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An effective and magnetic Fe_2O_3-ZrO_2 catalyst for phenol degradation under neutral pH in the heterogeneous Fenton-like reaction

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ABSTRACT

A novel Fe_2O_3-ZrO_2 catalyst was prepared by the sol-gel method, and investigated for phenol degradation in the Fenton-like reaction under neutral pH condition. The ZrO_2 addition increased the surface areas of the catalyst. Scanning electron microscopy (SEM) showed that ZrO_2 nano-particle dispersed on the surface of Fe_2O_3. X-ray photoelectron spectroscopy (XPS) indicated that the Fe^{2+} amount increased with the increase of the Zr content on the surface. The Fe_2O_3-ZrO_2 catalyst produced hydroxyl radicals ($OH^{\cdot}$) and superoxide radicals ($O_2^{\cdot -}$/$HO_2^{\cdot}$), and exhibited good catalytic performance in the reaction. Total phenol conversion and 56% TOC removal were achieved after 210 min under neutral pH at 60 °C in the heterogeneous Fenton-like reaction. In addition, the prepared Fe_2O_3-ZrO_2 catalyst had good magnetism.

1. Introduction

Severely environmental concerns for wastewater disposal result in the need to develop effective treatment technologies for different pollutants in the wastewater. Especially, the toxic contaminants are unfeasible for direct biological treatment. At last decades, advanced oxidation processes (AOPs) (photocatalysis, O_3, Fenton, wet air oxidation…) have shown great potential in destroying refractory organic compounds in the wastewater due to the formation of hydroxyl radicals ($OH^{\cdot}$) in the reaction, which exhibit highly reaction rate constants with most organic compounds in the range 10^8–10^{10} m^{-1} s^{-1} [1–3]. Among the AOPs, the Fenton process with simple equipment under mild operating conditions is the most cost-effective method to generate $OH^{\cdot}$ radicals, and hydrogen peroxide (H_2O_2) is a safe oxidant without lasting environmental threat. The conventional Fenton reagent, using Fe^{2+} salt as a catalyst in the presence of H_2O_2 under acidic condition (pH < 3), shows good pollutant removal [4], while low pH value and iron sludge generation limit its application in the wastewater treatment. Heterogeneous Fenton-like reaction has been paid attention and developed, due to the performance in the wide pH range and the decrease of iron sludge formation [5–10].

Iron oxides (Fe_3O_4, Fe_2O_3…), with environmental-friendly materials, have exhibited good catalytic performance in the heterogeneous Fenton-like reaction [11,12]. Magnetite (Fe_3O_4), the most widely used material, shows the better catalytic activity in the heterogeneous Fenton-like reaction for degrading pollutants. However, it is found that: (1) Fe_3O_4 has very low catalytic activity under near-neutral pH; (2) the passivation of the magnetite surface inhibits the catalytic efficiency in the reaction. Compared to Fe_3O_4, other iron oxides (α-Fe_2O_3, γ-Fe_2O_3…), with superior chemical stability, have the lower catalytic activity in the Fenton-like reaction [11,12]. Therefore, the development of the Fe-based catalysts with good performance and stability under neutral pH is a challenge in the heterogeneous Fenton-like reaction.

The addition of transition metal into iron oxides is an effective approach to enhance $OH^{\cdot}$ production, the electron transferation and specific surface area, leading to high catalytic activity of iron oxides in the Fenton-like reaction for degrading organic compounds. For example, the application of Ti^{4+}, Cr^{3+} and V^{3+} substituted Fe_3O_4 improved the degradation of methylene blue (MB) in the heterogeneous Fenton-like at neutral pH [8,13]. However, a few literatures involving the addition of transition metal into iron oxides in order to improve the Fe^{2+} regeneration from Fe^{3+} process, i.e., an important limited step, was investigated in the Fenton-like reaction. In this literature it is found that superoxide radical anion ($O_2^{\cdot -}$) accelerated the reduction rate of Fe^{3+} to Fe^{2+} in the presence of Mn^{2+} over Fe^{3+}-NTA complex as homogeneous catalyst in the Fenton reaction [14]. Pietrzyk found that ZrO_2 could generate reactive oxygen species ($O_2^{\cdot -}$, $HO_2^{\cdot}$…) in the presence of H_2O_2 [15]. The results indicate that the Zr addition could be

