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Enhanced inhibition of bromate formation in catalytic ozonation of organic pollutants over Fe–Al LDH/Al_2O_3

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ABSTRACT

Fe–Al layered double hydroxides (Fe–Al LDH, the molar ratio of Fe(II) to Fe(III) was about 1:10) was successfully supported and highly dispersed on mesoporous Al_2O_3 based on the X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis. Fe–Al LDH/Al_2O_3 was more efficient in inhibiting BrO_3^- formation and removing organic pollutant taking ozonation alone as control. Further investigation indicated that BrO_3^- reduction by surface Fe(II) was responsible to the complete inhibition of BrO_3^- formation. Fe(II) was reduced from the Fe(III)-intermediates complex via an electron transfer process and the reaction of Fe(III) and $HO_2^{\cdot-}/O_2^{\cdot-}$ in catalytic ozonation. The amount of surface Fe(II) in catalytic ozonation of amitrole (AMT), phenazone (PZ) and 2,4-dichlorophenoxyacetic acid (2,4-D) was 0.34, 2.47 and 3.30 μmol/g, which proved that most of Fe(II) was generated from the reaction of ozone and Fe–Al LDH/Al_2O_3 since 0.33 μmol/g of Fe(II) existed within the catalyst. The increase of ozone amount and the formation of Fe(III)-intermediates complex could enhance the Fe(II) generation, leading to more efficient inhibition of BrO_3^- formation. Finally, Fe–Al LDH/Al_2O_3 still showed effectiveness in the inhibition of BrO_3^- and TOC removal for a raw drinking water under the realistic conditions, which could be applied to the BrO_3^- mineralization in catalytic ozonation of Br^--containing drinking water.

1. Introduction

The application of ozonation in drinking water treatment is widespread throughout the world to address water quality problems caused by taste, odor, micropollutants, etc. [1]. However, there exists an important scientific challenge: controlling BrO_3^- formation as a result of the ozonation of Br^--containing water [1]. Hence, it is very important to minimize or eliminate BrO_3^- in water treatment due to its carcinogenicity and nephrotoxcity [2].

Three approaches could be used to control BrO_3^- contamination in the water supply: removal of Br^- before BrO_3^- formation via membrane filtration and ion exchange [3,4]; control of BrO_3^- formation during ozonation by lowering solution pH or adding H_2O_2 or NH_3 [5,6]; and removal of BrO_3^- after ozonation via adsorption or chemical reduction [7,8]. Among these methods, the minimization of BrO_3^- formation during ozonation appears as the most promising one since the combination with other treatment process is not necessary. Although the NH_3 addition and pH depression could result in bromate reduction of roughly 50% and may be applicable in treatment plants [9], if source waters have relatively high NH_3 concentration and alkalinity, the efficiencies of those processes may well be found insufficient [10]. Hence, novel methods are still urgently needed to minimize bromate formation during ozonation.

Recently, there are increasing interests on catalytic ozonation with various catalysts to improve the oxidation efficiency of ozonation [11–13]. Our and other studies have verified that more reactive oxygen species were generated from the interaction of ozone and surface Lewis acid sites of catalysts [14–16]. The organic compounds could be removed more efficiently, while few studies have been conducted to investigate the control of BrO_3^- formation during the heterogeneous catalytic ozonation [17,18].

In ozonation process, the removal of organic compounds and the oxidation of Br^- to BrO_3^- are competitive reactions in consuming the reactive oxygen species [9,19]. BrO_3^- is also a strong oxidant that can be reduced to Br^- in water by reduced iron species (Fe^{2+} or Fe^0) [8]. Moreover, our and other studies have verified that more Fe(II) could be generated from the reaction of Fe(III) and $HO_2^{\cdot-}/O_2^{\cdot-}$ due to the complexation of Fe(III) with the oxygen functional groups (–OH and –COOH) of intermediates [20,21]. For example, the reaction rate constant of Fe(III) with $HO_2^{\cdot-}/O_2^{\cdot-}$ was only $1.4 \times 10^5\ M^{-1}\ s^{-1}$, while it could be greatly enhanced to $2.0 \times 10^6\ M^{-1}\ s^{-1}$ due to the complexation of Fe(III) with ligand

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[22,23]. Thus, it is necessary to investigate the degradation process of organic compounds with different structure and its influence on the minimization of BrO_3^- formation in catalytic ozonation.

Recently, Fe–Al LDH has been used to reduce BrO_3^- in water via an adsorption process [24,25]. In this study, Fe–Al LDH was supported on mesoporous γ-Al_2O_3 by a hydrothermal hydrolysis process and its performance on catalytic ozonation of refractory organics and BrO_3^- control was also investigated. Three compounds with different structure were selected to evaluate the influence on BrO_3^- control during their degradation process. It has been proven that different amount of intermediates was formed in catalytic ozonation of organic compounds and the complexes of Fe(III) with intermediates (–OH and –COOH) resulted in different amount of surface Fe(II), leading to different BrO_3^- reduction rate over Fe–Al LDH/Al_2O_3. These findings will facilitate the development of catalytic ozonation for purification of Br^--containing water.

2. Experimental

2.1. Materials and reagents

Aluminum *i*-propoxide, glucose and NaOH were purchased from Beijing Chemical Reagents (Beijing, China). $FeCl_2{\cdot}4H_2O$, $AlCl_3{\cdot}6H_2O$, $KBrO_3$ and KBr were acquired from Yili Company (Beijing, China). 2,4-dichlorophenoxyacetic acid (2,4-D), phenazone (PZ), and amitrole (AMT) were purchased from Acros (Geel, Belgium) and their molecular structures were also provided (Table S1). Raw source water used in this study was obtained from Huanghe River, Zhengzhou, Henan Province, China. All other chemicals were analytical grade and used without further purification. All aqueous solutions were prepared with deionized water.

