



A promising ozone-based advanced oxidation process for effective generation of hydroxyl radicals in acidic solution



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ABSTRACT

The oxidative efficiency of $\text{H}_2\text{O}_2/\text{O}_3$ in the presence or absence of titanium silicalite of TS-1 was investigated at pH value of 3.0, in which acetic acid was selected as the target organic compound owing to its inert to ozone. The removal rate of acetic acid by $\text{H}_2\text{O}_2/\text{O}_3$ was negligible (5.6% in 30 min) because of the impossible deprotonation reaction of H_2O_2 in acidic solution. However, addition of titanium silicalite of TS-1 could greatly improve the oxidative efficiency of $\text{H}_2\text{O}_2/\text{O}_3$ (29% in 30 min). The results of effects of different parameters such as concentration of H_2O_2 , concentration of TS-1, rate of ozone input, and pH value, on the oxidative efficiency of TS-1/ $\text{H}_2\text{O}_2/\text{O}_3$ showed that the degradation of HAC by TS-1/ $\text{H}_2\text{O}_2/\text{O}_3$ was controlled by the transfers of reactants (including ozone and HAC) to the surface of TS-1. The tests of addition of tert-butyl alcohol and dimethyl sulfoxide (DMSO) both confirmed generation of hydroxyl radicals in this process. The rate of generation of hydroxyl radicals could be controlled by adjusting the concentration of H_2O_2 . The mechanism for generation of hydroxyl radicals might be the reaction of some reactive oxygen species (including Ti(IV)-superoxide and Ti(IV)-hydroperoxide/peroxide), which resulted from the interaction of TS-1 with H_2O_2 , with dissolved ozone. The results are of significance for the effective pretreatment of acidic wastewater containing refractory ozone-inert organic matter.

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1. Introduction

Ozonation has been demonstrated to be an effective oxidation technology for oxidation of organic pollutants in water [1–3]. However, some organic compounds are resistant to ozonation alone [4,5]. To enhance the efficiencies of degradation of ozone-inert compounds, ozone-based advanced oxidation processes (AOPs- O_3), such as $\text{H}_2\text{O}_2/\text{O}_3$, UV/O_3 , and catalytic ozonation, have been rapidly developed [6–9]. Considering the convenience of application and efficiency of oxidation, the combined process of hydrogen peroxide with ozone ($\text{H}_2\text{O}_2/\text{O}_3$) is considered as a most promising process for degradation of different contaminants because HO_2^- (the conjugate base of H_2O_2) can effectively promote the decomposition of dissolved ozone to produce hydroxyl radicals [4,8,10–12]. However, the oxidative efficiency of $\text{H}_2\text{O}_2/\text{O}_3$ process is always very low at pH less than 5.0 because the deprotonation reaction of H_2O_2 is difficult to proceed [13,14]. In fact, effective and controllable generation of hydroxyl radicals in acidic solution

is still a big difficulty in the research field of ozone-based AOPs at present [15].

In order to improve the efficiency of $\text{H}_2\text{O}_2/\text{O}_3$ in acidic solution, we have reported a Ti(IV)-catalyzed $\text{H}_2\text{O}_2/\text{O}_3$ (Ti(IV)/ $\text{H}_2\text{O}_2/\text{O}_3$) process whose oxidative efficiency is also high at pH 2.8 because a yellow complex compound of $\text{Ti}_2\text{O}_5^{2+}$ could effectively initiate the decomposition of dissolved ozone to produce hydroxyl radicals [16]. However, this method has a drawback of titanium ion loss, which limits its application. Therefore, to immobilize titanium ion in some substances with similar catalytic activity is an important research field for ozone-based AOPs. We once tried to degrade acetic acid by $\text{O}_3/\text{H}_2\text{O}_2$ in the presence of TiO_2 , but found that the results were not good when considering the removal rate of acetic acid and consumption of H_2O_2 .

Titanium silicon molecular sieves are a new kind of porous material and have been extensively investigated due to their high catalytic performances in the selective oxidation of some organic compounds under mild conditions [17–19]. It has been well demonstrated that some reactive oxygen species (including Ti(IV)-superoxide and Ti(IV)-hydroperoxide/peroxide) will be generated to oxidize organic compounds [20–22]. According to the mechanism of decomposition of ozone in water, the above reactive oxygen species can effectively promote the decomposition of

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ozone to produce hydroxyl radicals [23]. This fact suggests that the combination of titanium silicon molecular sieve and H_2O_2 may give a possible way to establish a highly efficient ozone-based advanced oxidation process in acidic solution.

In the present study, we prepared a titanium silicon molecular sieve (named TS-1) and further investigated the efficiency of TS-1-catalytic $\text{O}_3/\text{H}_2\text{O}_2$ for the oxidation of acetic acid in acidic solution. We selected acetic acid (always a final product of chemical oxidation) as the target compound because it is a typical probe compound for detecting hydroxyl radicals in ozonation process, which will benefit the quantitative study of generation of hydroxyl radicals. The experimental results will be of great significance for broadening the application of $\text{H}_2\text{O}_2/\text{O}_3$ in the pretreatment of refractory acidic wastewater, for example, effectively pre-treating chemical industrial wastewater (a typical refractory wastewater).

2. Experimental

2.1. Chemicals and reagents

Tetrapropylammonium hydroxide (TPAOH, 40 wt.%), tween 20, tert-butyl alcohol (TBA), tetraethyl orthosilicate (TEOS), tetrabutyl titanate (TBOT), isopropyl alcohol (IPA) and dimethyl sulfoxide (DMSO) were purchased from Shanghai Aladdin Chemicals Co., Ltd. Acetic acid (HAc, 99.5% by mass) was purchased from Hangzhou Chemical Reagent Co., Ltd. H_2O_2 Aqueous (30% by mass) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Potassium titanium oxide oxalate dehydrate was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Sulfuric acid (H_2SO_4 , 98% by mass) was purchased from Xilong Chemical Reagent Co., Ltd. All the chemicals were used without further purification. The pH of acetic acid solution was adjusted by sulfuric acid. All solutions in the experiments were prepared with ultrapure deionised water.

