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Synthesis of stable burger-like α-Fe_2O_3 catalysts: Formation mechanism and excellent photo-Fenton catalytic performance

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ABSTRACT

The application of iron-based photocatalysts has attracted wide attention. Herein, we reported a novel burger-like α-Fe_2O_3 catalyst, which was synthesized via facile hydrothermal method and used as a heterogeneous catalyst for photo-Fenton degradation of aquatic organic pollutants. More interesting, the α-Fe_2O_3 samples with spherical, elliptic, olive-like and burger-like morphologies could be obtained by adjusting the hydrothermal reaction time, respectively. Field emission scanning electron microscopy (FESEM) analysis showed that the burger-like α-Fe_2O_3 particles have convex waists and hemispherical ends, and are composed of many irregular nanoparticles. Furthermore, we proposed the probable growth mechanism involving oriented aggregation and Ostwald ripening of the burger-like structures. Under the optimum operating conditions, the burger-like α-Fe_2O_3 catalyst exhibited 98% degradation efficiency and 62% removal rate of COD for acid red G (ARG) in aqueous solution. In addition, the spheroidal structure showed the excellent stability, the burger-like α-Fe_2O_3 catalyst still remained high catalytic activity after six cycling experiments, and the leached iron value accounted for only 0.32 wt‰ of the iron content in the catalyst. This work might offer a new viewpoint for the development of sufficiently stable and highly efficient iron-based heterogeneous catalyst.

1. Introduction

Due to the rapid development of textile dyeing industry, hundreds of dyes are used in large quantities. Azo dyes with one or more the nitrogen double bond accounted for more than half of all dyes (Bokare et al., 2008; Sun et al., 2009; Zhang et al., 2012a). Azo dye wastewater with harmfulness, durability and non-biodegradability has brought kinds of troublesome pollution. The removal of dyes in the wastewater is urgent from the point of view of sustainable development. At present, there are several methods to remove dye pollutants in wastewater, such as biological, physical, chemical and physicochemical techniques. However, these methods cannot completely destroy the structure of the dye molecules and the secondary products need to be further disposed (Wang et al., 2013).

Advanced oxidation technologies are more promising for treating dye wastewater, which can produce a large amount of highly reactive radicals to degrade toxic organic contaminants completely in wastewater (García and Hodaifa, 2017; Rodríguez et al., 2016; Jiang et al., 2017; Guo et al., 2017). Fenton is one of the advanced oxidation technologies, which has been valued due to high efficiency, wide applicability, low cost and easy operation. However, the classical homogeneous Fenton reaction was limited by large amount of iron sludge, which easily caused secondary pollution (Huang et al., 2016; Deng et al., 2008). In order to overcome this drawback, heterogeneous Fenton was chosen to replace homogeneous Fenton (Fida et al., 2017; Wang et al., 2014; Qian et al., 2017). Zhou et al. prepared magnetic carbon material as a highly efficient heterogeneous Fenton catalyst to remove methylene blue and solved the iron sludge problem (Zhou et al., 2015). Nguyen et al. prepared the Zn-doped Fe_3O_4 hollow spheres catalyst, which exhibited high catalytic efficiency for organic pollutants in a heterogeneous photo-Fenton process (Nguyen et al., 2017). Heterogeneous catalysts have occupied an increasingly important position in Fenton reagent. Nevertheless, most of heterogeneous Fenton reactions have the problem of leaching large number of iron. Duan et al. prepared ordered mesoporous carbon supported

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iron catalyst, which showed high efficiency for the degradation of 4-chlorophenol in heterogeneous Fenton system, but the total leached iron accounted for 23.4% of the iron content in the catalyst after three runs (Duan et al., 2014). It is still meaningful to improve the stability and reduce iron leaching of the catalyst in heterogeneous Fenton.

Fe_2O_3 has attracted much attention owe to its cheapness, hypotoxicity, chemical inertness (Pouran et al., 2014; Huang et al., 2017; Xu et al., 2012). Recently, because of some important applications, many researchers have focused their efforts on the synthesis of α-Fe_2O_3 micro- and nanocrystals with various morphologies, such as nanorods (Woo et al., 2010), hollow tubes (Xiong et al., 2004), nanoplates (Vayssieres et al., 2010), rings (Hu et al., 2010) mesoporous (Jiao et al., 2006), microcubes (Xiong et al., 2011). As we all know, the morphology of catalyst has important influence on its chemical and physical properties (Rao et al., 2013). Various α-Fe_2O_3 particles with unique structures exhibited excellent properties in many fields (Jiao et al., 2014; Wu et al., 2006; Zhang et al., 2012b; Li et al., 2017). Lu et al. prepared a heterogeneous Fe_2O_3/γ-Al_2O_3 catalyst, which showed excellent efficiency for treatment of phenol wastewater in heterogeneous Fenton system (Lu et al., 2015). However, the iron leaching after reaction was approximately 19 mg/L. The spheroidal structure was beneficial to recover the catalysts and increase the light harvesting of the catalysts in the photo-Fenton degradation process, and improving the stability and degradation efficiency (Xu et al., 2014; Zheng et al., 2015). Thus, the synthesis of α-Fe_2O_3 with the special morphology has attracted much more attention in recent years.

