Cu-doped Bi_2O_3/Bi^0 composite as an efficient Fenton-like catalyst for degradation of 2-chlorophenol

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ABSTRACT

Cu-doped BiO_x composites were prepared with and without citric acid. In the presence of citric acid, Bi^0 and Cu^{2+}/Cu^+ were confirmed to coexist in the composite ($BiCu9/Bi^0$) by X-ray diffraction and X-ray photoelectron spectroscopy. The catalyst showed high Fenton activity and stability for the degradation and mineralization of 2-chlorophenol in the pH range of 6–8. H_2O_2 was predominately converted into ·OH radicals in $BiCu9/Bi^0$ suspension, as assessed by the electron spin resonance technique. In the composite, Bi^0 inhibited the oxidation of H_2O_2 by Cu^{2+} into O_2 and ·OH by reducing Cu^{2+}, enhancing the reaction of H_2O_2 with Cu^+ to produce ·OH. Intermediate determination showed that 2-chlorophenol was decomposed mainly by ·OH radicals into hydroxylation products, subsequently decomposed into short-chain organic acids, and eventually decomposed into CO_2 and H_2O.

1. Introduction

Iron-catalyzed hydrogen peroxide (H_2O_2) decomposition for generation of highly aggressive hydroxyl radicals (·OH) has been extensively developed as Fenton oxidation processes for environmental applications. A variety of catalytic iron species, including Fe^{2+} and Fe^{3+} salts [1,2], iron oxides [3–6], and iron-immobilized zeolites [7], have been exploited for degradation and mineralization of recalcitrant organic pollutants, as well as for disinfection. However, the widespread use of iron-based Fenton oxidation for pollution abatement and disinfection is still limited by the requirement for strict acidic conditions, the requirement for UV irradiation to accelerate the reductive generation of Fe^{2+} and the uncontrolled leaching of iron ions from the catalyst's surface [4,8]. Therefore, non-iron Fenton catalysts, such as Au [9], carbon materials [10], cerium oxides [11], manganese oxides [12], and Cu-containing catalysts [13–16], and their reactivity towards H_2O_2 activation have been explored to overcome these problems.

Among these non-iron catalysts, Cu-containing catalysts have attracted considerable attention because the redox properties of copper are similar to those of iron. Importantly, a Cu-based Fenton-like system could work over a broader pH range than the Fe-based redox system [13,14]. In particular, Cu^{2+}/Cu^+ cycling has been found to result in the generation of reactive oxygen species in the presence of H_2O_2 [17–19]. Compared to Fe^{3+}/Fe^{2+} cycling,

which is usually limited by the reduction of Fe^{3+} due to the low rate constants [20], the reduction of Cu^{2+} by H_2O_2 occurs more easily than that of Fe^{3+}, and Cu^+ can react efficiently with H_2O_2 to form ·OH with a higher reaction rate than Fe^{2+} [21,22]. However, the mobilization of Cu^+ limits its application due to its instability in water. The homogeneous reaction between Cu^+ and H_2O_2 is severely inhibited by O_2 in water because Cu^+ is quantitatively oxidized by O_2 to Cu^{2+}, which decreases the effective $[Cu^+]$ available for reaction with H_2O_2 [22]. Therefore, the immobilization of Cu^+ is required to overcome this problem. Two different methods for preparing copper-containing catalysts have been proposed: one yielding copper-doped samples and the other yielding copper supported on a porous solid substrate. Bismuth oxide (Bi_2O_3) is considered to be a good choice for a solid matrix because of its excellent catalytic, electrical, optical, and conducting properties [23,24]. Moreover, some reactions can proceed through a Bi(III)/Bi(0) or Bi(III)/Bi(I) redox couple in the presence of molecular oxygen [25]. Therefore, the aim of this work was to develop a highly active and stable heterogeneous Fenton-like catalyst by fixing Cu^+ and Cu^{2+} in a Bi_2O_3 structure.

In this paper, a composite catalyst with Cu^+/Cu^{2+} and Bi^0/Bi^{3+} was successfully synthesized by a citric acid-based sol–gel route. The performance of the catalyst was evaluated by degrading 2-chlorophenol (2-CP), which is a common model contaminant for the advanced oxidation process, a germicide/disinfectant, and an important precursor for synthesizing pesticides and other chlorophenols [26]. The Fenton-like degradation pathway of 2-CP was also investigated. The catalytic mechanism of Cu-doped

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Bi_2O_3/Bi^0 was systematically studied on the basis of the effect of multivalent Cu and Bi^0 on the generation of $\cdot OH$ from H_2O_2 decomposition.

2. Experimental

2.1. Materials

Bismuth nitrate $(Bi(NO_3)_3 \cdot 5H_2O)$, copper nitrate $(Cu(NO_3)_2 \cdot 3H_2O)$, ethylene glycol, citric acid, 2-methoxyethanol, and H_2O_2 (30%, w/w) were purchased from Sinopharm Chemical Reagent Co., Ltd. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was supplied by Sigma. 2-CP was obtained from Acros. All chemicals were at least analytical grade and were used as received without further purification. Deionized water was used throughout this study.

