Magnetic lanthanide oxide catalysts: An application and comparison in the heterogeneous catalytic ozonation of diethyl phthalate in aqueous solution

Junliang Wang [a], Yuanyang Lou [a], Chao Xu [a,*], Shuang Song [a], Weiping Liu [b]

[a] College of Environment, Zhejiang University of Technology, Hangzhou 310032, China
[b] College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310058, China

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ABSTRACT

Catalytic oxidation with nano magnetic catalysts has the advantages of easy recovery, good stability and high activity. In this study, three nano magnetic lanthanide catalysts with a core–shell structure of $Ce/SiO_2@Fe_3O_4$, $La/SiO_2@Fe_3O_4$ and $Pr/SiO_2@Fe_3O_4$ were prepared and characterized by Brunauer–Emmet–Teller, transmission electron microscopy, X-ray diffraction, energy dispersive X-ray spectrum and vibrating sample magnetometer analysis. All catalysts have Fe_3O_4 nanoparticles as cores, SiO_2 as the mid-layer, and CeO_2, La_2O_3, or Pr_6O_{11} as the outer layer, and have a good magnetic property. The catalyst activities followed the descending order of $Pr/SiO_2@Fe_3O_4$ > $La/SiO_2@Fe_3O_4$ > $Ce/SiO_2@Fe_3O_4$ upon the degradation of diethyl phthalate (DEP), and the catalytic ozonation process followed an ·OH reaction mechanism. The removal rate of DEP was small effected because of the presence of Cl^-, and addition of sodium carbonate had no obviously influence. The initial mineralization rate had a positive relation with the hydroxyl groups and pH value at the zero charge point (pH_{pzc}) of the catalysts, but had no significant relation with the surface area of the catalysts. The catalysts were relatively effective and stable after 3 repeated uses, and the leaching out concentrations of Ce, La and Pr were 1.33 mg/L, 0.138 mg/L and 0.115 mg/L after a 90 min reaction.

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1. Introduction

Ozonation is a popular technology for wastewater treatment because of its high redox potential [1,2]. However, the application of ozone is still limited because of the oxidation selectivity and relatively low efficiency, notably on the degradation of some persistent organic pollutants [3,4]. Recently, catalytic ozonation, especially heterogeneous catalytic ozonation, has been frequently reported for its relatively high efficiency [2,5]. Various metal oxides, including rare earth oxides, such as CeO_2, TiO_2, MnO_2, Ni_2O_3, Al_2O_3, Co_3O_4, CuO, ZnO, V_2O_5, La_2O_3, and Pr_6O_{11}, have been selected as catalysts [6–15]. Of these catalysts, the lanthanide oxides CeO_2, La_2O_3, and Pr_6O_{11} are considered to be promising for catalytic ozonation because of their chemical and biological inertness, strong oxidizing power, recyclability and extended stability against chemical corrosion [6,8,16]. In addition, the cerium ion and praseodymium ion can convert between trivalent and tetravalent states to release and absorb oxygen, this high oxygen mobility

increases the promise of these candidates for catalytic ozonation [17,18]. Faria et al. prepared a ceria–activated carbon composite ($Ce–O/AC_0$) and tested them as catalysts in the ozonation of two selected carboxylic acids, oxalic acid and oxamic acid, the results showed a notable catalytic effect [19]. Gonçalves et al. studied two catalysts containing ceria dispersed on the surface of multi-walled carbon nanotubes and activated carbon as ozonation catalysts for the mineralization of the antibiotic sulfamethoxazole (SMX), the results indicated that materials enhanced the mineralization of SMX relatively to single ozonation, and a strong synergetic effect between carbon materials and ceria was observed [20]. He et al. prepared a series of praseodymium-modified γ-Al_2O_3 (Pr/Al_2O_3) to degrade SA, they found significant enhancement of SA degradation using Pr/Al_2O_3 as a catalyst [6]. Li et al. prepared the catalysts of cerium supported on activated carbon (Ce/AC), which was employed to degrade dimethyl phthalate (DMP) in water, the results showed the catalysts had better catalytic activity and stability based on a 780 min sequential reaction [21].

