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Catalytic ozonation of toxic pollutants over magnetic cobalt and manganese co-doped γ-Fe_2O_3

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ABSTRACT

Magnetic Co- and Co, Mn-doped γ-Fe_2O_3 (FC and FCM) were prepared by co-precipitation method and characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), in situ attenuated total reflection FTIR (ATR-FTIR) spectroscopy and cyclic voltammetry (CV) analyses. FCM was found to be highly effective for the mineralization of 2,4-dichlorophenoxyacetic acid and its derivatives 2,4-diclorophenol, 2,4,6-trichlorophenol in aqueous solution with ozone. The characterization studies showed that Co and Mn incorporated in γ-Fe_2O_3 existed as multivalence oxidation states, and there were more Lewis acid sites on the surface of FCM. The interaction of ozone with chemisorbed H_2O and surface hydroxyl groups generated from dissociative adsorption of H_2O on Lewis acid sites initiated the production of reactive oxygen species. Moreover, a redox process was observed in the catalytic decomposition of O_3 at the water–catalyst interface by CV analysis. The results indicated that the introduction of Mn not only increased the surface Lewis acid sites of FCM to cause more surface hydroxyl groups and chemisorbed water, but also enhanced the interfacial electron transfer, resulting in higher activity.

1. Introduction

Heterogeneous catalytic ozonation has received increasing attention in recent years because of its potentially higher effectiveness in the degradation and mineralization of refractory organic pollutants and lower negative effect on water quality [1,2]. This method has been developed to overcome the limitations of ozonation processes, such as the formation of byproducts and the selective reactions of ozone designed to enhance the production of hydroxyl radicals ($^\bullet$OH), known as nonselective oxidants [3,4].

Supported and unsupported metals and metal oxides are the most commonly tested catalysts for the ozonation of organic compounds in water or air [5–7]. Experimental results indicate that the removal efficiencies of pollutants are significantly enhanced in the presence of catalysts compared to ozone alone. Despite these promising studies, one obstacle to its practical application is the separation of these materials from the finished water. Magnetite nanoparticles are easy to be separated from aqueous media due to their magnetic properties. Maghemite (γ-Fe_2O_3), the ferromagnetic cubic form of iron (III) oxide is technologically important, as it is being widely used for the production of magnetic materials and catalysts [8,9]. However, these magnetic catalysts have been hardly applied for the catalytic ozonation of organic pollutants in water.

The activity of the catalysts mentioned for heterogeneous ozonation is based mainly on catalytic ozone decomposition and the enhanced generation of hydroxyl radicals. The decomposition mechanism of gaseous ozone has been elucidated with in situ Raman spectroscopy and isotopic substitution [10,11]. The main redox steps were involved in the formation of superoxide or peroxide species on the surfaces of metal oxides, which suggested that transition metal oxides having easily accessible multiple oxidation states are good catalysts for ozone decomposition. In addition, the studies by our group and others [12,13] proposed that molecular ozone in aqueous solution should interact with the surface hydroxyl groups of the catalyst to initiate the formation of $^\bullet$OH. The amount of surface hydroxyl groups depended on the Lewis acid of the catalyst. Therefore, multiple oxidation states and surface Lewis acid sites are crucial factors for the high activity of catalyst in water.

In this present, cobalt/manganese substituted γ-Fe_2O_3 catalysts were prepared by co-precipitation method. 2,4-Dichlorophenoxyacetic acid (2,4-D) is the most widely used herbicide in the world [14]. It is poorly biodegradable and has been detected as a major pollutant in ground and surface waters. Most papers related to the treatment of chlorophenoxy herbicides in aqueous medium described the degradation of 2,4-D by advanced oxidation processes, where the mineralization of 2,4-D needed prolonging reaction time [15–17]. Therefore, 2,4-D and its derivatives 2,4-diclorophenol (2,4-DCP), together with other chlorophenols were selected to evaluate the activity and properties of the catalysts with ozone in aqueous solution. Cobalt

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and manganese co-substituted γ-Fe_2O_3 showed high efficiency for the degradation and mineralization of the tested toxic pollutants. This was mainly contributed to the enhanced interfacial electron transfer and the increased concentration of surface Lewis acid sites on the basis of cyclic voltammetry and in situ ATR-FTIR analyses.

2. Experimental

2.1. Materials and reagents

All reagents used in this work were analytical grade and were used without further purification. Ferric nitrate, cobalt nitrate and sodium carbonate were purchased from Beijing Chemical Reagent Company (Beijing, China). Manganese nitrate was acquired from Xilong Chemical Factory (Shantou, China). 2,4-D, 2,4-DCP and 2,4,6-trichlorophenol (2,4,6-TCP) were obtained from Yili Fine Chemicals Co., Ltd (Beijing, China). All solutions were prepared with deionized water.

2.2. Catalyst preparation

Cobalt doped γ-Fe_2O_3 (FC) was prepared by co-precipitation method. An aqueous solution containing nitrates of Fe^{3+} and Co^{2+} (molar ratio: Fe/Co = 2) was added slowly into sodium carbonate aqueous solution with continuous stirring. After aging, the precipitate was filtered and washed with deionized water, dried at 70 °C and calcined at 550 °C for 5 h in air. Cobalt and manganese co-doped γ-Fe_2O_3 (FCM) was obtained by the same method with a mixed solution of nitrates of Fe^{3+}, Co^{2+} and Mn^{2+} (molar ratio of ions: Fe/(Co + Mn) = 2, Co/Mn = 30). As a reference, iron oxide (F) was prepared by the same procedure with ferric nitrate solution.

