



Manganese oxides at different oxidation states for heterogeneous activation of peroxymonosulfate for phenol degradation in aqueous solutions

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ARTICLE INFO

Article history:

Received 12 March 2013

Received in revised form 6 May 2013

Accepted 6 June 2013

Available online 17 June 2013

Keywords:

Mn oxides

Peroxymonosulfate activation

Advanced oxidation

Phenol degradation

ABSTRACT

A series of manganese oxides (MnO, MnO₂, Mn₂O₃ and Mn₃O₄) were synthesized and tested in heterogeneous activation of peroxymonosulfate (PMS) for phenol degradation in aqueous solutions. Their properties were characterized by several techniques such as X-ray diffraction (XRD), thermogravimetric-differential thermal analysis (TG-DTA), scanning electron microscopy (SEM), and N₂ adsorption/desorption isotherms. Catalytic activities of Mn oxides were found to be closely related to the chemical states of Mn. Mn₂O₃ is highly effective in heterogeneous activation of PMS to produce sulfate radicals for phenol degradation compared with other catalysts (MnO, MnO₂, and Mn₃O₄). The activity shows an order of Mn₂O₃ > MnO > Mn₃O₄ > MnO₂. Mn₂O₃ could completely remove phenol in 60 min at the conditions of 25 mg/L phenol, 0.4 g/L catalyst, 2 g/L PMS, and 25 °C. After heat regeneration, the activity could be fully recovered. A pseudo first order model would fit to phenol degradation kinetics and activation energy was obtained as 11.4 kJ/mol.

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1. Introduction

Over the last decades, water treatment plays an important role in our lives, because of fresh water crisis and the increasing awareness of human health and ecological systems as a result of industrial waste pollution. Industrial activities generate large amounts of organic hazardous substances discharged into the environment. The organic wastes can be found in many industries as by-products such as petroleum refining, petrochemical, pharmaceutical, plastic, pesticides, chemical industries, agrochemicals, and pulp and paper industries [1,2]. The organic pollutants e.g. phenol, are toxic and cause considerable damage and threat to the ecosystem in water bodies and to the human health even at low concentrations [3]. It is important to dispose wastewater in a proper way in order to comply with environmental regulations. However, the organics in wastewaters from chemical and related industries cannot be well treated by conventional processes due to degradation of these pollutants being very slow or ineffective and not environmentally

compatible [4,5]. The most promising method for degradation of organic pollutants in wastewater is advanced oxidation processes (AOPs). AOPs are based on generation and utilization of reactive species, such as hydroxyl radicals (HO[•]) that have a high standard oxidation potential and react none selectively [6,7]. Heterogeneous catalytic oxidation systems have recently attracted much interest due to easily recovery and reuse of the catalysts [8].

Lately, manganese oxides, such as MnO, MnO₂, Mn₂O₃ and Mn₃O₄, have attracted much attention due to their physical and chemical properties for being used as catalysts, adsorbents, supercapacitors, and battery materials [9–15]. Kim and Shim [16] have conducted a study on the catalytic combustion of aromatic hydrocarbons (benzene and toluene) on manganese oxides. The results indicated that the catalysts showed high activity in the oxidation of hydrocarbons at temperatures below 300 °C. Furthermore, the reactivity of catalysts exhibited an order of Mn₃O₄ > Mn₂O₃ > MnO₂, which was correlated with oxygen mobility on the catalysts. Ramesh et al. [17] have studied CO oxidation over a series of manganese oxide catalysts and found that Mn₂O₃ is the best catalyst, with the sequence of catalytic activity as MnO ≤ MnO₂ < Mn₂O₃. Santos et al. [18] reported the synthesis of manganese oxide nanoparticles for ethyl acetate oxidation.

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Complete oxidation of ethyl acetate was achieved at temperature below 300 °C. However, few investigations have been conducted in the activity of a series of manganese oxides at different valence states in water treatment.

In the most of previous investigations in water treatment, MnO_x was usually used for Fenton-like reaction for production of hydroxyl radicals from H_2O_2 and oxidation of organic compounds. Recently, sulfate radicals (SRs) produced by Co^{2+} /oxone(peroxymonosulfate, PMS) or Ru^{3+} /oxone have attracted intense attention in degradation of organic compounds for water treatment [19,20]. However, Co^{2+} or Ru^{3+} may generate secondary pollution [21–23]. Therefore, alternative metal such as Fe^{2+} has been proposed by Zazo et al. [24]. They found that $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ have a high catalytic activity for degradation of phenol. In contrary, a recent study by Watts et al. [25] revealed that $\text{Mn}^{2+}/\text{H}_2\text{O}_2$ was significantly more reactive than $\text{Fe}^{2+}/\text{H}_2\text{O}_2$. Moreover, they found that catalytic activity was influenced significantly by pH. Saputra et al. [26] reported the oxidative removal of phenol from water by MnO_2 and studied the factors influencing the reactions. They found that MnO_2 exhibited as a promising chemical agent under certain conditions for phenol removal from wastewater. However, no further investigation has been reported for solid MnO_x for the activation of PMS to generate SRs.

In this research, we investigate the performance of a series of manganese oxides at varying valence states for heterogeneous generation of SRs for chemical mineralization of phenol in the solution. These catalysts will be an alternative for heterogeneous AOP. Several key parameters in the kinetic study such as phenol concentration, catalyst loading, PMS concentration and temperature were investigated. Regeneration of used catalysts was also investigated.

