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Carbon microspheres supported cobalt catalysts for phenol oxidation with peroxymonosulfate

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ABSTRACT

Heterogeneous catalytic oxidation of organic pollutants has been widely applied for wastewater treatment, in which the development of highly efficient catalysts is of critical importance. In this study, carbon microspheres supported cobalt catalysts (Co/CS) were prepared by a one-pot hydrothermal method for in-situ loading cobalt onto carbon spheres, followed by calcination at 300, 400 and 500 °C, respectively. Cobalt would distribute three-dimensionally in the spheres. Many characterization techniques, such as XRD, SEM, EDS and elemental mapping were applied to investigate the physicochemical properties of the supported catalysts. The catalytic activities were evaluated by decomposition of phenol solutions with sulfate radicals. It was found that the Co/CS catalysts were able to efficiently decompose phenol by activation of peroxymonosulfate (PMS). Co/CS-300, 400 and 500 can completely decompose 20 ppm phenol in 15, 5 and 10 min, respectively. Kinetics studies were carried out to investigate the effects of catalyst loading, PMS amount, and reaction temperature on phenol degradation efficiency.

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1. Introduction

Industrial synthesis processes of polycarbonates, epoxies, Bakelite, nylon, detergents, herbicides, resin paint, dyes, textile wood, pulp mill, and pharmaceutical drugs (Fleeger et al., 2003; Mukherjee et al., 1990; Mukherjee et al., 1991), have discharged a large range of hazardous organic pollutants into water body. Such pollution has posed a severe challenge to the sustainable development of the world. Organic pollutants such as phenolics are highly toxic and extremely refractory to natural degradation and causing significant risks to ecological system and public health (Shukla et al., 2010a, 2010b). Both source control and remediation technology are highly required. The industries need to manage the manufacturing sections to reduce the pollutants below permissible level in order to avoid harmful effects; meanwhile the techniques

need to be developed to remove organic compounds from natural water bodies and wastewater system.

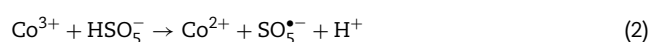
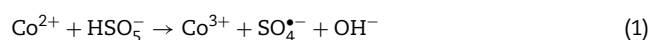
Owing to the complete degradation of organic pollutants in wastewater, advanced oxidation processes (AOPs) have attracted great interests in wastewater treatment. Various AOP techniques such as ozonation, wet air oxidation, thermal destruction, and homogeneous/heterogeneous oxidation, have been investigated, and proven effective in oxidizing organic compounds in wastewater to water and carbon oxide as final products (Agustina et al., 2005; Liang et al., 2012; Saputra et al., 2013; Wang, 2008; Wang and Hong, 1999; Wang et al., 2014; Yang et al., 2008; Zhou et al., 2011). Fenton reaction is a typical AOP involving formation of free hydroxyl radicals in the presence of Fe²⁺ ions. The free hydroxyl radicals are powerful, oxidative and non-selective compounds, and have been successfully employed in industries for decades (Fenton,

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1894). However, several barriers of the techniques have still been experienced: (a) requirement of low pH; (b) quenching of hydroxyl radical by carbonate species present in system; (c) production of sludge, (d) loss of iron in water and (e) difficulties in storage and transportation of hydrogen peroxide (Anipsitakis and Dionysiou, 2003; Chen et al., 2007; Madhavan et al., 2008; Shukla et al., 2010a; Yu et al., 2006). Recently, sulfate radicals as a promising alternative to hydroxyl radicals have been investigated. Many transition metal ions, such as cobalt can activate peroxymonosulfate (PMS, Oxone) to produce sulfate radicals for oxidation of organic pollutants (Anipsitakis and Dionysiou, 2003; Chan and Chu, 2005; Fernandez et al., 2004; Liang et al., 2012; Ling et al., 2010; Saputra et al., 2013, 2014; Sun et al., 2013). The activation reactions proceed as follows (Anipsitakis and Dionysiou, 2003; Bandala et al., 2007; Chen et al., 2007):



However, homogeneous catalytic oxidation process utilizing oxone and cobalt ions has several problems as well. The major concern is that cobalt ions are toxic and will lead to serious health issues (Shukla et al., 2011a). So, new types of heterogeneous cobalt based catalysts are highly demanded to avoid cobalt being discharged in water, and to improve the oxidation efficiency via support materials. Recently, cobalt catalysts supported by novel carbon materials, such as carbon nanofibers (Bezemer et al., 2006; den Breejen et al., 2009), carbon nanotubes (Xiong et al., 2011), and multi-walled carbon tubes (Kang et al., 2009), and micro/nano carbon spheres (Wang et al., 2014; Xiong et al., 2011; Xiong et al., 2010) were prepared and investigated in oxidation reactions. It was found that carbon spheres are promising support or barrier materials that can be easily produced by a green precursor of glucose and can uniformly distribute the effective components by in situ synthesis (Sun et al., 2012; Wang et al., 2014).

