

# Rapid decolorization of dyes in heterogeneous Fenton-like oxidation catalyzed by Fe-incorporated Ti-HMS molecular sieves



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## ABSTRACT

Fe-incorporated Ti-HMS molecular sieves were used as the new bimetallic catalysts for decolorization of methyl orange and methylene blue in heterogeneous Fenton-like oxidation. For comparison,  $\text{Fe}^{2+}/\text{HMS}$ ,  $\text{Fe}^{3+}/\text{HMS}$ ,  $\text{Fe}^{2+}/\text{Ti-HMS}$  and  $\text{Fe}^{3+}/\text{Ti-HMS}$  were synthesized via a room temperature crystallization method and characterized by a series of techniques including XRD, UV–vis spectroscopy, FT-IR, TEM and  $\text{N}_2$  physical sorption. UV–vis result confirmed that Fe species and framework Ti were successfully grafted in HMS. FT-IR result showed that the synergy effect of framework Ti on Fe species in Fenton-like catalysis possibly originated from the interaction between Fe–O–Si and Ti–O–Si bonds.  $\text{N}_2$  sorption showed that all the samples possessed the pores and surface properties of classic HMS, which provided sufficient space for adsorption and reaction.  $\text{Fe}^{2+}/\text{Ti-HMS}$  with the mole ratio of Si:Fe at 50:1 obtained the highest decolorization of dyes of the four samples, which was attributed to the valence change of  $\text{Fe}^{2+}$  and the promotion of hydroxyl radicals by framework Ti. This Fenton-like reaction should be performed at pH 3. Reaction temperature showed exactly the opposite effect on decolorization of methyl orange and methylene blue. Rapid decolorization for the two dyes solution with a concentration of  $10^{-4}$  M was able to be achieved over  $\text{Fe}^{2+}/\text{Ti-HMS}$  using a low concentration of  $\text{H}_2\text{O}_2$  as oxidant.

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## 1. Introduction

Dyes wastewater has become an increasing threat to the environment and the health of human beings because of its coloring, toxicity and non-biodegradable characteristics. It is estimated that the global consumption of dyes is over 10,000 t every year, and about 10% is discharged without any industrial treatment, for the lacking of effective technology or the high cost of treatment [1,2]. Many technologies such as precipitation [3], adsorption [4], chemical oxidation [5] and photocatalysis [6–8] have been put into practice for the removal of dyes to decontaminate drinking water and industrial wastewaters. The advanced oxidation processes (AOPs) based on the chemical destruction are effective and simple methods to give the complete solution to the problem of dye pollutants compared with others in which only a phase separation is realized with the subsequent problem of the final disposal [9,10]. AOPs generally include photocatalytic oxidation, Fenton's chemistry and ozonation. These processes have in common to generate hydroxyl radicals ( $\text{HO}^\bullet$ ) allowing the

mineralization of dyes molecules under mild conditions. Fenton process is considered as a mature AOP for dyes degradation by means of highly oxidative hydroxyl radical. Homogeneous Fenton process catalyzed by  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  systems were initially studied, based on which many Fenton-like ( $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ ) systems were reported [10–13]. Although high reaction rates were generally obtained with homogeneous Fenton-catalysts, such systems had significant disadvantages, such as the narrow pH range at 2.5–3.0, the difficulty of catalyst recovery and the secondary pollution caused by iron oxide sludges [10].