2.2. Preparation of TS-1

TS-1 catalyst was prepared according to the following steps: Firstly, 4 g of polyoxyethylene 20-sorbitan monolaurate (Tween 20) was dissolved in 48 mL ultrapure deionised water, and then the solution under the condition of being stirred in an oil bath at 308 K, was added by 54 mL of aqueous tetrapropylammonium hydroxide (TPAOH, 40 wt.%). Secondly, adding the obtained solution dropwise to 77.2 mL of tetraethyl orthosilicate (TEOS) in a polypropylene Erlenmeyer flask with vigorous stirring for 1 h. After then another solution of 3.6 mL of tetrabutyl titanate (TBOT) in 40 mL of anhydrous isopropyl alcohol (IPA) was also added dropwise to the solution in the polypropylene Erlenmeyer flask with vigorous stirring for another 1 h. Thirdly, the resulting solution was transferred into a Teflon autoclave that was subsequently heated at 443 K for 18 h. Finally the obtained solid was separated from the growth liquid via centrifugation, washed thoroughly with ultrapure deionised water twice, dried in vacuum oven at 323 K for 12 h, and calcined in air at 823 K for 5 h. The molar ratio of Si/Ti was always 35 for the synthesized TS-1 in this study. The detailed preparation method can be seen from literature [24]. For the convenience of description of experimental results, zeolite without Ti-doping (named S-1) was also prepared with similar procedure but no addition of tetrabutyl titanate.

2.3. Characterization of catalysts

Power X-ray diffraction (XRD) measurement of the sample was carried out using $\text{Cu K}\alpha$ radiation in the 2θ ranges of $5\text{--}40^\circ$ (wide angle) on a PANalytical X'Pert Pro X-ray diffractometer. Scanning

electron microscope (SEM) was used to analyze the surface morphology of TS-1 on a Hitachi S-570 model instrument.

2.4. Catalytic ozonation procedure

All experiments were performed in a semi-continuous process. Ozonation contactor was a 1.5 L cylindrical glass reactor (Fig. 1). Before the experimental operation, the reactor was pre-ozonated for 3 min and then was washed for several times with double-distilled water to exclude possible side effects of the impurities. Ozone was produced by a corona ozone generator (CFS-1A, Ozonia, Switzerland). Oxygen gas was dried and purified with silica gel prior to entering the ozone generator. Ozone concentration was regulated by varying the voltage and oxygen flow rate. The rate of gas flow was monitored by a rotor flowmeter and the mass percentage concentration of ozone in the mixed gas of O_2/O_3 is about 6%. The flow rate of ozonized oxygen was always 0.86 L min^{-1} and the rate of ozone input was 41.3 mg min^{-1} without any special instructions. Excess ozone was passed into two gas absorption bottles containing 2% KI solution before being emitted.

In a typical experiment of acetic acid degradation, the reactor was filled with 600 mL acetic acid aqueous solution containing the required amounts of TS-1 and hydrogen peroxide, and the temperature of the reactor was kept at room temperature (21 ± 0.5) °C. The ozonized oxygen passed from the ozone generator into the ozone reactor through the sintered inlet that enabled small bubbles to be produced at the bottom of the reactor. The sample was withdrawn for analysis at certain regular intervals, and dissolved ozone was removed by immediately bubbling nitrogen for 3 min after sampling to terminate oxidative reaction.

2.5. Analytical procedures

An ion chromatography (Dionex DX1500, USA) was used to measure the concentration of acetic acid (eluent: 18 mmol L^{-1} Potassium hydroxide, the flow rate was 1.0 mL min^{-1}). The concentration of ozone in gas was determined by the iodometric titration method [25]. The concentration of ozone dissolved in aqueous solution was analyzed by a spectrophotometer using the indigo method [26]. The concentration of H_2O_2 was determined by potassium titanium (IV) oxalate method [27]. The comparison tests showed that the presence of H_2O_2 did not interfere with the determination of the concentrations of ozone and acetic acid. The amount of $\cdot\text{OH}$ generation was determined by a product analysis of the reaction of dimethyl sulfoxide (DMSO) with $\cdot\text{OH}$ [28,29]. The pH value of the solution was recorded by a pH analyzer (PHS-3C, General Instrument Co., Ltd., Shanghai, China), and was controlled by adding 1 mol L^{-1} H_2SO_4 or NaOH solution.

3. Results and discussions

3.1. Characteristics of TS-1 catalyst

The crystalline phases of the TS-1 and S-1 samples were characterized by powder XRD (Fig. 2). Fig. 2 shows that both TS-1 and S-1 are composed of highly crystalline zeolite with the MFI structure. As evidenced by the peaks at $2\theta = 23.2^\circ$, 23.9° , and 24.4° , together with the disappearances of the diffraction peaks splitting at $2\theta = 24.5^\circ$ and 29.5° in TS-1 marked with arrows in Fig. 2, it could be deduced that the monoclinic structure of silicalite had changed to the orthorhombic structure with Ti-doping. This result indicated that Ti atom had incorporated into the framework of silicalite [24]. No diffraction peak is observed at $2\theta = 25.4$ in the XRD patterns of TS-1, which further suggests that Ti atom had completely incorporated into the framework of silicalite [30].

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