

Nanocrystalline cobalt oxide immobilized on titanium dioxide nanoparticles for the heterogeneous activation of peroxymonosulfate

Qiuqing Yang, Hyeok Choi, Dionysios D. Dionysiou*

Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati, OH 45221-0071, USA

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Abstract

Recently, sulfate radical-based advanced oxidation technologies have shown significant implications for environmental remediation to decompose water pollutants. In this study, we evaluated the performance of heterogeneous activation of peroxymonosulfate (PMS) to generate sulfate radicals using cobalt catalyst immobilized on titanium dioxide nanoparticles (Co/TiO₂). The Co/TiO₂ catalyst was prepared *via* an incipient wetness impregnation method employing Degussa P-25 TiO₂ and Co(NO₃)₂·6H₂O. The activity of Co/TiO₂ system was compared with those of Co(NO₃)₂ solution for homogeneous PMS activation and neat Co₃O₄ for heterogeneous PMS activation. More emphasis was given to the effect of cobalt loading and heat treatment on the physicochemical properties of Co/TiO₂ and cobalt leaching. The results showed that heat treatment of Co/TiO₂ at 500 °C, where cobalt existed as Co₃O₄, induced negligible Co leaching and enhanced catalytic activity to decompose 2,4-dichlorophenol. The Co/TiO₂ catalyst at Co/Ti molar ratio of 0.1 showed the highest activity *via* heterogeneous PMS activation. On the other hand, Co/TiO₂ catalysts with Co/Ti molar ratio of above 0.2 exhibited rather much lower activity which was initiated predominantly *via* a homogeneous pathway from leached cobalt, although they contained considerable amounts of Co₃O₄. The formation of Co–OH complexes at the surface of Co/TiO₂ nanoparticles, due to the ability of TiO₂ to dissociate H₂O for the formation of surface hydroxyl groups, was proposed to facilitate the heterogeneous PMS activation. However, high cobalt loading covering the TiO₂ surface diminished the beneficial role of TiO₂ due to the reduction in the concentration of surface hydroxyl groups and thus decreased the heterogeneous PMS activation. The activity of Co₃O₄ in Co/TiO₂ catalysts was much higher than that of neat Co₃O₄ due to the presence of surface hydroxyl groups and uniform distribution of well-defined 10–15 nm nanocrystalline Co₃O₄ particles at the surface of 30–40 nm TiO₂ nanoparticles.

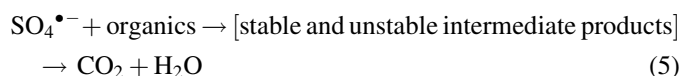
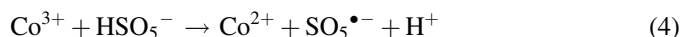
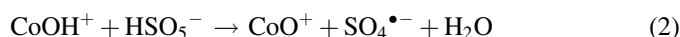
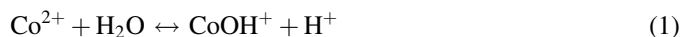
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1. Introduction

Recently, the growing interests in sulfate radical-based advanced oxidation technologies (AOTs) are driven by the increasing demand of cost-effective and environmentally benign routes for wastewater treatment [1–3]. Sulfate radicals, generated by catalytic decomposition of peroxymonosulfate (PMS) in a homogeneous pathway with the aid of transition metals and/or UV radiation, have been proven to be strong oxidizing species which are capable of readily attacking and decomposing recalcitrant organic molecules in water into nontoxic species, such as CO₂ and H₂O [4–8]. Of the transition metals investigated, cobalt ions (Co²⁺) showed the best

performance [5]. There are a few studies on the generation mechanism of sulfate radicals by cobalt-catalyzed decomposition of PMS in the homogeneous system [4,9,10]:



Although this system is promising for effectively abating environmental pollution in water, health concerns associated

* Corresponding author. Tel.: +1 513 556 0724; fax: +1 513 556 2599.

E-mail address: dionysios.d.dionysiou@uc.edu (D.D. Dionysiou).

with the adverse effect of dissolved cobalt in water still need to be addressed. Consequently, it is beneficial to activate PMS *via* a heterogeneous manner that may prevent the problem with dissolved or leached cobalt present in the polished water. In a recent article, Anipsitakis et al. explored this concept using commercially available Co_3O_4 and demonstrated the heterogeneous PMS activation [11]. The Co_3O_4 , however, is not fully utilized for the PMS activation since it exists as large macroparticles, which reduces dramatically the available surface area of the catalyst.

Consequently, the purpose of this study is to improve the catalytic activity of cobalt for the heterogeneous PMS activation by controlling the physicochemical properties of cobalt or Co_3O_4 material at the nanolevel. In this study, we focused on immobilizing cobalt catalyst at the surface of TiO_2 . TiO_2 nanoparticles were selected as the support material because: (i) the heterogeneous catalytic activity of cobalt can be maximized by evenly distributing cobalt on the TiO_2 nanoparticles with high surface area, (ii) deposition of cobalt on TiO_2 nanoparticles is the first step towards the development of a novel AOT where sulfate radicals and hydroxyl radicals can be generated simultaneously in the presence of UV radiation from PMS and TiO_2 , respectively, and (iii) TiO_2 as a support material is environmental friendly because it is relatively nontoxic and it can be recovered or used in immobilized form [12,13]. Interestingly, due to the well-known ability of TiO_2 to dissociate water for the formation of surface hydroxyl groups [12], TiO_2 as a support material might play a crucial role in the heterogeneous PMS activation by facilitating the formation of surface Co–OH groups, as depicted in Eqs. (1) and (2).