Heterogeneous Fenton-like process, which is able to overcome the shortcomings of homogeneous Fenton process, has received increasing attention primarily for environmental reasons. In this technique, the Fe-containing heterogeneous catalysts become the research focus. Researchers have developed various Fenton-like catalysts mainly including Fe-containing materials with catalytic activities similar to homogeneous Fe(II) ions. Fe ions or Fe species have been grafted in many kinds of substrates such as membrane [14], molecular sieves [15–17], carbon materials [18,19], and solid oxides [20,21]. It is worth mentioning that the immobilization and stability of Fe species in support should be first concerned to avoid the losing of activity center and the secondary pollution in water. Molecular sieves, which possess high specific surface area, are the

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most promising substrates for Fe species immobilization and dispersion. In addition, their adjustable pores and the capacious channels can facilitate the adsorption and conversion of bulky pollutant molecules. It has been reported that the molecular sieves such as ZSM-5 [15], MCM-41 [16] and SBA-15 [17] have been widely used as the substrates of Fenton-like catalysts. In order to enhance the catalytic performance for Fenton reaction, some active metal species (Al, Ce or Ti) was previously modified on molecular sieves and then a synergistic effect originating from metal-support can be obtained [22–24]. However, there are few reports on Fe contained catalysts promoted by Ti used in water treatment of Fenton process [24,25].

In this work, we present the synthesis and application of Fe<sup>2+</sup> or Fe<sup>3+</sup> incorporated Ti-HMS as a heterogeneous Fenton-like catalyst for decolorization of methyl orange and methylene blue. Methyl orange (MO) and methylene blue (MB), as shown in Scheme 1, are two typical organic dyes which are widely used in textile industry [26]. It is significant to remove methyl orange and methylene blue from the waste water because of their cancerogenic and teratogenic risk. HMS (Hexagonal mesoporous silica), which is a type of molecular sieve with wormlike mesopores and is easy to be decorated by other metal species, has been confirmed to be an excellent material for the conversion of many bulky reactants. Fe and Ti as the bimetallic active centers are expected to be synchronously introduced in HMS and to achieve a synergistic or promotion effect of Framework Ti on Fe species in Fenton reactions. A comparative study is focused on decolorization of dye with a high concentration over Fe<sup>2+</sup> or Fe<sup>3+</sup> incorporated Ti-HMS of HMS in order to find an idea material that can potentially improve the Fenton process, as well as improve the utilization of H<sub>2</sub>O<sub>2</sub>.

## 2. Materials and methods

### 2.1. Materials

Tetraethylorthosilicate (TEOS, AR), ethanol, isopropyl alcohol (IPA, AR) and H<sub>2</sub>O<sub>2</sub> (30 wt%, AR) were purchased from Tianjin Kaixin Chemical Co. Tetrabutylorthotitanate (TBOT, AR) and dodecylamine (DDA, AR) were purchased from Shanghai Chemical Co. HCl (AR) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (AR) were purchased from Beijing Wanchengyuanxing Chemical Co. FeSO<sub>4</sub>·7H<sub>2</sub>O (AR), methyl orange and methylene blue were purchased from Tianjin Hengxing Chemical Co.

### 2.2. Catalyst synthesis

Fe incorporated Ti-HMS was synthesized based on the synthesis of HMS and Ti-HMS via a room temperature crystallization method [27]. In detail, solution A was prepared by slowly adding the aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub> or FeSO<sub>4</sub> (14.25 mL) in the mixture of ethanol (9.6 mL) and DDA (1.25 g) under vigorous stirring, then the pH was adjusted by diluent HCl (2.1 mL, 0.24 M). Solution B was prepared by adding TEOS (5.6 mL) in the IPA solution of TBOT (2.1 mL) under stirring. Solution B was slowly dropped in solution A and crystallized at room temperature for 18 h under vigorous stirring. The product with a theoretical mole ratio of Si:Ti:Fe at 50:1:1 (unless otherwise noted) was filtered, washed and dried at 353 K. Finally, the sample denoted as Fe<sup>3+</sup>/Ti-HMS (or Fe<sup>2+</sup>/Ti-HMS) was obtained after the organic template DDA was removed under

913 K calcination. For comparison, we synthesized two other samples without adding IPA solution of TBOT, which were denoted as Fe<sup>3+</sup>/HMS and Fe<sup>2+</sup>/HMS.

