



Magnetic ordered mesoporous copper ferrite as a heterogeneous Fenton catalyst for the degradation of imidacloprid



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ABSTRACT

Highly ordered mesoporous copper ferrite (meso-CuFe₂O₄) with high surface area and large pore size was successfully fabricated and firstly proposed as a heterogeneous Fenton catalyst. It was synthesized through the nanocasting strategy by using KIT-6 as hard template. The morphology and physicochemical properties of meso-CuFe₂O₄ were characterized by SEM, TEM, XRD, XPS, FT-IR, Raman spectra, etc. The obtained results showed that the surface area and the pore size of meso-CuFe₂O₄ were 122 m² g⁻¹ and 9.2 nm, respectively. The meso-CuFe₂O₄ presented excellent catalytic activity for the degradation of imidacloprid, achieving almost complete removal of 10 mg L⁻¹ imidacloprid after 5 h at the reaction conditions of 0.3 g L⁻¹ catalyst and 40 mM H₂O₂. Kinetic analysis showed that the degradation of imidacloprid follows the pseudo-first order. The apparent rate constant for meso-CuFe₂O₄ was 1.0445 h⁻¹, which was 1.5, 2 and 2.5 times than those of meso-CoFe₂O₄, con-CuFe₂O₄ and nano-Fe₃O₄, respectively. The amount of hydroxyl radical (*OH) generated was directly proportional to the degradation efficiency of imidacloprid, suggesting the involvement of *OH in oxidizing imidacloprid. The obtained results indicated that meso-CuFe₂O₄ presented the highest activity, which was not only due to its ordered mesoporous structure with high surface area and large pore size, but also assigned to the redox recycle of Fe²⁺/Fe³⁺ and Cu⁺/Cu²⁺ in meso-CuFe₂O₄. The special effect of Cu was discussed in terms of the thermodynamically favorable Fe³⁺ reduction by Cu⁺, regenerating the active species Fe²⁺. The meso-CuFe₂O₄ presented very low iron leaching (<1 ppm) even in acidic condition and retained almost its high catalytic activity after 5 consecutive runs. Besides, meso-CuFe₂O₄ possessed medium saturation magnetization, which had provided a potential advantage for the recovery and reuse of catalyst.

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1. Introduction

Fenton technology is one of the powerful and widely used advanced oxidation processes (AOPs) for the treatment of industrial wastewater containing non-biodegradable organic pollutants. However, the classical homogeneous Fenton process has two significant defects: (i) limited by a narrow pH range (pH 2–3); (ii) producing a large iron sludge at the end of process, which increases the cost for the treatment of wastewater. To overcome these drawbacks of homogeneous Fenton, heterogeneous Fenton-like catalysis has been developed [1]. In the past decades, the potential applications of heterogeneous catalysts have been investigated widely. Various kinds of iron oxides and iron hydroxides, such as Fe₃O₄, α-Fe₂O₃ and α-FeOOH have already been used to catalyze the decomposition of organic pollutants. However,

many of them presented weak catalytic activity [2], which limited the practical application of heterogeneous Fenton-like catalysts. Moreover, the leaching of Fe contents from the bulk catalysts to the solution and the difficulty to separate them from the treated water leads to depletion of their catalytic activity in the long term [3]. Therefore, to fabricate a catalyst with higher activity, better stability and reusability is the goal of the scientists who are dedicating to heterogeneous Fenton-like catalysis.

Recently, various strategies have been developed to enhance the activity of heterogeneous Fenton catalyst, e.g. reducing the size of catalyst to nano-scales to increase the surface energy [4], loading the catalysts on carriers with high surface area to improve their dispersion [5], and introducing suitable transition metal (such as Ti, Co, Mn, Cr and V) into the structure of Fe₃O₄ to enhance the catalytic activity [6–13]. Particularly, the last one has been paid more attention due to the fact it could significantly improve the activity of catalysts. For example, Costa et al. [6,7] reported that the isomorphic substitution of Fe²⁺ by Co²⁺ and Mn²⁺ can remarkably increase the activity of Fe₃O₄. In addition, the stability and reusability of catalysts are also important for their practical application in the

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treatment of waste water. In previous reports, the stability of catalyst could be increased by modifying the surface of catalyst with inorganic or organic substance [14,15]. And the issue that catalysts are difficult to separate from the treated water could be solved by using magnetic materials as heterogeneous catalyst [16,17]. If one material possesses the advantages of high reactivity, good stability and ability to be magnetically separated, it can be applied in a wide range of fields.

Copper ferrite, CuFe_2O_4 , is a magnetic spinel material with cubic structure. Due to its medium saturation magnetization, excellent chemical stability and mechanical strengths, CuFe_2O_4 has already attracted extensive attention in the potential applications such as water gas shift reaction, CO oxidation, decomposition of gaseous pollutants and other reactions [18]. Recently, Zhang and Ding et al. [19,20] reported nanoscaled magnetic CuFe_2O_4 as a heterogeneous catalyst for the catalytic activation of peroxymonosulfate to generate sulfate radicals. However, the surface area of CuFe_2O_4 MNPs (magnetic nanoparticles) prepared by solid phase synthesis or sol-gel combustion method was very low (usually lower than $10\text{ m}^2\text{ g}^{-1}$). Such a low ratio of surface area to mass imposes limits on the resulting material's catalytic activity and applicability. This problem might be solved by fabricating heterogeneous catalyst with porous structure. As we all know, ordered mesoporous materials are ideal candidate as heterogeneous catalyst not only because of their high surface area but also the large pore in their structure network. The mesopore of 2–50 nm is in favor of the adsorption of the macromolecules and can largely reduce the mass transfer resistance [21]. For instance, Su et al. [22] synthesized mesoporous zinc ferrite by a hydrothermal process and used it as photocatalyst toward the degradation of Acid Orange II. Sahoo et al. [23] reported magnetic mesoporous manganese ferrite nanocomposites which were used as a catalyst for the degradation of methyl orange dye.