Co-based catalysts are widely used in CO hydrogenation or Fischer–Tropsch synthesis [14–18]. To the best of our knowledge, Co/ TiO_2 nanoparticles acting as an activator of PMS have never been reported so far. In this study, we synthesized Co/ TiO_2 nanoparticles *via* an incipient wetness impregnation method. More emphasis was given to the effect of Co loading at the TiO_2 surface and calcination temperature on the physicochemical properties of Co/ TiO_2 and leaching behavior of cobalt. The heterogeneous PMS activation using Co/ TiO_2 was examined in terms of 2,4-dichlorophenol (2,4-DCP) decomposition. 2,4-DCP is a well-known intermediate during the synthesis and degradation of 2,4-dichlorophenoxyacetic acid that is a regulated and widely used herbicide [19]. The chemical has been included in the drinking water contaminant candidate list by the USEPA because it is toxic, hardly biodegradable, and difficult to remove from the environment [20]. Finally, a possible mechanism for the heterogeneous PMS activation over Co/ TiO_2 was proposed, based on the widely accepted homogeneous pathway, and the crucial role of TiO_2 to generate surface hydroxyl groups was suggested.

2. Experimental

2.1. Preparation of Co/ TiO_2 catalysts

In order to immobilize Co at the surface of TiO_2 nanoparticles and control the properties of Co/ TiO_2 catalysts

at the nanolevel, we adapted an incipient wetness impregnation method. A desired amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.3%, Sigma) was dissolved in distilled water and then impregnated on Degussa P-25 TiO_2 nanoparticles (anatase/rutile mixture; BET surface area: $\sim 50 \text{ m}^2/\text{g}$; particle size: $\sim 30 \text{ nm}$) under vigorous stirring. This suspension was stirred for 24 h, and then dried under an infrared lamp at alleviated temperature of $50 \text{ }^\circ\text{C}$ to remove water. Finally, in order to control their crystal phase and enhance their mechanical stability, the catalysts were calcined in a furnace (Paragon model HT-22D, Thermcraft) at various temperatures ranging from 300 to $700 \text{ }^\circ\text{C}$ for 4 h with a ramp rate of $600 \text{ }^\circ\text{C}/\text{h}$. The resulting Co/ TiO_2 catalyst was ground thoroughly and labeled as XCo/ TiO_2 -Y, where X stands for the molar ratio of Co to Ti and Y stands for the calcination temperature. Heterogeneous PMS activation and homogeneous PMS activation are denoted as hetero-PMS-Act and homo-PMS-Act, respectively.

2.2. Evaluation of catalytic activity

The catalytic activities of three different systems (Co/ TiO_2 catalyst for hetero-PMS-Act partially combined with homo-PMS-Act at neutral pH (or basic pH), commercial neat Co_3O_4 powder for hetero-PMS-Act, and $\text{Co}(\text{NO}_3)_2$ solution for homo-PMS-Act) were evaluated in terms of 2,4-dichlorophenol degradation (2,4-DCP, 99%, Acros Organics). First, a quartz rectangular reactor (base: $10 \text{ cm} \times 10 \text{ cm}$; height: 25 cm) containing 1 L of 50 mg/L (0.307 mM) 2,4-DCP solution with adjusted pH of 7.0 using 5 mM NaHCO_3 and KHSO_4 was placed on a magnetic stirrer plate. After the addition of 0.1 g of Co/ TiO_2 catalyst in the solution, the solution was allowed to reach adsorption equilibrium between the catalysts and 2,4-DCP (there was no considerable 2,4-DCP adsorption on the catalyst surface). Then, Oxone (KHSO_5 as active component, Aldrich, manufactured by Dupont) was added into the solution at $\text{KHSO}_5/2,4\text{-DCP}$ molar ratio of 3:1. For measuring the concentration of 2,4-DCP during 2 h of reaction, 10 mL samples were withdrawn at specified time intervals and quenched with 5 mL of 2.47 M methanol (Aldrich) to prevent further reaction. The sample was filtered with $0.1 \text{ }\mu\text{m}$ filter (Magna Nylon, Fischer) and analyzed using a High Performance Liquid Chromatograph (HPLC, Agilent 1100 Series) with a QuatPump and a photo-diode-array detector. The column was an Eclipse XDB-C8 column (Agilent) and mobile phase was 70:30% (v/v) of 0.01N H_2SO_4 :acetonitrile. An atomic absorption spectrometer (Perkin-Elmer AA-300) equipped with an HGA-800 electrothermal atomizer and an AS-72 auto sampler was used to analyze the cobalt leaching from the catalyst. For the characterization of spent Co/ TiO_2 nanoparticles, the catalysts were collected after 2 h reaction and analyzed.

In parallel, the activities of commercially available neat Co_3O_4 ($\text{CoO} \cdot \text{Co}_2\text{O}_3$, Fischer) for hetero-PMS-Act and $\text{Co}(\text{NO}_3)_2$ (Sigma) solution for homo hetero-PMS-Act were tested for comparison. The amounts of neat Co_3O_4 , equivalent to 0.1 g of 0.1Co/ TiO_2 and 0.5Co/ TiO_2 were 9.1 and 33.4 mg, respectively, assuming that cobalt in Co/ TiO_2 exists in the form

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