the exploration and utilization of MOFs for environmental remediation.

## 1. Introduction

Recently, peroxymonosulfate (PMS) has received increasing attention as an emerging oxidizing agent because of its unique features. PMS is one of the most potent known oxidants in aqueous solutions and has a higher potential than $H_2O_2$. PMS is relatively stable and therefore can be transferred through considerable distances in a subsurface; furthermore, it can be activated to produce sulfate radicals ($SO_4^{\cdot-}$), which behave like hydroxyl radicals with an unselective oxidation pattern and are very reactive with a wide range of contaminants. There are many methods to activate $HSO_5^-$. For example, PMS can be activated through ultraviolet (UV) light irradiation and heat [1] or using low-valent metals ($Mn^+$), such as $Fe^{2+}$ and $Ag^+$ [2]. However, in these homogeneous processes, the poor circulation performance and the precipitation of the metal ion lead to secondary pollution and environmental harm [3].

Recent studies have revealed that photocatalysis is a highly valuable method for solar-to-chemical energy conversion, and it has been widely studied for environment cleaning. In photocatalysis technology, semiconductor materials are excited by visible light (Vis) to produce electron-hole pairs, which are then separated and transferred to target objects for redox reactions. PMS can act as an electron acceptor in photocatalytic reactions. The recombination of electrons and holes can be suppressed effectively by introducing PMS. Chen et al. found that PMS can be used as an efficient oxidant to accelerate the aqueous degradation of AO7 using visible light and $TiO_2$ [4].

MIL-53(Fe) is a three-dimensional porous solid composed of infinite one-dimensional —Fe—O—O—Fe—O—Fe— linkages and cross-linked by bis-bidentate terephthalate linkers. MIL-53(Fe) has advantages over conventional photocatalytic semiconductor systems such as more efficient harnessing of solar energy, small Fe-O cluster size, and limited recombination of the photogenerated charge carriers, and thus, superior photoactivities can be expected for such metal-organic frameworks. In an earlier study, it was found that MIL-53(Fe) can activate $H_2O_2$ and persulfate for potential environmental photocatalysis applications [5,6]. A study by Ai et al. [5] revealed that $H_2O_2$ could capture the photogenerated electrons to produce $\cdot OH$ radicals to degrade rhodamine B (RhB) when MIL-53(Fe) is irradiated with visible light. Gao et al. [6] reported that the introduction of persulfate accelerates the photocatalytic degradation of AO7 over MIL-53(Fe) under visible light irradiation by a light-emitting diode (LED). The fast recombination of photogenerated electron-hole pairs can be suppressed by adding persulfate to the catalytic system. However, the issue of electron migration remains to be solved.

In this study, the effect of the activation by PMS on the photocatalytic degradation of RhB over MIL-53(Fe) upon visible light irradiation was revealed. With the assistance of PMS, the photocatalytic degradation of RhB was faster. The electron migration in the Fe-O clusters was investigated through electron paramagnetic resonance (EPR) spectroscopy experiments.

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## 2. Experimental

### 2.1. Materials

$FeCl_3 \cdot 6H_2O$, terephthalic acid ($H_2BDC$), dimethylformamide (DMF), RhB, $H_2O_2$ (30%, v/v), HCl, and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. All chemicals used in this study were commercially available and of analytical grade.

### 2.2. Preparation of metal-organic framework MIL-53(Fe)

Metal-organic framework MIL-53(Fe) was prepared using a mild solvothermal process. Typically, a mixture of $FeCl_3 \cdot 6H_2O$, $H_2BDC$, and DMF in a molar ratio of 1:1:70 was stirred for 60 min at room temperature until a clear solution was formed; then, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 150 °C for 5 h for heat treatment, after which the autoclave was allowed to cool naturally to room temperature. Then, the resultant precipitate was separated by centrifugation and then washed repeatedly with deionized water and ethanol. Finally, the samples were dried at 60°C under vacuum overnight.

### 2.3. Sample characterization

Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 Advance diffractometer operating with a Cu-Kα source to investigate the crystal structures of the samples. The morphologies were examined with a Hitachi S4800 scanning electron microscope. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) was employed to investigate the chemical compositions of the samples. The Fourier transform infrared (FTIR) spectra were recorded on a NICOLET 5700 FT-IR Spectrometer using KBr pellets. UV–visible (UV–vis) diffuse reflectance spectra were recorded on a UV-Vis-NIR spectrophotometer (UV-U4100, Hitachi, Japan). The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. The pore volumes and pore diameter distributions were derived from the adsorption isotherms using the Barrett-Joyner-Halenda (BJH) model.

