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Catalytic degradation of bisphenol A by CoMnAl mixed metal oxides catalyzed peroxymonosulfate: Performance and mechanism

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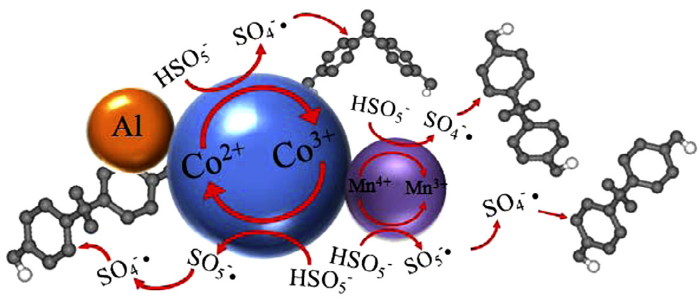
HIGHLIGHTS

- BPA was completely degraded by mixed metal oxides catalyzed of PMS.
- The $SO_4^{-\cdot}$ were recognized as the main species to oxidize pollutant.
- The hydroxyl radicals could induce the acceleration of PMS decomposition.
- The hydroxylation and cleavage of benzene-rings are major degradation pathways.

GRAPHICAL ABSTRACT

The mechanism of CoMnAl-MMO inducing PMS to oxidize BPA.



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ABSTRACT

In this study, CoMnAl mixed metal oxides (CoMnAl-MMO) were prepared and employed in heterogeneous activation of Oxone for bisphenol A (BPA) degradation. Typically, 10 mg L^{-1} of BPA could be completely degraded under the coexistence of 0.02 g L^{-1} of CoMnAl-MMO and 0.15 g L^{-1} of Oxone within 90 min at 25 °C. The degradation performance was evaluated in view of metal leaching and various effects, e.g., pH, Oxone dosage and temperature. The results indicated that the system of MMO/Oxone was suitable for the treatment of wastewater and presented favorable recycling and stability in both neutral and alkaline conditions. It was confirmed that BPA degradation catalyzed by CoMnAl-MMO followed well with the first order kinetics model and the an activation energy was calculated as 76.83 kJ mol^{-1}. The sulfate radicals were recognized as the main species to oxidize pollutants in the MMO/Oxone system. Particular attention was paid to the catalysis activation mechanism of peroxymonosulfate and the degradation pathway of BPA, which were analyzed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopic (XPS), LC–MS and GC–MS.

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1. Introduction

Bisphenol A [2,2-bis(4-hydroxyphenyl)propane, BPA], which is widely used as raw materials for the production of epoxy and polycarbonate resins, can affect growth, reproduction and development of aquatic organisms due to its xenoestrogenic activity [1]. BPA has a water solubility of 120–300 mg L^{-1} and is a low volatile compound in the environment. In 2010, the United States Environmental Protection Agency (EPA) reported that over one million pounds of BPA were released into the environment annually [2], of which the possible hazards to fetuses, infants and young children were identified by the United States Food and Drug Administration (FDA) in 2010. Therefore, extreme attention should be paid to the treatment of BPA wastewater.

Various technologies including physical, biological and chemical techniques have been developed to degrade BPA in aqueous solution, e.g., adsorption [3], biological degradation [4] and photocatalytic degradation [5]. BPA molecules can be quickly adsorbed from water by adsorbents but remain intact and pose potential threat to the environment. While the biodegradation method usually takes a long time and depends heavily on many environmental factors like nutrients, temperature and salinity [6]. Among these methods, advanced oxidation processes (AOPs) are considered as effective and promising techniques to completely degrade organic compounds in aqueous media. The organic pollutants can be oxidized and mineralized into simple compounds like CO_2 and H_2O by the reactive species such as hydroxyl radicals ($HO^{\cdot}$) and sulfate radicals ($SO_4^{-\cdot}$). Our previous researches have demonstrated the effective degradation of phenol, dye and dimethyl phthalate in aqueous media by AOPs [7,8].

Potassium peroxymonosulfate (PMS) which possesses a higher oxidizing potential (1.82 V) than H_2O_2 (1.76 V) is widely used as an oxidizing agent and its strong oxidation ability has been proved in both acid and alkaline solutions [9]. It has been reported that PMS can be activated to generate sulfate radicals by UV, heat, ultrasound, base, granular activated carbon or transition metals [10]. Wang et al. [11] fabricated three kinds of one-dimensional α-MnO_2 nanostructures including nanorods, nanotubes and nanowires, which were used as heterogeneous catalysts to activate PMS for phenol degradation. Saputra et al. [12,13] prepared different spinel structured transition metal oxides and manganese oxides with different crystallographic phases and different oxidation states as heterogeneous catalysts for the activation of PMS.