However, the difficulties associated with separation in catalytic ozonation systems limits their application in the water treatment field. Adding a magnetic component to the catalyst is a suitable

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* Corresponding author.
  E-mail address: chaoxu@zjut.edu.cn (C. Xu).

approach for recycling. To date, the magnetic catalyst using Fe_3O_4 as core has attracted attention because of its remarkable magnetic properties and low toxicity [22]. To avoid the oxidation of the Fe_3O_4 core by the outer atmosphere and the aggregation induced by the magnetic dipolar attraction between the magnetic nanoparticles, silica was usually covered on the surface of magnetic microspheres [23]. Catalysts with highly active oxides on the shell and the magnetized material $SiO_2@Fe_3O_4$ in the core would be helpful in the separation and recyclability.

Phthalic acid esters (PAE_S) are mainly used as a plasticizer to improve plastic flexibility and softness [24]. PAEs are also used in the production of pesticides, cosmetics, defoaming agents and lubricants. Diethyl phthalate (DEP) is one of the most widely used PAEs, it has a moderate water solubility ($\sim$1100 mg/L) and short-chain [25]. DEP is also a strong endocrine disrupter, inducing disorders in the male reproductive system, testicular cancer, and disorders of neuroendocrine system [26,27]. Furthermore, DEP is difficult to biologically and photochemically degrade [28]. Therefore, effective treatment methods are required for this pollutant.

In this study, the magnetic lanthanide oxide catalysts of $Ce/SiO_2@Fe_3O_4$, $La/SiO_2@Fe_3O_4$ and $Pr/SiO_2@Fe_3O_4$ were prepared with a ternary structure consisting of a Fe_3O_4 magnetic core, a silica membrane mid-layer and a lanthanide oxide outer layer. X-ray diffraction (XRD), transmission electron microscopy (TEM) energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), vibrating sample magnetometer (VSM) and B runauer–Emmet–Teller (BET) were used to probe the characteristics of these materials. Their catalytic activities were evaluated by the oxidation of DEP. Possible catalytic ozonation mechanisms and pathway were proposed, the effect of presence of chloride ion, carbonate and bicarbonate ions in the solution were investigated, and the leaching out and recyclability of magnetic catalysts were studied. In addition, the relationships between the initial mineralization rate, the concentration of surface hydroxyl groups, pH_{PZC} and surface area were related.

2. Materials and measures

2.1. Reagents and chemicals

All reagents used in this study were of analytical reagent grade. Deionized water obtained with a Milli-Q water purification system (Millipore, USA) was used in the preparation of all solutions. The ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), potassium hydroxide (KOH), potassium nitrate (KNO_3), trisodium citrate, ammonium hydroxide ($NH_3 \cdot H_2O$), ethyl alcohol (C_2H_5OH), and tetraethyl orthosilicate (TEOS) used for the preparation of $Fe_3O_4@SiO_2$ were purchased from Huadong Medicine Co. (Hangzhou, China). Diethyl phthalate (DEP), *Tert*-butyl alcohol (TBA), sodium carbonate (Na_2CO_3), chlorhydric acid (HCl) were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. (China). Cerous nitrate (99%), lanthanum nitrate (99%) and praseodymium nitrate (99%) tetrahydrate were purchased from Aladdin Reagent Co., Ltd. (China).

2.2. Synthesis of $Ce/SiO_2@Fe_3O_4$, $La/SiO_2@Fe_3O_4$ and $Pr/SiO_2@Fe_3O_4$ catalyst

2.2.1. Synthesis of Fe_3O_4 nanoparticles
Fe_3O_4 magnetic nanoparticles were prepared based on the Matijevic's method [29]. Briefly, KNO_3 (10.12 g) and KOH (5.62 g) were dissolved in 400 mL of anaerobic water (deoxygenated by bubbling N_2 gas for 1 h), then added dropwise 100 mL 0.2 mol/L $FeSO_4$ solution under mechanical stirring. The reaction was under N_2 protection at 60 °C in a water bath. After stirring for

approximately 6 h, the black precipitate was washed several times with absolute ethanol and distilled water until the pH of washing water has scarcely changed, then placed in a vacuum oven at 60 °C for 12 h.