In this study, carbon microsphere supported cobalt catalysts were prepared by a hydrothermal method using green precursors. The prepared catalysts were applied to activate PMS to produce sulfate radicals for phenol catalytic oxidation. It was found that the supported cobalt catalysts showed a high activity in phenol oxidation reactions and remained stable in multi-run tests. Kinetic studies were also carried out.

2. Experimental

2.1. Chemicals and materials

D-Glucose (99.5%) was purchased from Sigma. Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) from Sigma was used as the cobalt precursor. PMS (Oxone, peroxymonosulfate) was obtained from Aldrich, and used as the oxidant. Pure methanol was from Chem Supply. Phenol was obtained from Aldrich, and used to prepare pollutant solution. Urea (NH_2CONH_2) was purchased from Sigma-Aldrich.

2.2. Preparation of Co/CS catalysts

Carbon spheres supported cobalt catalysts were prepared by a hydrothermal method. In a typical synthesis, 2.97 g of cobalt(II) nitrate hexahydrate, 7.24 g of D-glucose and 1.20 g of urea were dissolved in 80 mL of ultrapure water. The mixture was stirred

for 6 h. Then the mixed solution was transferred into a 120 mL Teflon-lined autoclave. The autoclave was put in an oven and heated at 180 °C for 18 h. Then the reactor was naturally cooled down to room temperature. The obtained black precipitate was filtrated and washed with methanol twice and water three times. The precipitate was then dried in an oven at 70 °C in the air. Then, the dried samples were calcined in the air at 300, 400, or 500 °C for 2 h, respectively, in a crucible with a cover at a heating rate of 5 °C/min. Resulting samples were denoted as Co/CS-300, -400, and -500, respectively.

2.3. Characterization of catalysts

The crystalline structures of the supported catalysts were analyzed by powder X-ray diffraction (XRD). The spectra were obtained on a Germany Burker D8-Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and cobalt elemental mapping, performed on a Zeiss Neon 40EsB FIBSEM, were used to evaluate the morphology, size, and textural information of the samples.

2.4. Chemical oxidation of phenol

Oxidation of phenol was carried out in a 1L of Pyrex double-jacket reactor. A water bath and pump were used to maintain the reaction temperature at 30 °C. Typically, 0.25 g of Co/CS catalyst was added into 200 mL of 20 ppm phenol solution, and the mixture was stirred for 5 min. Then 0.4 g of PMS was added into mixed solution to start the oxidation reaction. At each set time interval, 1 mL solution was withdrawn by a 5 mL syringe and filtrated by a 0.25 μm Millipore film into a vial, which was filled with 0.5 mL of pure methanol as a quenching reagent. In stability tests, used catalysts were filtrated and washed by water twice, and then dried in an oven at 70 °C in the air. The concentrations of phenol solution samples were analyzed by a Varian high performance liquid chromatography (HPLC) with a UV detector set at $\lambda = 270 \text{ nm}$. 30% CH_3CN and 70% ultrapure water were mixed as the mobile phase at a flow rate of 1 mL/min. All experiments employing used catalysts were run in the same reaction conditions as mentioned above.

3. Results and discussion

3.1. Characterization of Co/CS catalysts

Fig. 1 shows XRD patterns of the supported cobalt catalysts prepared at different temperatures. XRD patterns of Co/CS-raw and pure carbon sphere were not shown here because they did not show any peaks. The fluctuation between 20° and 30° showed typical diffractions of carbon material (Fu et al., 2003). Co/CS-300 did not have peaks that could be assigned to Co_3O_4 . It was reported that the decomposition of the Co-B amorphous alloy can occur with the heat treatment above 300 °C (Lee et al., 2007). However, no peaks corresponding to metallic cobalt was detected with the decomposition of Co-B which might be caused by the small amount of formed metallic cobalt (Xu et al., 2008). This is also possible because the cobalt particles on this catalyst are too small to be detected by XRD (<4 nm) (Mukherjee et al., 1991; Wang, 2008). Therefore, it might show that cobalt(II) nitrate turned into cobalt(III) hydroxide or cobalt(II) hydroxide as precipitate after the hydrothermal reaction (Mukherjee et al., 1991).

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