### 2.3. Characterization

Fe content of the catalyst was determined by ICP (Leeman Plasma-Spec-II). The mole ratio of SiO<sub>2</sub>/TiO<sub>2</sub> was analyzed on a Bruker SRS-3400 sequential X-ray spectrometer (XRF). Powder X-ray diffraction (XRD) patterns were recorded using Rigaku D/Max 2400 diffractometer employing Cu K $\alpha$  radiation. N<sub>2</sub> adsorption isotherm was measured using an ASAP 2420 (Micrometrics Instruments) surface area analyzer. The pore size distribution was calculated from the Barrett–Joyner–Halenda (BJH) model. UV–vis spectra were obtained on a JASCO UV550 spectrometer with BaSO<sub>4</sub> as the internal standard. FT-IR spectra were recorded on a Nicolet Thermo 360 spectrometer, using the KBr pellet technique. Transmission electron microscopy (TEM) images were taken on JEM-2100HR (JEOL Company) with an acceleration voltage of 200 kV.

### 2.4. Decolorization experiments

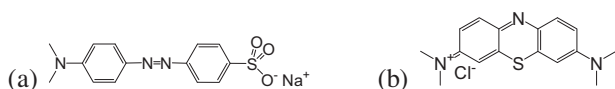
A series of experiments were performed to measure the activity of Fenton-like catalysts for degradation of methyl orange and methylene blue, respectively. All the experiments were carried out at desired temperature. In detail, 0.1 g of catalyst was added to 100 mL of methyl orange or methylene blue solution with an initial concentration of 10<sup>-4</sup> M, the pH of which was previously adjusted by diluent solution of HCl or NaOH. After the suspension reaching the adsorption equilibrium in 30 min, H<sub>2</sub>O<sub>2</sub> (0.05 M in reaction solution) was added to start the Fenton-like reaction. The reaction solution in a time interval was sampled, filtered and diluted, then analyzed using a TU-1800 UV–vis spectrophotometer immediately, during which the reaction was not stopped. The degradation effect was measured by  $D = C_t/C_0 = A_t/A_0$ , where  $C$  is concentration and  $A$  is absorbance. Total organic carbon (TOC) in treated water was determined by a TOC-4100 analyzer to evaluate the degree of dyes mineralization.

## 3. Results and discussion

### 3.1. Catalyst characterization

Fe content and SiO<sub>2</sub>/TiO<sub>2</sub> mole ratio of each sample was determined by ICP and XRF, respectively, which is listed in Table 1. The actual mole ratio of Si/Fe is close to the theoretical value, showing that Fe species is able to be effectively immobilized via room temperature crystallization method. The actual content of Ti denoted as SiO<sub>2</sub>/TiO<sub>2</sub> is reasonable compared with other report [27] and the introduction of Fe shows no affect on Ti content.

Fig. 1 gives the low-angle XRD patterns of the catalysts. Each of the samples shows a reflection peak at 2.4°. The peak is characteristic of wormhole structure of HMS which possesses short range order with uniform pore diameter [27]. We can also see that Fe<sup>2+</sup>/Ti-HMS and Fe<sup>2+</sup>/HMS show more intense peaks than



Scheme 1. Chemical structures of (a) methyl orange and (b) methylene blue.

Table 1  
Compositions of the catalyst samples.

Sample	Gel Si/Fe (mol/mol)	Product Si/Fe (mol/mol)	Gel SiO <sub>2</sub> /TiO <sub>2</sub> (mol/mol)	Product SiO <sub>2</sub> /TiO <sub>2</sub> (mol/mol)
Ti-HMS	–	–	50	41
Fe <sup>3+</sup> /Ti-HMS	50	47	50	41
Fe <sup>2+</sup> /Ti-HMS	50	48	50	41
Fe <sup>3+</sup> /HMS	50	46	–	–
Fe <sup>2+</sup> /HMS	50	47	–	–

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