2. Experimental methods

2.1. Preparation of Mn catalysts

A manganese dioxide (MnO_2) was purchased from Sigma–Aldrich Company and used without further treatment. Mn_2O_3 was obtained by treating the MnO_2 at 550 °C in air for 5 h. In addition, MnO_2 was calcined at 950 °C in air for 2 h to get Mn_3O_4 . Another catalyst (MnO) was obtained by a two-step method. First, MnCO_3 was synthesized by a hydrothermal method [27] and then calcination was made. Typically, KMnO_4 (3 mmol) and an equal amount of glucose were put into distilled water at room temperature to form a homogeneous solution, which was transferred into a 45 mL Teflon-lined autoclave. The autoclave was sealed and maintained at 150 °C for 10 h, and was then cooled down to room temperature naturally. The resulted solid product (MnCO_3) was filtered, washed with distilled water and dried in air at 100 °C overnight. Finally, MnO catalyst was obtained by calcination of MnCO_3 at 500 °C under argon flow at a rate 60 mL/min for 2 h.

2.2. Characterization of catalysts

Catalysts were characterized by X-ray diffraction (XRD), N_2 adsorption/desorption isotherm, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). XRD patterns were obtained on a Bruker D8 (Bruker-AXS, Karlsruhe, Germany) diffractometer using filtered $\text{Cu K}\alpha$ radiation source ($\lambda = 1.54178 \text{ \AA}$), with accelerating voltage 40 kV, current 30 mA and scanned at 2θ from 5° to 70°. N_2 adsorption/desorption was measured using a Micromeritics Tristar 3000 to obtain pore volume and the Brunauer–Emmett–Teller (BET) specific surface area. Prior to measurement the samples were degassed at 120 °C for 5 h under vacuum condition. The external morphology and chemical compositions of the samples were observed on a ZEISS NEON 40EsB scanning

electron microscope (SEM) equipped with an energy dispersive spectrometer (SEM-EDS).

2.3. Kinetic study of phenol oxidation

The catalytic oxidation of phenol was carried out in a 1 L glass beaker containing 25–100 mg/L of phenol solutions (500 mL), which was attached to a stand and dipped in a water bath with a temperature controller. The reaction mixture was stirred constantly at 400 rpm to maintain a homogenous solution. A fixed amount of peroxymonosulfate (using Oxone, Dupont's triple salt, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (PMS), Sigma–Aldrich) was added into the solution and allowed to dissolve completely before reaction. Further, a fixed amount of catalyst was added into the reactor to start the oxidation reaction of phenol. The reaction was carried on for 120 min and at a fixed time interval, 0.5 mL of solution sample was taken from the mixture using a syringe with a filter of 0.45 μm and then mixed with 0.5 mL methanol to quench the reaction. Concentration of phenol was analyzed using a HPLC with a UV detector at wavelength of 270 nm. The column used was C-18 with a mobile phase of 30% acetonitrile and 70% ultrapure water. For selected samples, total organic carbon (TOC) was obtained using a Shimadzu TOC-5000 CE analyzer. For the measurement of TOC, 5 mL solutions were extracted at a fixed interval and quenched with 5 mL of 3 M sodium nitrite solution and then analyzed on the TOC analyzer.

For recycled catalyst tests, two regeneration methods were used. One is simple washing treatment and the other is high-temperature calcination. In general, Mn oxides were collected by filtration after reaction, washing with water and drying at 80 °C overnight for reuse test. Some dried samples were further calcined at 500 °C in air for 1 h and then reused for test again.

3. Results and discussion

3.1. Characterization of manganese oxide catalysts

MnO_2 and MnCO_3 were studied by TGA under air and argon atmosphere, respectively (Fig. 1). The TGA pattern of MnO_2 (Fig. 1A) shows 5% weight loss below 300 °C, which corresponds to a loss of surface adsorbed water, organic and trace amount of oxygen. At around 550 °C, weight loss of about 8% corresponds to the loss of oxygen from MnO_2 lattice resulting in the phase transformation to Mn_2O_3 . Another 5% weight loss at around 950 °C corresponds to continuous loss of oxygen resulting in further phase transformation from Mn_2O_3 to Mn_3O_4 . For MnCO_3 , TGA pattern in Fig. 1B shows 10% weight loss below 350 °C, which corresponds to a loss of water, organic and trace amount of carbon dioxide, and another 29% weight loss at around 450 °C corresponds to loss of carbon dioxide from MnCO_3 lattice resulting in the phase transformation to MnO . The nature of TGA and different phase transitions are agreement with the previous reports for MnO_2 and MnCO_3 [28,29].

Fig. 2 shows XRD patterns of four manganese oxides. The four samples present different crystalline peaks. In Fig. 2A, the diffraction peaks occurred at 22.43°, 34.46°, 37.12°, 38.78°, and 57.36°, corresponding to the diffractions of $\gamma\text{-MnO}_2$ (JCPDS No. 14-0664, $a = 6.360 \text{ \AA}$). The diffraction peaks in Fig. 2B occurred at 34.94°, 40.57°, 58.72°, 70.19°, and 73.81°, confirming the structure of MnO (JCPDS No. 75-0626, $a = 4.444 \text{ \AA}$). In Fig. 2C, the diffraction peaks occurred at 28.91°, 30.99°, 32.38°, 36.08°, 38.09°, 44.40°, 50.83°, 53.86° and 59.90°, corresponding to $\gamma\text{-Mn}_3\text{O}_4$ (JCPDS No. 80-0382, $a = 5.749 \text{ \AA}$) while in Fig. 2D the diffraction peaks occurred at 23.08°, 32.84°, 38.14°, 45.05°, 49.22°, 55.04°, and 65.16°, confirming the crystalline structure of $\alpha\text{-Mn}_2\text{O}_3$ (JCPDS No. 89-4836, $a = 9.406 \text{ \AA}$). Those XRD results show the successful synthesis of MnO , Mn_2O_3

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