2.2. Catalyst preparation

Mesoporous Al_2O_3 was prepared as described previously [14]. Based on the reference [24], Fe–Al LDH was supported on Al_2O_3 by co-precipitation method with continuous nitrogen gas bubbling. In a typical procedure, $FeCl_2{\cdot}4H_2O$ and $AlCl_3{\cdot}6H_2O$ (Fe/Al molar ratio was 1:1) were dissolved in 3 mL of deionized water and 2 g Al_2O_3 was then added to this solution. After the pH was adjusted to 7.0 slowly using NaOH solution (3.0 mol/L), the resulting suspension was transferred immediately into Teflon tubes and kept at 373 K for 24 h. The solid product was isolated by centrifuging, washing with deionized water and finally drying overnight at 40 °C in a vacuum. The obtained Fe–Al LDH/Al_2O_3 was stored in tightly capped bottles for further use. For a reference, Fe–Al LDH was also prepared by repeating the same procedure described above except the addition of mesoporous Al_2O_3.

2.3. Characterization

Powder X-ray diffraction (XRD) of the catalyst was recorded on an XDS-2000 Diffractometer (Scintag, Cupertino, CA) with Cu K_α radiation ($\lambda = 1.54059$ Å). The X-ray photoelectron spectroscopy (XPS) data of Fe–Al LDH/Al_2O_3 was taken on an AXIS-Ultra instrument from Kratos using monochromatic Al Kradiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charge effects, the binding energies were calibrated using the C_{1s} hydrocarbon peak at 284.80 eV. The zeta potential of catalysts in the KNO_3 (1×10^{-3} M) solution was measured with a Zetasizer 2000 (Malvern, Worcestershire, UK) with three consistent readings.

2.4. Procedures and analysis

A 300-mL three-neck flask was used as a reactor and the reaction temperature was maintained at 20 °C. In a typical experiment, 220 mL deionized water was placed into the reactor, which was continuously magnetically stirred, and oxygen-ozone gas was bubbled into the reactor to obtain 2.0 mg/L ozone aqueous solution (the oxygen-ozone gas was stopped when the catalytic ozonation reaction started). Then, aqueous suspensions with the desired amount of catalyst and organic compounds, Br^- or BrO_3^- were added into the reactor, which was sealed and magnetically stirred, with a final total volume of 250 mL. In all experiments, the pH of the suspensions was not adjusted during the reaction. In general, the initial suspension pH was about 6, which remained the same within 0.3 units at the end.

Samples were taken at given time intervals (the residual O_3 was liberated by N_2 purging) and filtered through a Millipore filter (pore size 0.45 μm) to remove particles. The filtrates were then divided into several parts for respective measurements of total organic carbon (TOC), BrO_3^- and Br^- by TOC analyzer (TOC-VCPH, SHIMADZU) and ICS-2000 ion chromatography (Dionex Corporations, USA). The ozone was generated by a 3S-A5 laboratory ozonizer (Tonglin Technology, China). All of the experiments were repeated three times.

Fe(II) on the surface of Fe–Al LDH/Al_2O_3 was determined using a phenanthroline spectrophotometric method [26]. 1,10-phenanthroline was used as a probe agent for the detection of Fe(II), and could take up Fe(II) from the surface of the solid-phase Fe–Al LDH/Al_2O_3 via a specific chelating reaction. The samples were prepared as follows: the catalyst dispersions under different conditions were filtered and the resulting solid was resuspended in 10 mL of deionized water. After the addition of 1.0 mL of 1,10-phenanthroline solution and reaction for 10 min, the new dispersion was filtered and the filtrates were analyzed by recording the absorbance at 510 nm. As a reference, no Fe(II) was detected in the filtrates from Fe–Al LDH/Al_2O_3 dispersions from different reaction conditions. The concentration of ozone dissolved in the aqueous phase was determined with the indigo method [27].

The samples for GC–MS analysis were prepared by the following procedure. The suspensions of Fe–Al LDH/Al_2O_3 with different pollutants after reaction with ozone for 15 min were filtered. The resulting solution and Fe–Al LDH/Al_2O_3 particles were evaporated by the freeze-drying method separately. The residues were dissolved with 2.0 ml dichloromethane and the main products on the surface of Fe–Al LDH/Al_2O_3 could be extracted by dichloromethane. Then, the suspension was trimethylsilylated with 0.1 ml of hexamethyldisilazane and 0.05 ml of chlorotrimethylsilane at room temperature. The mixture was shaken vigorously for about 60 s and then allowed to stand for 5 min at room temperature. Precipitate was separated by filtration prior to chromatographic analysis. GC–MS analysis was carried out on Agilent 6890GC/5973MSD with a DB-5 MS capillary column. The chromatographic conditions were as follows: the initial column temperature was held for 20 min at 353 K, ramped at 3.5 K/min to 553 K.

3. Results and discussion

3.1. Characterization of Fe–Al LDH/Al_2O_3

As shown in Fig. 1, the as-prepared Fe–Al LDH exhibited symmetric reflections of the basal (003) and (006) planes, which were the characterization of typical layered structure of LDH. However, no XRD diffraction peaks of LDH structure were observed in the supported sample, which was presumably due to its low loading