



K₃MB₅O₁₀ (M = Zn and Cd) with d¹⁰ configuration: Efficient and reusable catalysts for dehalogenation of halophenols

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ABSTRACT

Two isostructural d¹⁰ configuration non-centrosymmetric materials: K₃ZnB₅O₁₀ (KZBO) and K₃CdB₅O₁₀ (KCBO) can act as efficient and reusable catalysts in the dehalogenation of halophenols. More than 90% of the 2, 4-DXP were degraded within 10 min with the dehalogenation efficiency 2, 4-DBP > 2, 4-DCP > 2, 4-DFP, the dehalogenation efficiency is almost 10 times higher than that of commercial P25 TiO₂ catalyst in the present reaction conditions. The internal electric field due to the distorted [MO₄] tetrahedral and [BO₃] units promote the charge separation in the initial process of photoexcitation and d¹⁰ configuration of Zn and Cd with large dispersion is useful for photoexcited electron transfers without recombination, thus enhance the photocatalytic activity. The dehalogenation pathways with KCBO outlined both oxidative and reductive dehalogenation. Our work is expected to offer new insight into photocatalytic theory for better understandings to photocatalytic reactions and rational design and synthesis of photocatalysts with high activity.

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1. Introduction

Halophenols (XPs) represent one of the largest chemical classes of environmental contaminants and have great toxic effect on our ecosystem and health [1]. They are released to the environment via industrial discharge, accidental spills, and excessive usage of related products, and can also be formed during water disinfection or the pulp bleaching processes. XPs are generally resistant to biodegradation and difficult to remove from the environment, in particular, the halogen atoms in XPs play a very crucial role in directing, substituting, and blocking some positions in the aromatic ring [2]. Therefore, the cleavage of the C-X (X = F, Cl, Br) bond is a critical step in the degradation process of XPs usually occurring at the first stage of reactions by which these compounds are degraded and detoxified [3]. Chlorophenols, such as 2-dichlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol are listed as priority pollutants and have perhaps received the most attention, as they are ubiquitous environmental contaminants. Bromophenols (BPs) usually found in high concentrations in sponges

and algae. Meanwhile, the rapidly increasing levels of fluorinated organic pollutants in the environment has also been given much attention in recent decades. Conventional processes used for removal of XPs include physical, [4,5] chemical, [6–8] and biological methods [9]. However, these methods are limited by the toxicity of XPs to microbes or merely transfer the pollutants with the risk of secondary contamination.

Photocatalysis, which can be classified as an advanced oxidation method, is considered a promising technology for elimination of most organic contaminants in water. One of the most important problems limiting the applications to a great extent is the low photocatalytic activity caused by the photo-induced carrier recombination in semiconductor photocatalyst, which causes neutralization of the photo-induced electrons and holes before they can initiate the photocatalytic processes [10]. Although many approaches have been proposed and put into practice to solve this problem, the efficiency is still too low to separate electron-hole pairs completely during photocatalysis [11]. A photocatalyst particle with built-in electric field has been proposed to promote the separation of photo-induced charge carriers in recently. The existence of the built-in electric field provides a driving force which can easily transport the photo-induced charge carrier to the different directions, thus enhancing their separation and directly enhancing the photocatalytic performance [12,13].

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Non-centrosymmetric materials can easily polarization which is the simplest way to obtain built-in electric field. [14] Thus, how to synthesize the polar structure efficiently remains a problem. Usually, there are three methods to obtain a non-centric structural materials. The first one is to direct borate-based noncentric materials by using π -conjugated planar borate rings; the second one is to acquire asymmetric building units by adopting transition metals existing second-order Jahn-Teller (SOJT) distortions; the third one is add to the polarization of structure by incorporating halide anions with large electronegativities [15]. According to the SOJT effect, the Jahn-Teller distortion can occur in Zn^{2+} and Cd^{2+} with fully occupied d -orbitals, which is favorable for the formation of the non-centrosymmetric structure [16]. And the conduction bands of d^{10} metal cations consist of sp orbitals which are dispersed well resulting in high mobility of photogenerated electrons [17]. Moreover, the flexible coordination of the Zn and Cd tetrahedra makes borate anion framework much variable. Therefore incorporation of borates with asymmetric π systems and d^{10} metal cations is an eminent strategy to prepare catalysts with high photoactivity. [18]

Herein, we demonstrate that two isostructural d^{10} configuration non-centrosymmetric materials by introducing alkali K metal atoms with a large radius into the borate system, KZBO and KCBO, which can function as effective photocatalysts for dehalogenation of XPs under UV light irradiation. More than 90% of the 2, 4-DXP were degraded within 10 min with the dehalogenation efficiency 2, 4-DBP > 2, 4-DCP > 2, 4-DFP, which is closely related to the physical properties of 2, 4-DXP, and approximately 82.50% of the fluoride content, 90.50% of the chloride content, and 95.75% of the bromide content was converted into F^- , Cl^- , and Br^- anions by KCBO, while the conversion percentage for KZBO is 80.25%, 83.11% and 89.77%. The distorted $[\text{MO}_4]$ tetrahedral and $[\text{BO}_3]$ units are responsible for the formation of the non-centrosymmetric structure, which facilitates producing an internal electric field that can provide a driving force for the separation of photogenerated electrons and holes and d^{10} configuration of Zn and Cd with large dispersion is useful for photoexcited electron transfers without recombination, thus enhance the photocatalytic activity. The dehalogenation pathways with KCBO outlined both oxidative and reductive dehalogenation.