2.3. Characterization

Powder X-ray diffraction (XRD) of the catalyst was recorded on a XDS 2000 Diffractometer (Scintag Inc., CA) with Cu Kα radiation (λ = 1.54059 Å). Magnetic measurements were conducted on a 7307 vibrating sample magnetometer (Lake Shore Cryotronics Inc., USA). The X-ray photoelectron spectroscopy (XPS) data were taken on an AXIS Ultra instrument (Kratos Analytical, UK) using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV). The determination of acid groups was carried out following the method proposed by Boehm [18].

Electrochemical experiments were performed on a basic electrochemical system (Princeton Applied Research Co., U.S.A.). All experiments were done using a three-electrode cell configuration with a catalyst modified conductive glass (prepared by dip coating and drying in air at 70 °C) as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode as the reference electrode.

In situ ATR-FTIR spectroscopy: To prepare an ATR sample, a desired amount of catalyst particles was added to H_2O or D_2O solution and sonicated. The manipulations were performed under nitrogen atmosphere when D_2O was employed. A short time before running the spectra, the samples were centrifuged, half of the supernatant was used as reference, the solid resuspended in the other half was used as the sample. This procedure yielded a solid concentration of 100 g L^{-1}. The ATR-FTIR spectra were recorded using a TENSOR 27 infrared spectrometer with a DLaTGS detector and a ZnSe horizontal ATR cell. Infrared spectra over the 4000–650 cm^{-1} range were obtained by averaging 32 scans with a resolution of 4 cm^{-1} at room temperature. The spectrum of the particles in suspension is the result of subtracting the spectrum of the supernatant (reference) from the spectrum of the slurry (sample). The cell remains in place throughout the running of every single-beam spectra of the empty cell, reference, and sample so that its transmittance and average angle of incidence are constant.

2.4. Procedures and analysis

Semi-batch experiments were carried out with a 1.2 L reactor. The reaction temperature was maintained at 20 °C. In a typical experiment, 1 L of 20 mg L^{-1} 2,4-D aqueous solution was introduced into the reactor. 1 g catalyst was added into this solution under magnetically stir. 30 mg L^{-1} gaseous O_3 oxygen–ozone was then bubbled into the reactor through the porous plate of the reactor bottom at a 12 L h^{-1} flow rate. Ozone gas was generated by a 3S-A5 laboratory ozonizer (Tonglin Technology, China). Samples were withdrawn at given intervals. After the residual ozone was instantly quenched with 0.1 M $Na_2S_2O_3$, each sample was filtered through a 0.45-μm cellulose acetate membrane for analysis. The gaseous ozone concentration was measured using the iodometric titration method. Concentrations of 2,4-D, 2,4-DCP and 2,4,6-TCP were measured using 1200 series HPLC (Agilent, U.S.A.) with a ZORBAX Eclipse XDB-C_{18} column (4.6 × 150 mm, 5 μm). The total organic carbon (TOC) of each solution was analyzed with a Phoenix 8000 TOC analyzer (Tekmar-Dohrmann Co., U.S.A.). The amounts of Fe^{3+}, Co^{2+} and Mn^{2+} in the supernatant were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) on an OPTIMA 2000 (Perkin Elmer Co., U.S.A.) instrument.

The experiments of O_3 decomposition were carried out in sealed three-mouth 260 ml bottle. The gaseous O_3 30 mg/L (oxygen–ozone) was bubbled into the reactor to get 200 ml O_3-saturated aqueous solution (about 4 mg L^{-1}) with 60 ml, 30 mg of gaseous O_3/L oxygen–ozone mixture gas above solution. 0.2 g catalyst was added into the reactor and stirred magnetically. At given time intervals, the concentration of residual ozone in aqueous solution was monitored by UV spectrophotometer (Hitachi, Japan) using the indigo method.

3. Results and discussion

3.1. Characterization of catalysts

Fig. 1 shows the XRD patterns of different samples. The predominant crystalline phase of FC and FCM is maghemite with the reflections 2θ at 30.2, 35.6, 43.2, 57.2 and 62.7°. Weak diffraction peak was also observed at 2θ 33.2° which is related to the presence of small amounts of hematite. The results suggested that Fe, Co and Mn formed binary and ternary oxides. In contrast, the iron oxide F

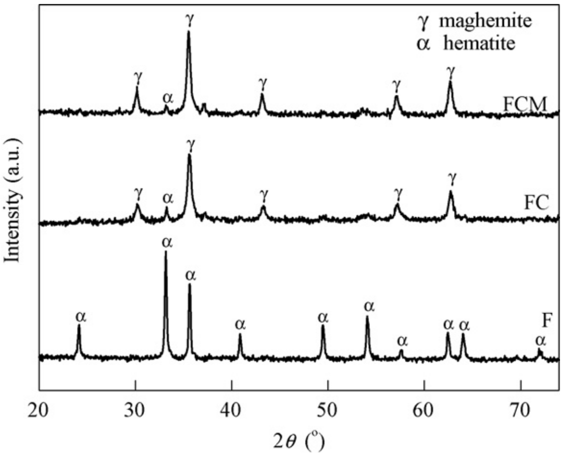

Fig. 1. XRD patterns of different catalysts.