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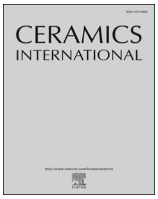

Spinel-type cobalt-manganese oxide catalyst for degradation of Orange II using a novel heterogeneous photo-chemical catalysis system

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ABSTRACT

A spinel-type Co-Mn oxide was designed and synthesized through a two-step oxidation-precipitation method at modest temperatures. The Co-Mn oxide was applied as the catalyst in the presence of $NaHSO_3$ under visible light irradiation in order to establish the superiority of heterogeneous photo-chemical catalysis system. In the above system, the Co-Mn catalyst exhibited much better catalytic capability than that in either single photocatalysis or chemocatalysis system, implying that the Co-Mn catalyst could well combine photocatalysis and chemocatalysis to obtain the highest degradation efficiency of up to 94% within 40 min when using Orange II as the target pollutant. Recycling experiments results showed that the as-obtained catalyst has excellent stability and recyclability. Powder X-ray diffraction (XRD) analysis showed that the as-obtained Co-Mn catalyst had a cubic $MnCo_2O_{4.5}$ spinel structure. Because of relatively low temperature (180 °C) synthesis, the catalyst was formed with nanoparticles (25–65 nm) and high specific surface area as confirmed by SEM and BET analyses. XPS indicated the presence of both manganese and cobalt species that serve as reactive sites for the catalytic oxidation reactions. Rational degradation mechanisms responsible for superior catalytic activity and durability were proposed based on a series of experimental results. The active species such as Mn(III), holes and sulfate and hydroxyl radicals were proposed to be responsible for the outstanding degradation results.

1. Introduction

In developing countries, large amounts of organic hazardous substances generated in industrial activities are being discharged indiscriminately into the environment. Among the multifarious organic pollutants, pollution from dyes has become an issue of great concern due to their high toxicity, chemical stability, non-biodegradability and carcinogenic effects [1]. In order to follow environmental guidelines, disposal of wastewater in an appropriate way is absolutely imperative. Thus far, advanced oxidation processes (AOPs) have been one of the most promising ways to degrade organic pollutants in wastewater.

The concept of AOPs was first proposed by Glaze et al., [2], namely, using the highly active and nonselective hydroxyl radicals (·OH) which are generated in the reaction to aggressively attack most refractory compounds by oxidative degradation gradually or complete mineralization at the end [3]. Great majority of AOPs adopt a combination of catalysts (e.g. transition metal ions) with strong oxidizing agents (e.g. O_3, H_2O_2) and irradiation (e.g. visible, ultraviolet, ultrasound). Researchers realized that light could accelerate some AOP (such as Fenton) reactions markedly [4], inspiring the investigators to combine these processes in order to achieve higher degradation efficiency.

It is well known that the photocatalytic performance depends largely on the band structure, morphology, particle size and specific surface area of the semiconductor materials. Due to unfilled valence d-orbitals, transition metals are prone to lose or seize electrons, thus they have strong redox and semiconductor properties. Furthermore, transition metal oxides have heat resistance, photosensitivity, thermal sensitivity and impurity sensitivity that were more favorable to the modification of catalyst performance [5,6]. Mixed transition metal oxides (MTMOs), typically binary metal oxides with two different metal cations, could lead to rich redox reactions due to the coupling of two metal species [7]. Cobalt and manganese oxides not only are widely available and rich in species, but also have stable chemical properties, large specific surface area, good adsorption and catalytic properties and that is why they play an important role in environmental chemistry and catalytic materials. Li et al. [8] synthesized cobalt–manganese spinel

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oxides with simultaneously controllable phase and composition and coordinated the tetragonal and cubic crystallographic symmetry of spinel over an unparalleled wide compositional range. Pi et al. [9] prepared well-crystallized $Co_xMn_{3-x}O_4$ spinel catalysts with porous micro-nano hierarchical structures and found that they have lower oxidation potentials and more redox-active sites compared to Mn_2O_3 and Co_3O_4 catalysts with similar microstructures. Bazuev et al. [10] showed that $MnCo_2O_{4+\delta}$ prepared at low temperatures had the structure of the cation-deficient spinel with enhanced oxygen content and manganese or cobalt (or a part of these elements) in this phase had a higher valence than that in the stoichiometric spinel ACo_2O_4 (A = Mn, Zn). Liang et al. [11] used nucleation and growth mechanism to design a $MnCo_2O_4$/N-doped graphene hybrid material and found that the increased activity of catalytic sites in the hybrid materials may result from the partial substitution of Co^{3+} sites by Mn^{3+}. Zhang et al. [12] found that the cubic $CoMn_2O_4$ spinel contains mixed-valence Mn and Co cations that can be catalytic sites, and the presence of multivalent 3d metals would promote electron conduction (through hop) and charge transfer (by redox reactions) to enhance the photocatalytic reaction. Habibi et al. [13] found that cobalt manganese oxide coated on glass could efficiently mineralize 92% of azo textile dye within 3 h of irradiation and inferred that the eximious photocatalytic activity may be due to the heightened photo-induced charge separation caused by the formation of coupling of two oxides as a composite.