2. Experimental

Materials. 2,4-difluorophenol (2,4-DFP), 2,4-dichlorophenol (2,4-DCP), 2,4-dibromophenol (2,4-DBP), and terephthalic acid (TA) were purchased from Sinopharm Chemical Reagent Co., Ltd. K_2CO_3 , KNO_3 , ZnO, CdO, Na_2SO_4 , and H_3BO_3 were obtained from Tianjin Chemicals, Inc. Methanol and acetonitrile were chromatographic grade (Sinopharm Chemical Reagent Co., Ltd). Deionized water was used throughout this study.

Synthesis of KMBO. KZBO powder were prepared by employing a conventional solid-state reaction method with a stoichiometric mixture of K_2CO_3 , ZnO and H_3BO_3 . After grounded in an agate mortar and packed into crucible, the raw materials were heated to 400°C , held for 12 h and at 600°C for 48 h. Under the same condition, a stoichiometric mixture of KNO_3 , CdO and H_3BO_3 were prepared for the synthesis of KCBO powder.

Characterization. X-ray diffraction (XRD) patterns of the samples were recorded by a Bruker D8 Advance X-ray diffractometer equipped with a diffracted-beam monochromator set for Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphologies of KMBO were observed on a scanning electron microscope (SEM) using a ZEISS SUPRA55VP apparatus and the energy dispersive X-ray spectroscopy (EDX) were obtained by the EDX8000. The diffuse reflectance absorption spectra (DRS) were recorded in the range from 200 to 800 nm using a Solidspec-3700 DUV spectrometer with BaSO_4 as a reference. The Brunauer-Emmett-Teller (BET) surface area was obtained

from the N_2 adsorption/desorption isotherms recorded at 77K (QUADRASORB IQ, Quantachrome Instrument Corp.). High performance liquid chromatography (HPLC) (Ultimate 3000, Dionex) were carried out with a C18 column ($4.6 \text{ mm} \times 250 \text{ mm}$). The size of the sample loop was $20 \mu\text{L}$. For XPs, a mixture of methanol and water [85/15 (v/v)] was used as an effluent with the flow rate 1 mL/min , detector wavelength 273 nm , 282 nm , and 285 nm for 2,4-DFP, 2, 4-DCP, and 2, 4-DBP, respectively. The intermediate products during 2, 4-DXP degradation were qualitatively analyzed by a liquid chromatography-mass spectrometry (LC-MS, Agilent 1290). Ion chromatography (IC) was measured by the ICS 5000. The photocurrents of UV light on and off studies were determined on a CHI660E electrochemical system using a standard three-electrode cell with a working electrode ($10 \text{ mm} \times 10 \text{ mm}$), a platinum plate as the counter electrode, and a standard calomel electrode (SCE) as the reference electrode. The KMBO film was prepared on ITO glass, followed by air-drying. The experiments were performed in a 50 mL quartz cylinder reactor which was placed in front of a 500 W mercury lamp ($\lambda > 254 \text{ nm}$; Perfect Light Company, Beijing, China). The photoelectron chemical (PEC) activities of the samples were all evaluated in a $0.1 \text{ M Na}_2\text{SO}_4$ solution. Atomic force microscopy (AFM) combined with Kelvin probe force microscopy (KPFM) measurements were performed with an atomic force microscope (Bruker Multimode 8). Images were obtained in tapping mode with a scan rate of 1 Hz and an AC mode for a scan size of $1 \mu\text{m} \times 1 \mu\text{m}$. In the experiment, KMBO nanoparticles were first dispersed in water and then sprayed on a Pt substrate to form a film. The sample was baked in a dry oven at 600°C for 4 h. For the light irradiation experiment, a mercury lamp and a convex lens with a focusing spot size (d) of 1.5 cm were used to introduce focused UV light onto the measurement region between the tip of the atomic force microscope and sample. Fluorescence spectra were measured on a Hitachi fluorescence spectrophotometer F-7000. The $\cdot\text{OH}$ radical trapping experiments were carried out using the following procedure: terephthalic acid (TA) (8.3 mg) was first dissolved in 100 mL of dilute NaOH solution ($2 \times 10^{-3} \text{ M}$), followed by addition of 50 mg of photocatalysts, and stirred for 20 min in dark. The suspension was irradiated by a 500 W mercury lamp. The fluorescence emission spectrum (excited at 312 nm) of the solution was measured every 2 min during irradiation.

Photocatalytic Activity. Typically, 50 mg catalysts was added into 100 mL aqueous solution of XPs (50 mg/L) (2, 4-DFP, 2, 4-DCP, and 2, 4-DBP) in a 250 mL glass beaker, then stirred for 20 min in the dark to attain adsorption equilibrium, and irradiated by a 500 W mercury lamp (the light intensity at the test samples = 0.287 W/cm^2). The percentage of residual contaminants solution at a selected time of irradiation is given by C/C_0 , where C_0 is the concentration of the contaminants solution at the initial stage, and C is the concentration at selected irradiation times. To test the reproducibility and uncertainty of the degradation experiments, the photochemical reactions were repeated three times.

3. Results and discussion

The as-prepared samples crystallize in the monoclinic system with space group $P21/n$ [19,20] and cell parameters, $a = 7.6391(5) \text{ \AA}$, $b = 19.2304(13) \text{ \AA}$, $c = 7.6905(5) \text{ \AA}$. The structure exhibits a three-dimensional (3D) network, consisting of ZnO_4 , KO_n ($n = 7, 8$) distorted polyhedra, and isolated B_5O_{10} units. The Zn atoms are coordinated to four O atoms. The ZnO_4 tetrahedra are isolated; they connect each other by sharing the B_5O_{10} group. (Fig. 1). The morphology also be investigated, which shows a unregularly shape (Fig. S1) with $0.951 \text{ m}^2/\text{g}$ [18] and $1.54 \text{ m}^2/\text{g}$ BET surface areas for KZBO and KCBO, respectively (Fig. S2).

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