In spite of the high catalytic performance of Co oxides and Mn oxides, the poor chemical and thermal stabilities of these single metal oxides have led to the aggregation of particles and limitation of applications. Layered double hydroxides (LDHs) are a family of common inorganic materials and are facile to be synthesized in the laboratory. A key structural characteristic of LDHs is that the M^{II} and M^{III} cations are distributed in a uniform manner in the hydroxide layers [14]. Therefore, LDHs can be employed as precursors or templates for fabricating catalysts with high dispersion due to the lattice orientation/lattice confinement of LDHs [15].

In our previous study [16], oxidized Multi-Wall Carbon Nanotube coupled with CoMnAl layered double oxides were synthesized and characterized as heterogeneous catalysts, which showed superior catalytic performance for BPA degradation by using PMS as oxidant. However, the activation and degradation mechanism had not been investigated in detail. In this study, the physicochemical properties of the obtained catalysts were characterized, and the effects of pH, Oxone concentration, and temperature on the catalytic activity in AOPs reactions were evaluated. The reaction kinetics, activation energy, chemical stability and recycle of the catalysts, as well as the catalysis mechanism and degradation pathway were also studied.

2. Experimental

2.1. Synthesis of catalysts

The CoMnAl-LDHs precursor with Co:Mn:Al molar ratio of 4:1:1 was prepared by the hydrothermal method. $Co(NO_3)_2{\cdot}6H_2O$ (20 mM), $Mn(NO_3)_2$ (5 mM), $Al(NO_3)_2{\cdot}9H_2O$ (125 mM) and urea (125 mM) were dissolved in distilled water to form a homogeneous solution at room temperature, which was then transferred into a 300 mL Teflon-lined stainless steel autoclave, sealed and maintained at 100 °C for 48 h. After the reaction was completed, the resulting solid products were filtered, washed with distilled water to remove ions possibly remnant in the final products and finally dried in air. The dried products were calcined for 5 h at 500 °C and denoted as MMO.

2.2. Characterization

The external surface microstructure of the samples was observed by a ZEISS Merlin Scanning electron microscopy (SEM, Carl Zeiss, Germany). The X-ray diffraction (XRD) patterns were measured by a X-ray diffractometer (D/MAX-III A, Rigaku Ltd., Japan) equipped with Cu Kα radiation. The measurement of particle surface areas and pore sizes was carried out by N_2 adsorption/desorption isotherm analysis with a Chemi-sorption Surface Area Analyzer (ASAP 2010, Micromeritics, America). The X-ray photoelectron spectra (XPS) were measured with an X-ray photoelectron spectrometer (AES430S, ANELVA, Japan) and the binding energy of C 1S was shifted to 284.6 eV as an internal reference. The FTIR spectra were recorded using the KBr pellet technique on a PerkinElmer 1725X FTIR spectrometer, over the spectral range of 4000–400 cm^{-1} with 4 cm^{-1} resolution.

2.3. Catalytic activity test

The degradation of BPA was carried out at 25 °C in a 1 L glass vessel with 500 mL of 10 mg L^{-1} BPA solution under constant stirring. The reactor was attached to a stand and dipped into a water bath with a temperature controller (5, 25, or 45 °C). After the addition of 0.01 g catalyst into the BPA solution, the Oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, Aladdin), which is the source of the strong oxidant PMS, was added into the solution at a range of 0.1–0.25 g L^{-1}. It must be noted that Oxone addition in unbuffered water will lead to a significant decrease of solution pH values. Therefore, the pH of solutions was adjusted by NaOH. At predetermined time intervals, samples (1 mL) were withdrawn by syringe and filtered by 0.45 μm PES (polyethersulfone) membranes. The BPA concentration in filtered solution was then quantified by high performance liquid chromatography (HPLC, Hitachi, L-2000) with an HP UV detector at 276 nm. A Synergi 4u Polar-RP 80 column (diameter, 250 × 4.60 mm) and a guard column (diameter, 4.6 × 12 mm) were used. The mobile phase was consisted of water and acetonitrile (50:50) at 1.0 mL min^{-1}. In order to assess the degree of mineralization, total organic carbon (TOC) was determined by Liqui TOC (liqui TOC, Elementar, Germany). In addition, the leaching amounts of cobalt and manganese were measured by zeeman atomic absorption spectrometry (AAS, Hitachi, Z-2000) after 2 h to evaluate the stability of the catalysts.

For the recycle tests, the catalysts were recycled by filtration, thoroughly washed several times with distilled water, and then dried overnight at 60 °C after each run. The regeneration of the catalysts was achieved by calcination at 500 °C.

To determine the radical species formed in different experimental conditions, two sets of quenching experiments were performed by the addition of tert-butyl alcohol (TBA) and ethanol (EtOH). A