2.2. Preparation of catalysts

Cu-doped Bi_2O_3/Bi^0 was prepared by a citric acid-based sol–gel route. The synthesized samples were designated as $BiCux/Bi^0$, where x indicated the Bi/Cu molar ratio. In the following, synthesis description for $BiCu9/Bi^0$ is given. Typically, 9 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 1 mmol $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in 20 mL of 2-methoxyethanol, followed by adding 20 μL of 0.1 M HNO_3, 10 mmol citric acid (as a complexant) and 10 mL ethylene glycol (as a dispersant). After stirring for 1 h at 60 °C, the synthesis medium was incubated at 100 °C for 10 h to form the gel. Finally, the gel was calcined at 500 °C for 2 h in air. As a reference, BiO/Bi^0 was prepared as described above without $Cu(NO_3)_2 \cdot 3H_2O$ added. Cu_2O was also synthesized using a previously reported process [27]. To clarify the formation and effect of Bi^0, BiO and BiCu9 were prepared as described above without the addition of citric acid.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Scintag-XDS-2000 diffractometer with Cu Kα radiation (λ = 1.540598 Å). The generator voltage and tube current used were 40 kV and 40 mA, respectively. The X'Pert HighScore Plus software (version 2.2.4) was used to semi-quantitatively determine the weight fraction of constituents. X-ray photoelectron spectroscopy (XPS) data were measured via an AXIS-Ultra instrument from Kratos using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charge effects, binding energies were calibrated using the C1s hydrocarbon peak at 284.8 eV. Electron spin resonance (ESR) spectra were obtained using a Bruker model ESP 300E electron paramagnetic resonance spectrometer.

2.4. Procedures and analysis

Unless indicated otherwise, 0.07 g of catalyst powders was dispersed in 50 mL of a 0.078 mM 2-CP solution at natural pH (approximately 6.0). The solution pH was not adjusted or controlled because it did not vary by more than 0.2 pH units during the catalytic reaction. The suspensions were stirred for approximately 20 min to establish an adsorption/desorption equilibrium between the solution and catalyst. Afterwards, the reaction was started by adding 20 mM H_2O_2 as an oxidant. At given time intervals, part of the suspension sample was withdrawn and filtered to remove catalyst powders for analysis. The concentrations of 2-CP and the intermediates catechol, p-benzoquinone and phenol were measured using high-performance liquid chromatography (1200 series; Agilent) with a Zorbax SB-Aq column (5 μm, 4.6 × 250 mm; Agilent). The analysis was carried out at 275 nm

using a 60/40% v/v mixture of methanol/ultrapure water as the mobile phase. The total organic carbon (TOC) of the solution was analyzed using a TOC-V_{CPH} analyzer (Shimadzu). The measurements of chloride ions (Cl^-) and short-chain organic acids were conducted using a Dionex model ICS 2000 ion chromatograph (IC) equipped with an IonPac AS11-HC analytical column (4 × 250 mm) and using 40 mM KOH as an eluent.

In addition, the possible cation leaching (Bi, Cu) was monitored by inductively coupled plasma optical emission spectrometry (ICP–OES) on an Optima 2000 (PerkinElmer, Inc.) instrument. To test the stability and recyclability of $BiCu9/Bi^0$, the catalyst was filtered, washed with water, dried at 70 °C and used again in the second cycle. This process was repeated several times.

All of the above experiments were repeated in triplicate, and the data are presented as the average of the triplicates, with a standard deviation of less than 5%.

3. Results and discussion

3.1. Characterization of catalysts

The XRD patterns of the synthesized samples were shown in Fig. 1. The characteristic peaks of α-Bi_2O_3 (JCPDS 71-0465) and Bi^0 (JCPDS 85-1329) were present in all of the samples prepared in the presence of citric acid. The lattice parameters decreased with increasing copper content in Bi_2O_3 up to a Bi/Cu ratio of 9:1 as shown in Table 1, indicating that Cu^{2+} was incorporated into the Bi_2O_3 structure to replace Bi^{3+}, due to the smaller ionic radius of Cu^{2+} (72 pm) than that of Bi^{3+} (96 pm) [28]. However, further increase in Cu content resulted in the occurrence of the impurities Bi_2CuO_4 (JCPDS 80-1906) and Cu_2O (JCPDS 78-2076) in $BiCu3/Bi^0$ (Fig. 1). Therefore, there was an upper limit of Cu content that could be incorporated inside the Bi_2O_3 structure. When citric acid was not added in the preparation process of BiO and BiCu9, pure α-Bi_2O_3 was produced and no Bi^0 was found (e, f in Fig. 1), indicating that the formation of Bi^0 depended on the presence of citric acid in the course of synthesis.

XPS analysis was used to confirm the oxidation states of the Bi and Cu elements on the surface of $BiCu9/Bi^0$. The binding energy of Bi $4f_{7/2}$ was 158.4 eV, which was assigned to Bi^{3+} [29]. Surface Bi^0 was not observed, but it appeared in the XRD patterns of $BiCu9/Bi^0$, indicating that Bi^0 was in the interior of the catalyst and coated with Bi_2O_3. Peaks corresponding to Cu $2p_{3/2}$ were observed at 932.4 and 934.2 eV for reduced copper species and Cu^{2+},
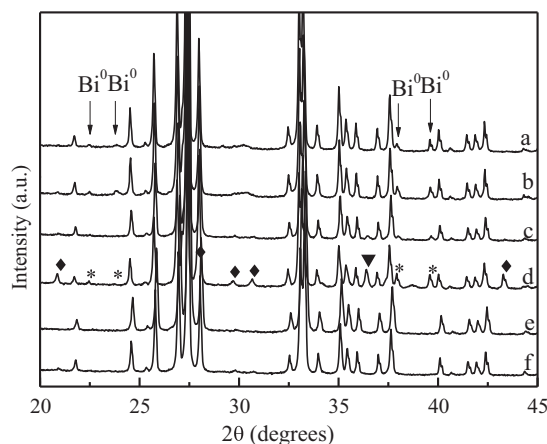

Fig. 1. XRD patterns of (a) BiO/Bi^0, (b) $BiCu19/Bi^0$, (c) $BiCu9/Bi^0$, (d) $BiCu3/Bi^0$, (e) BiO and (f) BiCu9. Some characteristic peaks in the patterns: (*) Bi^0, (♦) Bi_2CuO_4, (▼) Cu_2O.