### 2.4. Degradation experiments

The visible light photocatalytic degradation of RhB over MIL-53 (Fe) in the presence of PMS was carried out in a visible-light LED photoreactor, which consisted of a 500 mL glass beaker; the reactions were stirred at 25 °C at a distance of 12 cm from the LED lamps. Into a 500 mL glass beaker were added 0.05 g of MIL-53 (Fe) and 50 mL of RhB solution (40 mg $L^{-1}$). The solution was magnetically stirred in the dark for 30 min to ensure adsorption/desorption equilibrium. Afterward, PMS (100 mg $L^{-1}$) was added into the glass beaker, and then the solution was stirred at a constant speed with a magnetic stirrer and illuminated by the LED lamps. During the reaction, 1 mL of the sample solution was removed from the glass beaker at certain time intervals and centrifuged to remove the particles. Residual RhB was diluted by one-third using deionized water. Then, it was measured using a UV–vis spectrophotometer (UV-5100B, Metash, Shanghai) at a wavelength of 554 nm.

## 3. Results and discussion

### 3.1. Characterizations

The PXRD results for MIL-53(Fe) are shown in Fig. 1(a). The pattern of MIL-53(Fe) is in good agreement with the simulated one and indicates that MIL-53(Fe) is highly crystalline [7,8], the characteristic peaks of were at 2θ of 9.3°, 12.6°, 17.3°, thus demonstrated that pure MIL-53(Fe) was prepared successfully in this condition. The intensity of the sample diffraction peaks is low, because the synthesis time of the sample is 15 h, and the synthesis time is short, which results in the crystals being in the process of crystallization without complete growth. The chemical structure of MIL-53(Fe) was determined using FTIR spectroscopy. The FTIR spectra of $H_2BDC$ and MIL-53(Fe) are shown in Fig. 1(b). The characteristic absorption peaks of MIL-53(Fe) were observed at 1687, 1535, 1390, 750, and 534 $cm^{-1}$. The absorption band at 1687 $cm^{-1}$ corresponds to the stretching vibration of C=O bonds. The two sharp peaks at 1535 and 1390 $cm^{-1}$ were assigned to the asymmetric and symmetric vibrations of carboxyl groups, respectively, confirming the presence of dicarboxylate linkers within the sample [8]. The band located at 750 $cm^{-1}$ was attributed to the C—H bending vibrations of the benzene rings in the organic linker [9,10]. The peak at 534 $cm^{-1}$ corresponds to the stretching vibration of Fe—O bonds, indicating the formation of the Fe—O cluster between the inorganic metal and the carboxylic group of terephthalic acid [11].

The particle size and specific surface area of the MIL-53(Fe) sample were examined using scanning electron microscopy (SEM) (Fig. 2(a)). Fig. 2(b) show the nitrogen adsorption-desorption isotherms of MIL-53(Fe). MIL-53(Fe) is composed of sphere-like particles with a particle size distribution of 100–600 nm. MIL-53(Fe) is built up from terephthalate anions and trans chains of metal(III) octahedra are sharing OH groups, creating a

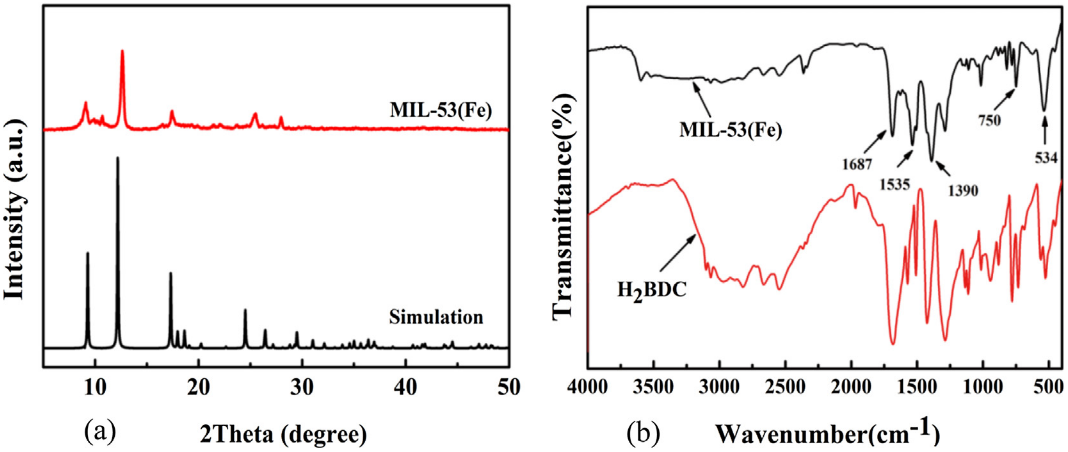

**Fig. 1.** (a) XRD patterns of MIL-53(Fe) and calculated MIL-53(Fe). (b) FTIR spectrum spectra of MIL-53(Fe) and $H_2BDC$.