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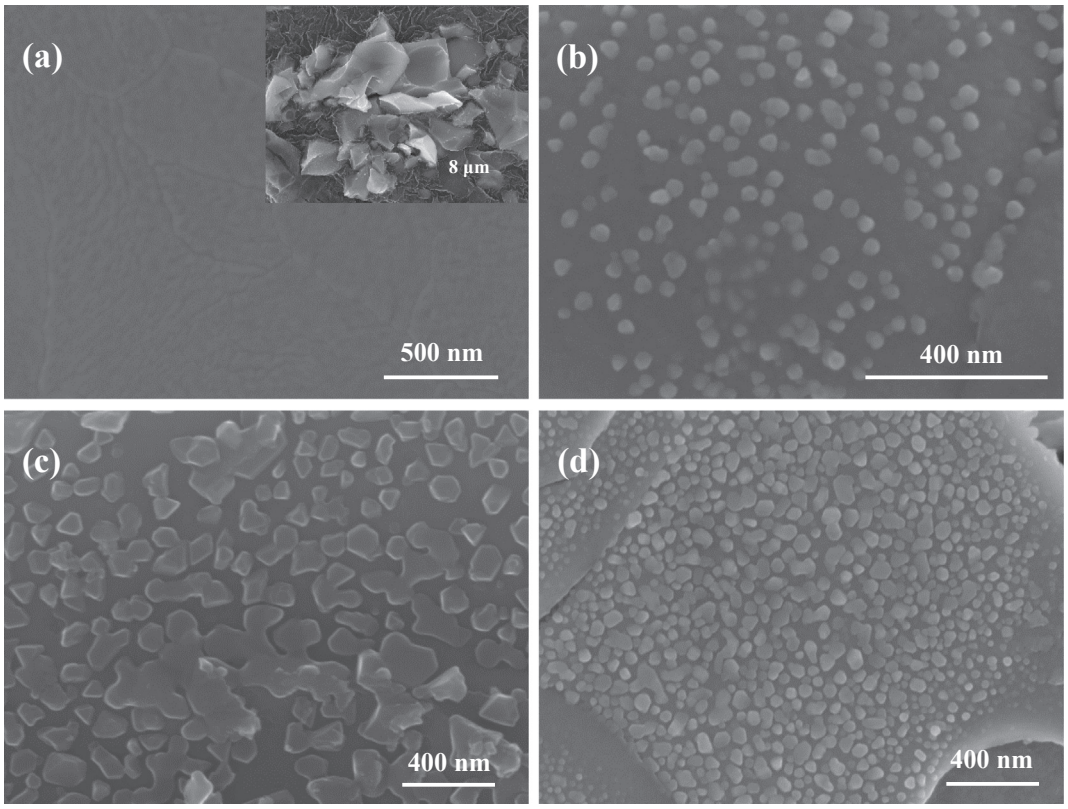

Fig. 1. SEM images of the different catalysts.

helpful for the Fe^{2+} regeneration from Fe^{3+} and improve the $OH^{\cdot}$ formation and catalytic activity of iron oxides in the heterogeneous Fenton-like reaction. However, the iron oxides adding ZrO_2 as a catalyst and the relative reaction mechanism are not studied in the heterogeneous Fenton-like reaction.

In this study a novel Fe_2O_3-ZrO_2 catalyst was prepared and investigated in the Fenton-like reaction under neutral pH. Phenol, a common toxic and priority pollutant, was selected as model organic compound. We compared the activity of our-prepared catalyst with that of other Fe-based catalyst (Fe_3O_4, Fe^0…) [16,17] under neutral pH condition. Moreover, the mechanism of the Fe_2O_3-ZrO_2 catalyst was discussed in the Fenton-like reaction for phenol degradation.

2. Experimental

2.1. Materials and chemicals

In the experiment, chemical reagents without further purification were obtained from Aladdin Industrial Corporation. Methanol, acetic acid and H_2O_2 (30 wt%) were purchased from Sigma-Aldrich Company.

2.2. Synthesis of the catalysts

The catalysts were prepared by sol-gel method. $Fe(NO_3)_3{\cdot}9H_2O$ and $Zr(NO_3)_4{\cdot}5H_2O$ were dissolved in the deionized water, and then citric acid was added with strong stirring at room temperature. The mixed solution was heated to 80 °C and kept for 5 h to obtain a yellow gel. The gel was dried at 110 °C overnight. The resulting solid was grinded and calcined at 500 °C for 3 h under air. The mole ratio of metal salts and citric acid was 1. The atom ratio of Fe and Zr was 9/1, 7/3 and 5/5, and the prepared catalyst was named as Fe-Zr-1, Fe-Zr-2 and Fe-Zr-3, respectively. Pure Fe_2O_3 and ZrO_2 were prepared with the same method.

2.3. Catalyst characterization

The catalyst morphologies were investigated by means of scanning electron microscope (SEM) with a HITACHI S-4500 using an accelerating voltage of 15 kV and Oxford ISIS300 energy-dispersion microanalysis system. The specific surface areas of the catalyst were measured by N_2 adsorption at 77 K using an Autosorb iQ-MP system. Before analysis, the catalyst was outgassed at 200 °C for 4 h. X-ray diffraction (XRD) patterns of the catalyst were obtained on a Siemens D5005 diffractometer using the Cu K_α radiation (λ = 0.15406 nm). X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5400 ESCA analyzer with an Al K_α X-ray source (h_ν = 1486.60 eV). The C1s peak (E_b = 284.60 eV) was used as a reference for the calibration of the binding energy. The pH at the point of zero charge (pH_{PZC}) of the catalyst was measured with the method developed by Noh et al. [18].

2.4. Catalytic activity tests

The heterogeneous Fenton-like reaction was performed in a 500 mL grass reactor in the dark, equipped with a stirrer and thermocouple. The pH value of phenol solution was adjusted by adding 0.1 M NaOH to 7.0 ± 0.05. First, a certain amount catalyst and 250 mL phenol solution (100 mg/L) were loaded into the reactor with stirring. The reactor was heated to a desired temperature, and then maintained for 30 min to achieve the adsorption equilibrium of a catalyst. Second, H_2O_2 was added into the reactor to initiate phenol degradation. Samples were periodically withdrawn from the reactor, quenched with methanol, and then filtered through 0.22 μm filter film. Each experiment was measured in triplicate. The experiments of the radical identification were performed by adding tert-butanol and p-benzoquinone to have an insight into the primary oxidative species formed in the heterogeneous Fenton-like reaction [12,19]. Phenol concentration was analyzed by an Agilent 1260 HPLC with a C18 column at 254 nm. The mobile phase was a mixture solution containing methanol and 0.2% acetic acid