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Short communication

Heterogeneous catalytic ozonation of *p*-chloronitrobenzene (*p*CNB) in water with iron silicate doped hydroxylation iron as catalyst

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ABSTRACT

In this communication, synthesis of iron silicate (IS) doped hydroxylation iron (IS-FeOOH) and its catalytic activity in ozonation of *p*-chloronitrobenzene (*p*CNB) was reported and the mechanisms of *p*CNB removal were deduced. The XRD and HR-TEM analyses indicated that the IS-FeOOH were mainly composed by amorphous IS and FeOOH. IS-FeOOH exhibited significant catalytic activities. The EPR spectrum results showed that IS-FeOOH could promote ozone decomposition into hydroxyl radicals (·OH), resulting in the increased removal of *p*CNB. The catalytic reusability studies demonstrated that IS-FeOOH kept its catalytic activity in five consecutive cycles.

1. Introduction

Heterogeneous catalytic ozonation has gained increasing attention in water and wastewater treatment field, owing to its higher oxidation, lower negative influence on water quality, less cost and more feasible for practical application [1]. To date, several researchers have been successfully using various materials as heterogeneous catalyst in ozonation process to degrade organic pollutants in aqueous solution, such as metal oxides [2], supported metals [3], oxyhydroxide [4], and some porous materials [5]. Compared with the ozonation alone, these catalysts can significantly enhance the degradation efficiency of organic pollutants. Different catalytic mechanisms for degradation different organic matter were also proposed, including the promoted generation of hydroxyl radicals (·OH), the promotion of the mass-transfer efficiency through the surface of the catalyst adsorption on the ozone and pollutants in aqueous solution [6,7]. Our previous work also indicates that heterogeneous catalytic ozonation using manganese silicate enhances the ozone degradation [8]. In continuation of searching for new and efficient catalysts for catalytic ozonation processes, herein we report iron silicate (IS) doped hydroxylation iron (IS-FeOOH) as a catalytic material candidate for the first time.

IS which is a common Fe-Si complex has been used as the catalyst for ozonation, due to its high density of surface hydroxyl groups and stable structure. Furthermore, the complexation of Fe and Si may increase the physical strength of the IS [9]. FeOOH is a common catalyst in the heterogeneous catalytic ozonation system, which plays an important role in catalysis through promotion of ozone decomposition into ·OH [10,11]. In this study, IS doped FeOOH was prepared and used for catalytic ozonation.

p-Chloronitrobenzene (*p*CNB) is a typical halogenated nitro aromatic compound, and which is frequently used as an important intermediate in the fields of the production of dyes, pesticides, pharmaceuticals and rubber chemicals. And large amount of it is detected in some main drinking water sources after it usage [12]. Moreover, it possesses a wide range of toxicities for humans and animals such as genotoxicity, immunotoxicity and carcinogenis [13]. *p*CNB scarcely reacts with ozone alone, because the reaction rate constant of *p*CNB with O_3 is only 1.6 $(M \cdot s)^{-1}$. However, with ·OH is 2.6×10^9 $(M \cdot s)^{-1}$. Therefore, *p*CNB was selected as the model pollutant to test the catalytic activity of the IS-FeOOH in this study.

In this communication, we have reported on the preparation of IS-FeOOH and degradation of *p*CNB by using the synthesized IS-FeOOH. The synthesized mechanism, catalytic activity and reusability of the IS-FeOOH on the degradation of *p*CNB were investigated.

2. Experimental section

2.1. Materials and reagents

The *p*CNB stock solution was prepared by dissolution 100 mg *p*CNB (99.5% purity, Merck, Germany) into 1 L Milli-Q ultra-pure water (18 MΩ cm, Millipore Q Biocel system), and stored in an amber flask.

Abbreviations: IS, iron silicate; FeOOH, hydroxylation iron; IS-FeOOH, iron silicate doped hydroxylation iron; DMPO, 5, 5-dimethyl-1-pyrroline N-oxide.

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Other chemicals used in this study were analytical grade, except as noted.

The volumetric flasks were washed by soaking them into chromic acid and rinsing with distilled water. The other glassware was muffled overnight at 673 K.

2.2. Catalyst preparation

The IS-FeOOH was prepared using Fe $(NO_3)_3$ and Na_2SiO_3 as precursor. A 150 mL volume of 0.1 M Na_2SiO_3 was slowly added to 150 mL of 0.1 M $Fe(NO_3)_3$ solutions (pH < 2.0, adjusted by HNO_3 solution) at room temperature under magnetic stirring at the speed of 100 rpm. When the pH of the suspension was 7.0, the dropping of Na_2SiO_3 solution was stopped. Then pH of the suspension was adjusted higher than 12 by NaOH solution, and it was incubated at 313 K for 24 h. The precipitate was then collected, washed and dried according to our previous publication [14]. To further study the catalyst IS-FeOOH, we also synthesized IS according to the literature [9].

