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Preparation of $FeCeO_x$ by ultrasonic impregnation method for heterogeneous Fenton degradation of diclofenac

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ABSTRACT

$FeCeO_x$ has been successfully synthesized by ultrasonic impregnation method and applied in diclofenac removal in heterogeneous Fenton process. The effects of ultrasonic density, impregnation time, mole ratio of Fe and Ce and calcination temperature were investigated. Nitrogen adsorption/desorption, SEM, XRD, HRTEM, Raman and XPS analyses were characterized. Stability and reusability of $FeCeO_x$ were evaluated. The results indicated that 83% degradation efficiency of diclofenac was achieved by $FeCeO_x$ under the optimum preparation conditions. Fe ions were distributed uniformly in crystal structure and the solid solution structure of $FeCeO_x$ with a lattice constriction was formed. Exposed crystalline plane (200) with a relatively high surface energy may be the main reason to provide high catalytic activity of $FeCeO_x$. Oxygen vacancies took part in catalytic process and a portion of them were oxidized after reaction. $FeCeO_x$ showed an excellent chemical stability and reusability in heterogeneous Fenton process.

1. Introduction

Cerium oxide (CeO_2) is a multifunctional rare earth metal oxide, and has unique structure of oxygen vacancy defects and properties of redox cycle of Ce^{4+}/Ce^{3+} and high oxygen storage capacity. Moreover, there is a positive correlation between the oxygen storage capacity of CeO_2 and the concentration of oxygen vacancies at surface [1]. Thus, the performance of oxygen storage capacity can be modified by doping various transition and lanthanide metal ions, where the lattice changes occur due to the difference of ionic radius and electrons. Since the doping modification can improve the catalytic performance of CeO_2, ceria-based materials (ceria doped with other ions) have attracted widely attention in heterogeneous catalysis [2,3], fuel transform [4] and gas sensors field [5]. Recently, ceria-based materials have been reported as heterogeneous Fenton catalysts for the degradation of organic pollutant in water [6–8]. In particular, Fe-doped CeO_2 can produce large amounts of oxygen vacancies, which facilitate the activation and transportation of active oxygen species in reaction process [9]. This feature has an obvious advantage in Fenton-like process, in which free radicals' oxidation dominates the reaction.

Various techniques have been used to synthesize Fe-doped CeO_2 catalyst, including hydrothermal [10], co-precipitation [9], sol–gel [11] and impregnation methods [12]. However, hydrothermal method usually needs a long ageing time to achieve crystalline at low temperature. Co-precipitation and sol–gel methods frequently lead to particle agglomeration and weak uniformity. Impregnation is a common and simple method that allows the active component dispersing onto the surface of support. But it may cause the low dispersion of metal species or need a long dipping time due to the small driving force of mass transfer in the preparation process [13].

In order to overcome the disadvantages of impregnation method, ultrasound was introduced to assist the impregnation process. The ultrasound wave can improve mass transfer and thermal heating effects by the phenomenon of cavitation which involves formation, growth and collapse of bubbles in the liquid medium [14]. Consequently, ultrasound assisted impregnation method can promote the dispersion of active species onto the surface of support and may introduce the active components in the structure, thus leading to more active sites and better catalytic performance. Besides, faster mass transfer rate by ultrasound can significantly shorten the preparation period [15]. Based on the above analysis, Fe-doped CeO_2 prepared by ultrasonic impregnation method is worthy of study, but it has not been studied previously. Therefore, we prepared Fe-doped CeO_2 by ultrasonic impregnation method,

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anticipating excellent catalytic performance in heterogeneous Fenton process.

In this work, Fe-doped CeO_2 ($FeCeO_x$) was successfully synthesized by ultrasonic impregnation method and applied in removal of diclofenac in heterogeneous Fenton process. Diclofenac, an emerging organic pollutant in water, was chosen as the target pollutant here. Effects of ultrasonic density, impregnation time, mole ratio of Fe and Ce, and calcination temperature were investigated in detail. N_2 sorption–desorption, Scanning electron microscopy (SEM), X-ray diffraction (XRD), High resolution transmission electron microscope (HRTEM), Raman spectrometer (Raman) and X-ray photoelectron spectroscopy (XPS) were used to investigate the morphologic and physical/chemical properties of $FeCeO_x$. The stability and reusability of $FeCeO_x$ were detected to evaluate its applicability. The aim of this study was to use an improved method to synthesize $FeCeO_x$ and use it to remove diclofenac in heterogeneous Fenton process.

2. Experimental

2.1. Reagents and materials

All chemicals used in this study were of analytical grade and used without further purification. Ferrous chloride hexahydrate ($FeCl_2{\cdot}4H_2O$) and sodium hydroxide (NaOH) were purchased from Xilong Chemical Co., Ltd, China. Cerous nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) was purchased from Tianjin Guangfu Fine Chemical Institute, China. Hydrogen peroxide (H_2O_2, 30%, *V/V*) and sulfuric acid (H_2SO_4, 98%) were obtained from Beijing Chemical Works, China. Solutions were prepared with deionized water purified by a Millipore Milli Q UV Plus system (USA).

