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ORIGINAL RESEARCH

Photocatalytic degradation of benzene in gas phase by nanostructured $BiPO_4$ catalysts

Baihua Long[a], Jianhui Huang[a,b], Xinchen Wang[a,*]

[a]*Research Institute of Photocatalysis, State Key Laboratory Breeding Base of Photocatalysis, Fuzhou University, Fuzhou 350002, PR China*
[b]*Department of Environment and Life Sciences, Putian University, Putian 351100, PR China*

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Abstract A rod-shaped $BiPO_4$ photocatalyst was prepared by a simple hydrothermal method for light-induced catalytic degradation of stable aromatic compounds such as benzene in gas phase under ambient conditions. The samples were subjected to various technical characterizations including X-ray diffraction (XRD), transmission electron microscopy (TEM), UV/vis and FTIR spectrum, to determine the crystal structure, morphology, and optical properties of the as-prepared photocatalysts. Results indicate that $BiPO_4$ exhibits much higher photocatalytic activity and stability under UV light irradiation than that of commercial TiO_2 (Degussa P25) in the degradation of benzene to CO_2. The active radical species involved in the degradation reactions over $BiPO_4$ photocatalyst have been investigated by the spin-trapping electron paramagnetic resonance (EPR) spectra and a photoluminescence technique. Theoretical calculations reveal that $BiPO_4$ contains highly-dispersive conduction bands, enabling high mobility of the photo-generated carries and therefore leading to fast charge transfer and separation.

1. Introduction

Benzene is a toxic chemical that occurs naturally in the environment but is used by human in a wide range of products such as mucilage, paints, plastics, rubber and gasoline. Therefore, benzene is an important pollutant in the urban and indoor air. It is already confirmed that exposure to benzene for a long-time or at high levels can result in a number of ailments including drowsiness, dizziness, headache, lightheadedness, nausea and even cancers. Thus, this chemical has been

*Corresponding author. Fax: +86 591 83738608.
E-mail address: xcwang@fzu.edu.cn (X. Wang).

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classified as a class A carcinogenic by the Environmental Protection Agency [1,2]. Many technologies such as thermal incineration, catalytic incineration [3,4], oxidation with ozone or supercritical water [5,6], degradation using a plasma-based system [7] have been developed for completely removing benzene from the air. Unfortunately, most of these technologies are not efficient and economic in treating benzene at low concentrations, for examples at ppb or ppm level.

Photocatalytic oxidation of benzene and other aromatic compounds at low levels over titanium dioxide (TiO_2) has been examined by several research groups [8–10]. Although its photocatalytic oxidation has proven to be effective, continuous-flow photocatalytic reactors for the treatment of gas-phase aromatics generally yield moderate conversion only. In addition, the fast and apparent catalyst deactivation typically occurred during the operation. Recently, our group and others have reported that some non-TiO_2 photocatalysts such as Ga_2O_3, InOOH, $Sr_2Sb_2O_7$, Zn_2GeO_4, $ZnGa_2O_4$, and $Cd_2Ge_2O_6$ can catalyze the efficient degradation of benzene under UV irradiation to CO_2 and water. The main feature of these kind of metal oxide photocatalysts in the treatment of benzene is that they did not suffer from a significant catalytic deactivation during prolonged reaction time [11–16] due to their high redox potentials associated with the wide band gap. This is distinctly different from the TiO_2 photocatalysts that are susceptible to surface carbonization during treatment of benzene. The carbonization blocks the surface active sites of TiO_2 and thereafter passivates and deactivates TiO_2 photocatalysts, irreversibly. Despite the high stability of these materials, these new metal oxide photocatalysts are composed of metal components such as Ga, In, Ge and Sb that are too rare and expensive to be used broadly. Thus, it calls for the design and development of more powerful and durable photocatalysts for the treatment of benzene.

