



Magnetic carbon-supported cobalt prepared from one-step carbonization of hexacyanocobaltate as an efficient and recyclable catalyst for activating Oxone



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ABSTRACT

To develop an easy-to-prepare magnetic carbon-supported cobalt (MCC) catalyst, hexacyanocobaltate salt, as the first time, was employed as a precursor to prepare MCC via a simple one-step carbonization. The magnetism, porosity and carbon-supported cobalt of MCC allow it to be a promising catalyst to activate Oxone for generation of sulfate radicals which can degrade toxic Amaranth dye. Parameters influencing the Amaranth degradation were examined including catalyst loading, Oxone dosage, temperature, pH, co-existing compounds as well as inhibitors. While increases in MCC loading and Oxone dosage both enhanced the degradation extent and kinetics, the Amaranth degradation was more sensitive to the variation of Oxone dosage. The degradation was also preferable at elevated temperature and low pH. In addition, the Amaranth degradation by MCC-activated Oxone remained quite stable in the presence of salts and anionic surfactant. Through the effect of various inhibitors and ESR spectroscopic analysis, the Amaranth degradation primarily involved sulfate radicals. MCC also exhibited a consistent catalytic activity over multiple degradation cycles and stable chemical composition. Considering the magnetically controllability of MCC together with the aforementioned features, MCC can be a promising heterogeneous catalyst to activate Oxone for degradation of toxic contaminants.

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1. Introduction

Wet chemical oxidation (WCO) is extensively employed in chemical synthesis [1] and environmental remediation [2–4]. Specifically, WCO reactions for treating contaminants are classified as Advanced Oxidation Processes (AOPs) [2,5–7], in which high-oxidation-potential radicals, including hydroxyl (OH[•]) and sulfate (SO₄^{•-}) radicals [8,9], can be generated to degrade organic pollutants. Although OH[•]-generating reactions, such as Fenton reaction, have been intensively developed, recently SO₄^{•-}-generating reactions also receive enormous attention owing to the following reasons [10]. First, SO₄^{•-} exhibits a similar or even higher oxidation potential (*i.e.*, 2.5–3.1 V) than OH[•] (*i.e.*, 2.8 V) [11]. Second, SO₄^{•-} possesses a higher selectivity for unsaturated and aromatic electrons [11,12]. Third, the half-life of SO₄^{•-} (~40 μs) is relatively long compared to that of OH[•] (<1 μs) [13,14].

To generate SO₄^{•-} radicals, Oxone (potassium peroxydisulfate) has been recognized as an environmentally-friendly and

easily-accessible [10] source. The generation of SO₄^{•-} from Oxone, however, is quite slow; therefore several techniques have been proposed to activate Oxone, including thermal treatment [15,16], UV irradiation [15,17], sonication [18,19] and catalysts [20–23]. Due to the intensive and continuous energy input needed during the thermal treatment, UV irradiation and sonication, the addition of catalysts is a more efficient and cost-effective approach [24]. Up to date, cobalt is considered as the most efficient metal to activate Oxone [24,25]. Several studies have added cobalt ions directly to solutions for activating Oxone [26–29]. Nevertheless, cobalt ions added to solutions cannot be easily recovered, leading to secondary contamination. Therefore, attempts have been made to immobilize cobalt on supports including mesoporous silica [30,31], TiO₂ [32,33], SiO₂ [32], Al₂O₃ [32], and Fe₃O₄/Carbon [34], as well as to prepare core/shell metal/carbon composites [35,36]. Some studies also proposed to use Co₃O₄ nanoparticle as a heterogeneous catalyst to activate Oxone to avoid the release of Co ions to solutions [20,37,38]. Nevertheless, immobilizing Co₃O₄ particles on appropriate supports is still considered a preferable technique in order to evenly disperse Co₃O₄ particles on high-surface-area supports for maximizing catalytic activity [39], to easily recover catalysts [39], and to prevent aggregation of nanoscale catalysts [40].

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Therefore, various supports have been proposed to immobilize Co_3O_4 , such as SiO_2 [41], MnO_2 [42], TiO_2 [39], graphene [23,43,44], graphite [45], fly ash [46] as well as carbon microspheres [47].

For either cobalt ions or Co_3O_4 , carbonaceous materials appear to be an attractive support because carbon is non-metal, earth-abundant, chemically inert and electrically conductive. Huang et al. reported that using activated carbon fiber as a cobalt support could facilitate electron transfer to improve catalytic activity of cobalt [48]. Shi et al. also immobilized Co_3O_4 on graphite and found that graphite-supported Co_3O_4 outperformed unsupported Co_3O_4 owing to a synergy between Co_3O_4 and graphite. While these findings indicate that carbonaceous materials are promising supports, the preparation of such carbon-supported cobalt materials involves complex post-modification techniques and relatively long preparation time. In addition, carbon-supported cobalt, as a heterogeneous catalyst, must be easily recovered [34,49]. Therefore, it is necessary to develop a simple-to-prepare, easy-to-recover and highly efficient carbon-supported cobalt material for the activation of Oxone. To this end, we propose to employ a commercially available hexacyanocobaltate salt, which consists of cobalt, carbon and nitrogen, as a precursor to prepare magnetic carbon-supported cobalt (MCC) via simple one-step carbonization. The magnetism, porosity and carbon-supported cobalt of MCC allow it to be a promising catalyst to activate Oxone for generation of sulfate radicals which can degrade organic pollutants.