2.3. Ozonation procedure

The catalytic ozonation experiments were performed in batch mode at 293 ± 1 K in a 1.2 L glass flat-bottomed flask equipped with gas inlet and outlet. Ozone was produced from pure oxygen using the CF-G-3-010 g ozone generator (Qingdao guolin, China) and bubbled into the bottom of the reactor through a silica bubble diffuser for a desired period to reach the desired dissolved ozone concentration. The desired amounts of catalysts and *p*CNB stock solution were then immediately dosed into the reactor, and the reactor was instantly sealed by the cap. Then, the magnetic stirrer was turned on to initiate the experiment. The samples were withdrawn at a predetermined time intervals (0, 1, 3, 5, 10, 15 min) and the reaction was quenched by $Na_2S_2O_3$ solution (0.1 mol/L). All the experiments were conducted three times and the average date and error bars were shown in the figures. For comparative purposes, adsorption on IS-FeOOH, IS catalytic ozonation experiment, five reusability experiments and the ozonation alone experiments were performed with the same system under identical experiment conditions.

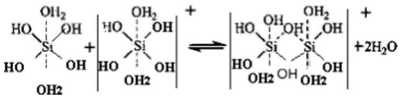
2.4. Analytical method

The concentration of ozone in aqueous solution was measured using the indigo method via spectrophotometry [15]. The concentration of *p*CNB was analyzed according to our previous publication using a liquid chromatograph (HPLC, LC-1200, Agilent, USA) with UV detection at 265 nm [14]. The structure and morphology of the prepared IS-FeOOH catalyst was investigated by Transmission Electron Microscope (TEM) (Japan, with a FEI Tecnai G^2 F30) and powder X-ray diffraction (XRD) patterns were on a BrukerD8 Advance Diffractometer with Cu Kα radiation (λ = 1.5418 Å). The saturated deprotonation method was used to measure the density of surface hydroxyl groups of the catalyst according to the described by Laiti [16]. The electron paramagnetic resonance (EPR) spin-trapping experiments were used to determine the ·OH generated in the ozonation processes and the EPR spectrum was measured with an EPR spectrometer (Bruker EMX-8/2.7 ESR spectrometer with ER4102ST cavity) under the following experimental conditions: X-field sweep; sweep width 100.00 G; center field 3480.00 G; frequency 9.751 GHz; static field 3490.00 G; power 4.0 mW. The samples were scanned and accumulated to 10 times for 20.972 × 10 s. The metals leached from the catalyst into solution were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Optima 5300DV, Perkin Elmer, USA).

3. Results and discussion

3.1. The preparation mechanism and characterization of the IS-FeOOH

Sodium silicate is an ionic compound and a strong base-weak acid salt. It can easily dissolve in water to form silicic acid. Under the weak alkaline or neutral conditions, silicic acid exit in the form of $H_3SiO_4^-$ and H_4SiO_4. As shown in the Seq. 1, during the process of silicic acid polymerization, it mainly occurs four coordinating combined reaction between silicate molecule and anion of silicic acid. Under the acid condition, silicic acid exits in the form of $H_5SiO_4^-$ and H_4SiO_4, and the polymerization occurs mainly in the following manner (Seq. 2) [17].


(Seq.1)


(Seq.2)

In the process of IS-FeOOH synthesis, when the $Fe(NO_3)_3$ solution as strong acidic solution, is mixed with the solution of Na_2SiO_3, the above reactions (Seq. 2) should occur simultaneously. Due to the instability of OH_2 bonds, Fe-Si complexes are most likely to form, and form IS. When the pH of the suspension was 7.0, the titration of sodium silicate solution into $Fe(NO_3)_3$ solutions was stopped, which makes the polymerization occur along the Seq. 2. Then the pH of the suspension was adjusted to >12 by sodium hydroxide solution. The objective of adjusting pH was (1) to generate FeOOH according to the following reaction (Seq. 3);

$$Fe^{3+} + OH^- \rightarrow FeOOH + H_2O \quad \text{(Seq. 3)}$$

(2) to make the unsaturated surface of FeOOH and IS adsorb abundant of hydroxyl ion, resulting in the formation of surface hydroxyl groups.

According to the saturated deprotonation results, the density of surface hydroxyl groups on IS is 2.573×10^{-2} mol/g and IS-FeOOH is 3.169×10^{-2} mol/g, respectively. In addition, the condensation reaction may occur between the surface hydroxyl groups of the FeOOH and IS to form IS-FeOOH. In other words, IS-FeOOH is not a simple physical mixture of FeOOH and IS. This viewpoint was confirmed by the results of XRD.

Fig. 1 showed the XRD pattern of the synthesized IS-FeOOH and IS. The broad peak in the range of 2 θ from 20° to 30° was typical of amorphous silica [14]. The weak peaks observed at 18.083°, 35.9°, 41.3° and

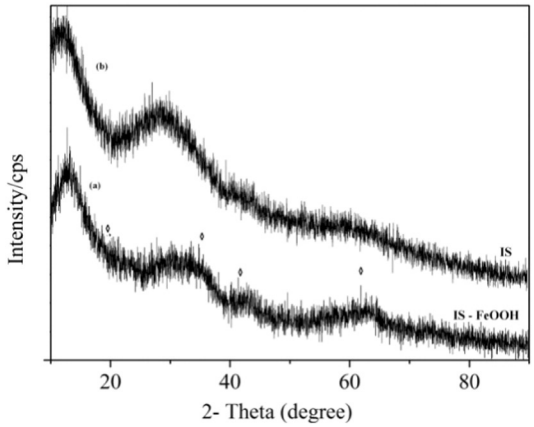


Fig. 1. The XRD pattern of IS-FeOOH and IS.