2.2. Synthesis of $FeCeO_x$

The preparation of CeO_2 was carried out by a precipitation method [16]. $Ce(NO_3)_3{\cdot}6H_2O$ (0.01 mol) was dissolved in 200 ml deionized water under vigorous mechanical stirring. A stoichiometric amount of NaOH was added drop-wise and kept reaction temperature at 35 °C. After 4 h reaction, the solution was centrifuged at 3000 rpm for 3 min to separate the products. The settled products were aged 12 h at room temperature, and then dried at 100 °C for 3 h. The obtained CeO_2 was dipped in $FeCl_2{\cdot}4H_2O$ solution under ultrasonic irradiation for 20 min, then the mixture was filtered. The solid was calcined for 2 h at 400 °C in muffle furnace. Finally, $FeCeO_x$ catalyst was obtained.

2.3. Characterization of $FeCeO_x$

Specific surface area and porosity of catalyst were measured by nitrogen adsorption/desorption isotherms at 77 K on a BeiShiDe 3H-2000PS2 specific surface and pore size analysis instrument. The surface morphology of samples was investigated by using a Hitachi S 4700 scanning electron microscope (SEM) analyzer with secondary electron detector at different scales and magnifications. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-rc diffractometer employing Cu radiation. High-resolution transmission electron microscopy (HRTEM) equipped with energy dispersive spectroscopy (EDS) and selective area electron diffraction (SAED) were conducted on a JEOL JEM-2010 at an accelerating voltage of 200 kV. Raman measurements were performed at room temperature using a Via+ Reflex Raman spectrometer with the excitation light of 514 nm. The X-ray photoelectron spectra (XPS) were measured on an EScalab 250Xi spectrometer equipped with a XR6 mononchromated X-ray source.

2.4. Determination of diclofenac removal

All experiments for diclofenac degradation were conducted in 150 ml beakers. Experimental conditions were as follows: initial concentration of diclofenac 20 mg/L, pH 5, dosage of $FeCeO_x$ 0.5 g/L, concentration of H_2O_2 10 mmol/L. The solution was adjusted with diluted NaOH and H_2SO_4 to the desired initial pH, and the final volume was 100 ml. The desired dosage of $FeCeO_x$ catalyst and H_2O_2 was introduced into the reaction solution immediately. Then the beaker was placed in an electronic stirrer at ambient temperature with continuous stirring. At set intervals, 1.0 ml supernatant of the sample solution was analyzed immediately after filtration by 0.45 μm membrane filter. Control experiments were also performed under the same conditions.

Determination of diclofenac was performed with a Waters e2695 high-performance liquid chromatography instrument (HPLC) equipped with a C18 reversed phase column (4.6 × 150 mm I.D.). Elution conditions: mobile phase was composed of 70/30 v/v acetonitrile and acetic acid solution (0.2%); flow rate: 1 ml/min; injection volume: 10 μL; column temperature: 30 °C; λ_{max} was 275 nm.

3. Results and discussion

3.1. Feasibility study

To evaluate the feasibility of ultrasonic impregnation method, comparison on catalytic performance of $FeCeO_x$ was carried by using ultrasonic impregnation and traditional impregnation separately. As shown in Fig. 1, the removal efficiency of diclofenac with H_2O_2 alone was only 2.2% in 40 min, which had little contribution to diclofenac removal. $FeCeO_x$ prepared with ultrasonic impregnation method showed a very good diclofenac removal of 78.50% in 20 min and 85.25% in 40 min, which was better than $FeCeO_x$ prepared with traditional impregnation method. In fact, traditional impregnation process might lead to a non-uniform dispersion and agglomeration of Fe species on the surface of CeO_2 [15]. Ultrasonic impregnation has an important advantage of distributing the active species and reducing the agglomeration during the immersion. This can attribute to the favorable effect of acoustic cavitation and induced turbulences on solid–liquid transport, mass transfer and distribution status [17]. In ultrasonic impregnation process,

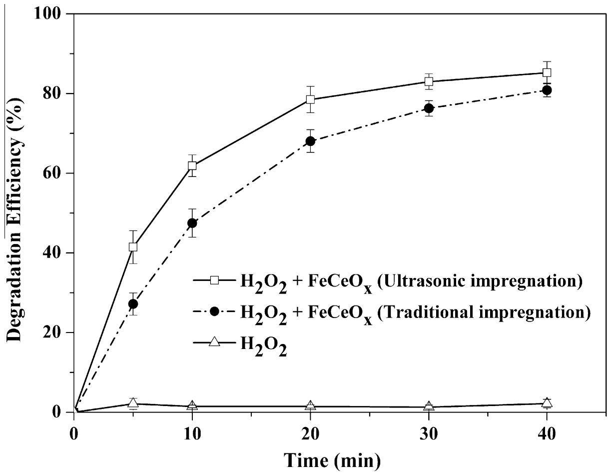

Fig. 1. Catalytic performance of $FeCeO_x$ prepared by ultrasonic impregnation and traditional impregnation. Preparation conditions: ultrasonic density = 0.3 W/cm^3, impregnation time = 20 min, mole ratio of Fe and Ce = 3:7, calcination temperature = 450 °C.