There are a large number of nonmetal salts based semiconductors such as phosphates, sulphates in the nature which is much cheaper than precious metal oxide or precious metal salts, allowing their practical applications in industry. For example, Zhu and his coworkers [17–22] reported that $BiPO_4$ shows improved photocatalytic activity for the degradation of organic pollutants in aqueous phase over commercial TiO_2 (P25). So far, it remains unknown whether $BiPO_4$ catalyst can act as an effective and stable photocatalyst towards the degradation of volatile organic compounds including benzene in the gas phase. This motivates us to explore the potential applications of $BiPO_4$ for the degradation benzene in the air under ambient conditions, without applying co-catalysts.

In the present study, we applied a simple hydrothermal method to fabrication nanostructued $BiPO_4$ for the treatment of benzene in gas phase. The prepared materials were fully characterized by XRD, TEM, UV/vis, and FTIR techniques. The study results demonstrated that photocatalytical activity of $BiPO_4$ is much higher than that of commercial TiO_2 (P25) for the decomposition of benzene under the same experimental conditions. In addition, our investigations also demonstrated that the post-calcined treatment of $BiPO_4$ can further enhance the photocatalytic activity of $BiPO_4$ photocatalysts. The electronic band structure of $BiPO_4$ was therefore investigated to reveal the physical insights accounting for its high photocatalytic activity in the treatment of stable benzene molecules. The photoactive radical species involved in the degradation reaction were also described.

2. Experimental

2.1. Catalyst preparation

All of the reagents were analytically pure and without further purification before used. $BiPO_4$ was synthesized by a hydrothermal method. In a typical synthesis, 3.88 g $Bi(NO_3)_3 \cdot 5H_2O$ was added to 75 mL of phosphoric acid (1 mol/L) with strongly magnetic stirring at room temperature. The resulting mixture was stirred for 1 h and then transferred to a 100 mL stainless telflon-lined autoclave. The autoclave was maintained at 160 °C for 12 h under autogenous pressure, followed by cooling naturally to room temperature. After centrifugation, washing and drying, the resulting sample was denoted as $BiPO_4$-160. The above-mentioned $BiPO_4$-160 was further calcined at 750 °C in air for 2 h to obtain the heat-treated sample denoted as $BiPO_4$-750.

2.2. Characterization

The phase composition of the samples was determined by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer at 40 kV and 40 mA with Ni-filtered Cu Kα radiation. Transmission electron microscopy (TEM) characterizations were collected on a JEOL model 2010 EX instrument operating at an accelerating voltage of 200 KV, to which an energy dispersive X-ray emission analyzer (EDX) was attached. Nitrogen sorption experiments were carried out at 77 K by using the Micromeritics ASAP 2020 equipment. The optical properties were analyzed by UV–vis diffuse reflectance using a UV–vis spectrophotometer (Cary-500, Varian Co.) equipped with an integrating sphere attachment. FTIR spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer at a resolution of 4 cm^{-1}. X-ray photoelectron spectroscope analysis was conducted on an ESCA lab250 photoelectron spectrometer (thermo Fisher Scientific) by using monochromatic Al *K*α X-ray beam as the excitation source and all binding energies were calibrated by the C 1 s peak of the surface adventitious carbon at 284.6 eV. The photoluminescence (PL) excitation and emission spectra were taken on a FL/FS 900 time-resolved fluorescence spectrometer. Electron spin resonance spectra were obtained using a Bruker model A300 instrument with a 200 W mercury–xenon lamp with a wavelength centered at 254 nm as irradiation light source. The band structure and density of states (DOS) calculations were performed by using the CASTEP program belonging to a DFT plane-wave pseudopotential method. The flat-band potentials (V_{fb}) of $BiPO_4$ were determined from Mott–Schottky plots by electrochemical method, which was carried out in conventional three electrode cell using a Zenuium electrochemical workstation (Zahner Co.).

2.3. Photocatalytic activity measurement

The gas-phase photocatalytic degradation of benzene was conducted with a fixed bed tubular quartz reactor operated in a continuous-flow mode. The weights of the catalysts were 0.3 g, with a particle size of 0.21–0.25 mm. The light source was provided by four 4 W UV lamps with a wavelength centered at 254 nm (Philips, TUV4W/G4 T5). A bubbler that contained benzene was immersed in an ice-water bath and