2.2.2. Synthesis of $SiO_2@Fe_3O_4$ nanoparticles
The $SiO_2@Fe_3O_4$ was prepared according to the following procedure. First, Fe_3O_4 (1 g) nanoparticles were added to 50 mL of 0.5 mol/L sodium citrate solution and was ultrasonically treated for 1 h. The sample was then mechanically stirred under N_2 protection for 6 h at 60 °C in a water bath. The precipitate was washed with ethanol and distilled water several times and placed in a vacuum oven at 60 °C for 12 h. Furthermore, the modified Fe_3O_4 nanoparticles (1 g) were added to 80 mL of ethanol and 20 mL of distilled water and were ultrasonically treated for 1 h. Then, 5 mL of TEOS were added to the solution under mechanical stirring at room temperature, 5 mL $NH_3 \cdot H_2O$ was added dropwise. After 4 h, the precipitate was washed with ethanol and distilled water several times until the pH of washing water has scarcely changed, and placed in a vacuum oven to dry at 60 °C for 12 h.

2.2.3. Synthesis of rare earth (RE)/$SiO_2@Fe_3O_4$ nanoparticles
The RE/$SiO_2@Fe_3O_4$ nanoparticles were synthesized via a chemical precipitation and subsequent calcination process. The $SiO_2@Fe_3O_4$ nanoparticles (0.232 g) were dispersed using ultrasonic treatment in 100 mL of 0.05 mol/L cerium nitrate, lanthanum nitrate or praseodymium nitrate solution for 1 h, respectively. Then, 50 mL of 0.5 mol/L KOH was dropwise added under mechanical stirring. After 4 h, the precipitate was washed with water and ethanol several times and placed in an oven to dry at 60 °C for 12 h. Subsequently, the dried powder was calcined in a tube furnace from ambient temperature to 600 °C at a heating rate of 5 °C/min and maintained at that temperature for 2 h under N_2 protection. After calcination, the RE/$SiO_2@Fe_3O_4$ nanoparticles were obtained. The nanoparticles were washed several times with deionized water until the pH of washing water has scarcely changed, and then placed in a vacuum oven to dry at 60 °C for 12 h.

2.3. Characterization of the magnetic nanoparticles

The morphologies of Fe_3O_4, $Fe_3O_4@SiO_2$, $Ce/SiO_2@Fe_3O_4$, $La/SiO_2@Fe_3O_4$, and $Pr/SiO_2@Fe_3O_4$ nanoparticles were characterized by transmission electronic microscopy (TEM). The samples for TEM were obtained by placing drops of each sample on a copper grid. The elemental composition of samples was determined by energy-dispersive X-ray spectroscopy (EDX). Powder X-ray diffraction (XRD) of the catalyst was recorded on a Thermo ARL SCINTAG X'TRA diffractometer at room temperature (25 °C) using a Cu Kα irradiation at 45 kV and 40 mA. The specific surface area was measured by a Brunauer–Emmet–Teller (BET) apparatus (Micrometritics ASAP 2020, USA). The X-ray photoelectron spectroscopic (XPS) measurements were performed on a RBD upgraded PHI 5000C ESCA system (Perkin–Elmer) with Mg KR radiation (300 W, 14.0 kV, 93.9 eV). The binding energies were calibrated by using the contaminated carbon (C1s = 284.6 eV). The magnetic properties of $Ce/SiO_2@Fe_3O_4$, $La/SiO_2@Fe_3O_4$ and $Pr/SiO_2@Fe_3O_4$ nanoparticles were measured at room temperature with a vibrating sample magnetometer (VSM7407, LAKESHORE, USA). The pH value at the point of zero charge (pH_{PZC}) was measured by the drift method as described [30]. The determination of surface hydroxyl groups was carried out as described by Ref. [31].

2.4. Catalytic ozonation activity measurements

The experimental apparatus in this study included a cylindrical Pyrex glass reactor (diameter 80 mm, height 260 mm), an O_3 sup-