Recently, advanced oxidation processes (S-AOPs) based on sulfate radical ($SO_4^{\bullet-}$) and hydroxyl radical have attracted intensive attention for rapidly oxidizing organic compounds at nearly diffusion controlled rates [14,15]. Sulfate radical has extremely strong standard electrode potential ($E_0 = 2.5\ V - 3.1\ V$) [16] and it has almost the same oxidation ability as the hydroxyl radical ($E_0 = 2.7\ V - 2.8\ V$) [17]. Studies have shown that sulfate radicals can persist longer after they are produced which can increase the contact with organic compounds and prolong the oxidation time, achieving the degradation effect that is better theoretically than hydroxyl radicals under the same conditions. Moreover, sulfate radicals can also decompose some organic compounds that cannot be oxidized by hydroxyl radicals, and hence, their removal capacity will be superior. Similar to the method of Fenton activation to produce ·OH, $SO_4^{\bullet-}$ can be generated using various transition metal ions (Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ce^{3+} etc.) to catalyze sulfite, bisulfite (BS), persulfate (PS) etc. Via a two-electron oxidation process, the sulfite can be enzymatically oxidized with the formation of $SO_3^{\bullet-}$ anion radicals, which can rapidly react with dioxygen and cause the formation of $SO_5^{\bullet-}$, $SO_4^{\bullet-}$ and ·OH radicals [18]. Xie et al. [19] reported an efficient degradation/debromination of para-bromophenol in the UV/sulfite process and found that the degradation was enhanced with increasing pH and sulfite concentration but inhibited by the presence of oxygen and organic solvent. As it can produce highly active species during oxidation process, sulfite is considered to have great application potential in wastewater treatment. Actually, the homogeneous iron–sulfite system has been authenticated as an efficient system for degradation of organic pollutants [20,21]. However, heterogeneous catalysts have not been used to a significant extent in the oxidation reaction so far.

Sun et al. [22] proposed a novel advanced chemocatalysis oxidation process that employed HSO_3^- to activate manganese oxidants and suggested that reactive intermediate(s) such as manganese(III) species with minimal stabilization by complexation are responsible for the extraordinarily fast oxidation rates. Mn(III) is a strong and important oxidant for one electron transfer reactions, which may play an important role in the transformation of organic contaminants in biogeochemical redox processes and water treatment. However, as soluble and free Mn(III) are unstable under general conditions, the interaction mechanism between organic contaminants and free Mn(III) has not been fully appreciated or understood. Furthermore, Mn(III) centers on the surface of manganese oxides are also involved in the redox processes of manganese minerals as heterogeneous catalytic oxidation systems, which have recently attracted much interest due to their easy recovery and reuse of the catalysts. The combination of several advanced oxidation processes is an extraordinarily promising method in water treatment that conforms to current development trend and needs.

Herein, we have designed and synthesized a spinel-type cobalt-manganese oxide through a two-step oxidation-precipitation process under modest temperature conditions. Then, the as-obtained cobalt-manganese oxide was used as the catalyst and $NaHSO_3$ as the co-catalyst in a system where decomposition of Orange II pollutant was tested. This system was supplemented by visible light irradiation in order to establish heterogeneous photo-chemical catalysis as a superior process and investigated the influence of material morphology, composition and chemical environment on the reaction during the process. Moreover, cycling experiments were conducted to examine the stability and recyclability of the catalyst.

2. Experimental

2.1. Chemicals

Manganese nitrate tetrahydrate [$Mn(NO_3)_2 \cdot 4H_2O$], cobalt nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$], ammonium hydroxide solution (25 wt %), sodium bisulfite ($NaHSO_3$), ethanol (EtOH), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) were purchased from the Shanghai Titan Scientific Co., Ltd. (Shanghai, China). Tert-butanol (TBA) and p-benzoquinone (BQ) were obtained from the Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Orange II sodium salt was supplied by the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals procured for this study were at least of analytical grade and were used as received. Deionized water was used throughout the experiments.

2.2. Synthesis of spinel Co-Mn catalyst

According to a previously reported procedure [8], the spinel-type cobalt-manganese oxides were prepared through a two-step oxidation-precipitation method under modest temperature conditions. The preparation method is briefly described as follows: Firstly, 8 mL ammonium hydroxide solution (25 wt%) was dropped into 10 mL 0.2 mol L^{-1} $Co(NO_3)_2$ solution under stirring at room temperature. Then, 20 mL of 0.2 mol L^{-1} $Mn(NO_3)_2$ solution was added to the mixture followed by stirring for an additional 120 min in air. Afterwards, nitrates were fully decomposed and the mixtures were dried by heating at 180 ℃ for 6 h, yielding the Co-Mn oxide catalyst powder.

2.3. Characterization

The crystallinity and phase purity of the catalyst were investigated by powder X-ray diffraction (XRD) analysis using an X-ray diffractometer (Rigaku D/Max-2500 PC) with Cu Kα ($\lambda = 1.54056$ Å) radiation (40 kV, 300 mA) of 0.154 nm wavelength. The morphology of the catalyst was characterized by the JSM-6360LA scanning electron microscope (SEM, JEOL, Japan). The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method using an adsorption apparatus (Micromeritics, ASAP 2010C, USA). The chemical oxidation states of Co, Mn and O species in the catalyst were investigated by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific, Escalab 250Xi spectrometer with Al X-ray source (Al Kα, $h\nu = 1486.7$ eV).

2.4. Catalytic degradation of Orange II

Three different catalytic degradation processes of Orange II, i.e., photocatalysis, chemocatalysis and photo-chemical catalysis were carried out, the latter is a combination of photocatalysis and chemocatalysis processes. Testing the catalytic activity of the Co-Mn sample was