Herein, a burger-like α-Fe_2O_3 catalyst was synthesized via the hydrothermal process without further thermal treatment. We observed the different morphologies of α-Fe_2O_3 at different reaction stages, revealing the possible formation mechanism of burger shaped α-Fe_2O_3. Then, the catalytic activity of burger-like α-Fe_2O_3 was evaluated using ARG as a model pollutant. The influence of catalyst dosage, concentration of H_2O_2 and pH value on catalytic activity of the burger-like α-Fe_2O_3 was researched systematically. Moreover, the stability of the burger-like α-Fe_2O_3 catalyst was also studied.

2. Experimental

2.1. Synthesis

All of the reagents in this work were analytical purity, which were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai China). In a typical procedure, 45 mL ethanol aqueous solution (the volume ratio of deionized water and ethanol was 1:2) was added to a noncorrosive steel reactor with a Teflon liner of 100 mL. In addition, 0.025 mol NaOH and 0.06 mol $FeCl_3 \cdot 6H_2O$ were added to reactor under vigorous stirring, the suspension was further stirred for 40 min at room temperature. After that, the mixed solution was heated at 160 °C for 24 h and then cooled to room temperature naturally, the products were washed with deionized water and ethanol for three times respectively. Finally, the obtained black products were dried in a vacuum dryer at 60 °C for overnight. In order to research the formation mechanism of burger-like α-Fe_2O_3, an array of synthetic experiments were carried out at different reaction times. The as-prepared samples were named as x-Fe_2O_3, where x represented the reaction time of the hydrothermal process (x = 6, 12, 18, 24 h). Especially, 24-Fe_2O_3 represented the burger-like α-Fe_2O_3.

2.2. Characterization

The crystal structure of the samples was determined by X-ray diffraction (XRD) on a D8 diffractometer with Cu Kα radiation (λ = 0.1542 nm) over diffraction angle range from 5° to 70°. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB II XPS system and operated at a pass energy of 30 eV, using Al Kα as an exciting X-ray source. The morphologies of samples were investigated by scanning electron microscopy (SEM, JSM-5610LV) and field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan). The element distribution of the as-prepared samples was observed by energy-dispersive X-ray mapping. The N_2 adsorption/desorption isotherm was measured by a micromeritics ASAP2020 adsorption instrument. The stability of samples was further confirmed by Fourier transform infrared (FT-IR) spectroscopy (Thermo Nicolet, USA). The iron concentration of leaking was measured using an inductively coupled plasma optical emission spectrometer (Prodigy 7). The fluorescence spectrophotometer (RF-5300PC, Shimadzu) was used in detection of •OH radicals.

2.3. Photo-Fenton degradation activity evaluations

0.1 g of the burger-like α-Fe_2O_3 catalyst was added into 100 mL of ARG aqueous solution (50 mg/L, pH = 2) and was stirred quickly in the dark for 30 min to reach the adsorption balance. Afterwards, the degradation reaction was carried out under LED lamp (λ = 420 nm) irradiation after adding 0.3 mL of aqueous H_2O_2 solution (30 wt%). 6 mL of the suspension was collected and then centrifuged (5000 rpm, 10 min) to remove the residual catalyst. Eventually, the concentration of ARG was detected immediately by using a UV–vis spectrophotometer (UV-1100) at 505 nm. All experiments and tests were performed at room temperature.

3. Results and discussion

3.1. Characterizations and properties of burger-like α-Fe_2O_3

The XRD patterns of products obtained under different reaction time were shown in Fig. 1a. All peaks were consistent with the standard card of α-Fe_2O_3 [JCPDS: 33–0664]. The diffraction peaks at 2θ = 24.1°, 33.1°, 35.6°, 40.8°, 49.4°, 54.1°, 57.4°, 62.4° and 63.9° corresponded to the reflection planes of (012), (104), (110), (113), (024), (116), (122), (214) and (300), respectively. Moreover, no peak of impurities was found, denoting that well-crystallized α-Fe_2O_3 has been successfully synthesized.

In order to further study the element composition and chemical state of the burger-like α-Fe_2O_3, XPS analysis was conducted. The survey spectrum was displayed in Fig. 1b indicating the main existence of Fe and O in the catalyst, C was the background value of the instrument itself. The Fe 2p was characterized by doublet spin orbit components and peaks appeared at binding energies of 711.0 eV and 724.8 eV in the burger-like α-Fe_2O_3 corresponded to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, meanwhile, a Fe $2p_{3/2}$ carrying satellite peak was located at binding energy of 718.6 eV, suggesting that Fe presented in Fe^{3+} state (Yamashita and Hayes, 2008; Xia et al., 2017; Patil et al., 2011; Dghoughi et al., 2006). For O 1s, the first peak obtained at 529.5 eV could be attributed to the lattice oxygen, the second peak located at 532.2 eV implied there were the hydroxyl groups at the surface of α-Fe_2O_3 (Özer and Tepehan, 1999).

The morphologies of the as-prepared samples were examined by SEM and FESEM analysis. Uniformly dispersed micro-burger with uniform sizes (an average length of 5 μm) can be clearly observed in Fig. 2a. Fig. 2b shows that the surface of burger-like α-Fe_2O_3 is rough. From the high-magnification FESEM image (inset of Fig. 2b), we can see that the surface is composed of many irregular nanoparticles with the sizes in the range of 20–40 nm. As shown in