The resultant MCC was characterized using transmission electronic microscopy (TEM) to observe its morphology. Chemical characteristics of MCC were determined using X-photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Raman spectroscopy. Physical features of MCC were obtained by thermogravimetric (TG) analysis, N_2 sorption/desorption measurement as well as the saturation magnetization. To evaluate whether MCC can be used in AOPs to activate Oxone, degradation of Amaranth was selected as a model test because Amaranth is potentially carcinogenic and used extensively as additives for manufacturing foods and cosmetics [50,51]. Parameters influencing Amaranth degradation were investigated, including catalyst loading, Oxone dosage, temperature, pH, co-existing compounds and inhibitors. Electron Spin Resonance (ESR) spectroscopy was employed to identify radical species occurring during the activation of Oxone by MCC in order to probe into the degradation mechanism. To evaluate reusability of MCC, a multi-cycle Amaranth degradation test using MCC was also performed without regeneration treatments on MCC.

2. Experimental

2.1. Materials

All chemicals used in this study were purchased from commercial reagent suppliers and used directly without purification. Potassium hexacyanocobaltate ($\text{K}_3\text{Co}(\text{CN})_6$), Oxone[®] (potassium peroxymonosulfate), ascorbic acid and sodium dodecyl sulfate (SDS) were obtained from Sigma-Aldrich (USA). Sodium fluoride (NaF), potassium iodide (KI) and urea were purchased from Showa Chemicals (Japan). Sodium bromide (NaBr) and sodium chloride (NaCl) were obtained from Merck (Germany). *tert*-butyl alcohol (TBA) was purchased from Alfa Aesar (USA). Cobalt nitrate ($\text{Co}(\text{NO}_3)_2$) was obtained from Choneye Pure Chemicals (Taiwan). Deionized (DI) water was prepared to less than 18 MOhm-cm.

2.2. Preparation and characterization of MCC

The preparation of MCC is illustrated in Fig. 1. $\text{K}_3\text{Co}(\text{CN})_6$ powder was placed in a tubular furnace and then carbonized in nitrogen at 600 °C for 6 h. The resultant black-colored particles were

washed thoroughly with D.I. water and then dried in a conventional oven at 85 °C overnight to yield the final production, MCC. MCC was characterized first by TEM (JEOL JEM-2010, Japan) for observing its morphology. The XRD pattern of MCC was determined using an X-ray diffractometer (Bruker D8 Discover, USA) with copper as an anode material (40 mA, 35 kV). Raman spectroscopic analysis of MCC was conducted using a Raman spectrometer (Tokyo Instruments Inc. Nanofinder, Japan). Surface chemistry of MCC was investigated using X-ray Photoelectron Spectroscopy (XPS) with Versa Probe/Scanning ESCA Microprobe (PHI 5000, ULVAC-PHI, Inc., Japan). Saturation magnetization of MCC was measured by a SQUID Vibrating Sample Magnetometer (Quantum Design MPMS, USA) at 27 °C. Thermogravimetric (TG) analysis of MCC was conducted using a thermogravimetric analyzer (ISI TGA i1000, USA) at increments of 20 °C min^{-1} from 20 to 800 °C in nitrogen or air atmosphere. N_2 sorption and desorption isotherms of MCC was measured by a volumetric gas adsorption analyzer (Micromeritics ASAP 2020, USA).

2.3. Activation of Oxone using MCC for Amaranth degradation

Amaranth degradation using MCC-activated Oxone was investigated by batch-type experiments. In a typical experiment, 20 mg of Oxone was added to 200 mL of Amaranth solution with an initial concentration (C_0) of 50 mg L^{-1} . When Oxone powder was fully dissolved (less than 1 min), a certain amount of MCC (e.g., 20 mg) was immediately added to the Amaranth solution which was stirred at 300 rpm and maintained at a pre-set temperature. Sample aliquots were withdrawn from the Amaranth solution at pre-set intervals and the residual Amaranth concentration (C_t) at a given t was determined using a UV-vis spectrophotometer at 520 nm (Chrome-tech S-2200, Taiwan). Co_3O_4 , which was prepared hydrothermally [52], and cobalt nitrate were used to activate Oxone for comparison with MCC. Effects of MCC loading and Oxone dosage were also examined by changing MCC loading from 100 to 300 mg L^{-1} while fixing Oxone to 100 mg L^{-1} and varying Oxone dosage from 50 to 200 mg L^{-1} with a fixed MCC loading of 100 mg L^{-1} . To investigate effect of temperature, the solution temperature was varied from 20 to 60 °C. In addition, effect of pH was also investigated by adjusting the initial pH of solution to 3.5, 6 and 11, representing an acidic, a neutral and a basic condition, respectively. Considering that Amaranth is an anionic compound the degradation competition between Amaranth and other potential anions were also studied, including F^- , Br^- , Cl^- and a common anionic surfactant, SDS. Several radical-scavengers, such as ascorbic acid, KI, methanol and TBA, were added to Amaranth solutions in order to investigate their inhibitive effects on the Amaranth degradation and on the activation of Oxone by MCC. Furthermore, electron spin resonance (ESR) spectroscopy was used to determine radical species generated during the activation of Oxone by MCC using Bruker ESR spectrometer (EMX-P, Germany). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) as a radical-trapping agent. The recyclability test of MCC was conducted first by collecting the used MCC by a permanent magnet and then adding it to another batch of degradation experiment without regeneration. Cobalt leaching out from MCC during activation of Oxone was determined using Perkin Elmer Analyst 100 Atomic Absorption Spectrometer.

3. Results and discussion

3.1. Characterization of MCC

As revealed in Fig. 1, $\text{K}_3\text{Co}(\text{CN})_6$ powder are transparent crystals which are a few millimeters in size. After carbonization, the transparent crystals were converted to black-colored MCC powders as

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