In this work, highly ordered mesoporous CuFe_2O_4 was synthesized through the nanocasting strategy and used as a powerful candidate of heterogeneous Fenton-like catalyst for the degradation of imidacloprid. Imidacloprid, one of the insecticides most used in agricultural areas, was selected as a model pollutant for evaluating the catalytic activity of spinel catalyst, because it is highly soluble in water (0.58 g L^{-1}) and remains stable in it for more than 30 days [24]. The main purpose of this study is to elucidate the effect of ordered mesoporous structure and the role of copper and iron on the catalytic activity of CuFe_2O_4 in the heterogeneous Fenton reaction. For comparison, ordered mesoporous CoFe_2O_4 synthesized by the same method, conventional CuFe_2O_4 synthesized by solid-phase method and Fe_3O_4 were prepared as reference catalysts. Additionally, the possible mechanism was proposed on the basis of the detected $\cdot\text{OH}$ radical and the surface reaction revealed by comprehensive characterizations. Finally, the stability and reusability of the catalyst was evaluated.

2. Experimental

2.1. Reagents

Tetraethylorthosilicate (TEOS), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), butyl alcohol, hydrochloric acid (HCl), sodium hydroxide (NaOH), *n*-hexane for preparation of ordered mesoporous CuFe_2O_4 and CoFe_2O_4 were obtained from Sinopharm Chemical Reagent Co., Ltd., SCRC, China. H_2O_2 (30%, v/v), ethanol, isopropanol and imidacloprid (IMI) were supplied by Aladdin Co., China. Triblock copolymer Pluronic P123 ($M_w = 5800$, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) was purchased from Sigma-Aldrich. All of the chemicals were reagent grade and used as received without further purification. Deionized water was used in all the experiments.

2.2. Preparation of samples

KIT-6 was synthesized according to the previous literature [25]. Highly ordered mesoporous CuFe_2O_4 and CoFe_2O_4 (denoted as meso- CuFe_2O_4 and meso- CoFe_2O_4 , respectively) were prepared through the nanocasting strategy [26], using the as-prepared KIT-6 as hard templates. The classical procedure for preparing meso- CuFe_2O_4 was carried out as follows: firstly, 0.288 g $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.962 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were per-mixed together with 0.5 g as-prepared KIT-6 powder and ground in an agate mortar in the presence of 10 mL of *n*-hexane to yield a homogeneous mixture. Afterwards, the resulting mixture was subsequently dispersed in 30 mL *n*-hexane and stirred overnight under reflux at 70°C . After cooling down, the solid products were recovered by filtration, dried in an oven at 70°C and calcined in a tubular furnace under air atmosphere with the heating rate of 1°C min^{-1} , then keeping the temperature at 600°C for 5 h. Finally, the silica template was selectively dissolved by 2 M NaOH solution in 60°C water bath under continuously vigorous stirring for 24 h, and the brown product was obtained by washing with distilled water and ethanol for three times and drying at vacuum oven. The meso- CoFe_2O_4 was fabricated in the same way. And the conventional CuFe_2O_4 and CoFe_2O_4 without mesoporous structure (denoted as con- CuFe_2O_4 and con- CoFe_2O_4) were prepared by using the traditional solid-phase method, the specific steps are as follows: the corresponding mixture in stoichiometric proportion of the $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were calcined at 600°C for 5 h with a heating rate of 1°C min^{-1} in air atmosphere. The Fe_3O_4 magnetic nanoparticles were synthesized by the chemical coprecipitation method [27] as previously reported in the literature, and the product was denoted as nano- Fe_3O_4 .

2.3. Characterization methods

Power X-ray diffraction (XRD) patterns were measured on a Bruker D8 Advance X-ray diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.540562\text{ \AA}$, 40 kV, 40 mA) as the X-ray source. The high-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL JEM-2100 transmission electron microscope. The scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 scanning electron microscope. N_2 adsorption-desorption analysis was measured on a Micromeritics TriStar 3000 instrument, Brunauer-Emmet-Teller (BET) special surface area was estimated from the relative pressure range from 0.05 to 0.20, pore volumes were determined using the adsorbed volume at a relative pressure of 0.99033, and the pore size distributions of the as-prepared samples were analyzed using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the N_2 adsorption-desorption isotherm. Fourier transform infrared spectra (FT-IR) were collected in the region from 400 to 4000 cm^{-1} at room temperature using a Nicolet 6700 spectroscopy on KBr pellets. Raman spectroscopy was performed by a Renishaw Raman microspectrometer using an Ar^+ ion laser (514.5 nm line) as the excitation source. X-ray photoelectron spectroscopy was recorded on a Kratos ASIS-HS X-ray photoelectron spectroscopy equipped with a standard and monochromatic source (Al $\text{K}\alpha$) operated at 150 W (15 kV, 10 mA). H_2 -TPR measurements were performed using AutoChem II 2920 instrument (Micromeritics). Prior to the TPR run, the fresh sample was pretreated in situ for 1 h at 200°C in air flow. After cooling and a step of purge of the lines in Ar flow, an H_2 :Ar mixture (H_2 :Ar volume ratio of 10% and total flow of 50 mL min^{-1}) was sent through the sample while increasing the temperature up to 800°C with a rate of $10^\circ\text{C min}^{-1}$. Finally, the magnetic properties were measured by a Lakeshore 735 vibrating sample magnetometer (VSM) at room temperature.

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