Catalysis Communications 87 (2016) 57–61

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

A novel low-cost method for Hg^0 removal from flue gas by visible-light-driven BiOX (X = Cl, Br, I) photocatalysts

Anchao Zhang [a,*], Weibo Xing [a], Dan Zhang [b], Hua Wang [a], Guoyan Chen [a], Jun Xiang [c,*]

[a] School of Mechanical and Power Engineering, Henan Polytechnic University, Jiaozuo 454000, China
[b] School of Civil Engineering, Henan Polytechnic University, Jiaozuo, 454000, China
[c] State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

ARTICLE INFO

Article history:
Received 24 May 2016
Received in revised form 2 August 2016
Accepted 1 September 2016
Available online 3 September 2016

Keywords:
Photocatalysis
Bismuth oxyhalides
Elemental mercury removal
Fluorescent light

ABSTRACT

BiOX (X = Cl, Br, I) photocatalysts were synthesized by a simple coprecipitation method and were characterized by SEM, TEM, HRTEM, XRD, TG, DRS, PL, and ESR techniques. The photocatalytic activity of Hg^0 removal and the effects SO_2 and NO were investigated under fluorescent light. The Hg^0 removal performance was in the sequence of BiOI > BiOBr > BiOCl. Compared with BiOBr, BiOI showed much excellent SO_2 resistance on Hg^0 removal. In the BiOBr reaction system, h^+ and $\bullet O_2^-$ could play key roles in Hg^0 removal, while for BiOI photocatalytic system, I_2 might be an important species for higher Hg^0 removal.

1. Introduction

The high toxicity, volatility, and bioaccumulation of mercury emitted from coal-fired flue gas have attracted increasing concern in recent years. China is the largest mercury emission country in the world due to the large amounts of coal consumption [1]. In coal-fired flue gas, mercury is mainly in three forms: elemental (Hg^0), oxidized (Hg^{2+}) and particle-bound (Hg^p) [2]. Among them, Hg^0 is very difficult to be removed due to its high volatility and low solubility [3].

In recent years, the wet scrubbing technologies such as $NaClO_2$ [4], $K_2S_2O_8/Ag^+/Cu^{2+}$ [5], $H_2O_2/Na_2S_2O_8$ [6], UV/Fenton [7], UV/H_2O_2 [8], and $Fe_{2.45}Ti_{0.55}O_4/H_2O_2$ [9] for Hg^0 abatement were extensively researched. Among them, the advanced oxidation processes (AOPs) with much strong oxidizing hydroxyl radicals (•OH) produced have been widely studied to remove Hg^0 [7–9]. This method is much attractive since it can be performed even at room temperature. However, the approach requires plenty of UV light irradiation and some amount of H_2O_2, and the cost of providing continuous UV light in power plant remains a challenging issue. Therefore, it is appropriate for us to synthesize a photocatalyst that can produce many reactive free radicals with strong oxidation under visible light or free sunlight irradiation [10].

To date, many attempts have been devoted to finding and synthesizing of visible-light-driven photocatalysts, such as carbon-deposited TiO_2 [10], Ag/AgCl [11], Ag_3PO_4 [12], AgI [13], and bismuth oxyhalides (BiOX, X = Cl, Br, and I) [14–17]. In the photocatalysis field, BiOX (X = Cl, Br, and I) have been recognized as one of the most promising photocatalysts due to their superior optical properties, structural variability, excellent photocatalytic activity and stability [14–20]. In addition, the use of visible-light-responsive BiOX photocatalysts would be much cheaper than silver-based photocatalysts because the prices of BiOX are lower, which could be suitable for their commercial applications in the future. During the photocatalytic processes of BiOX (X = Cl, Br, I) under visible light, lots of reactive radicals, such as superoxide radicals ($\bullet O_2^-$), hydroxyl radicals (•OH), and holes (h^+), would be photogenerated under visible light [18–21], which might greatly oxidize Hg^0 due to their much strong oxidizing ability. However, to our knowledge, until now, the experimental study of Hg^0 removal by visible-light-responsive BiOX photocatalysts has not yet been reported and the mechanism for higher Hg^0 removal was still unclear.

Since solar radiation contains more visible light (about 43%), the appropriate use of this fraction through the utilization of efficient visible-light photocatalysts to remove Hg^0 is promising. Thus, in the present work, we fabricated BiOX (X = Cl, Br, I) photocatalysts via a facile coprecipitation method. The photocatalytic activity of Hg^0 removal by BiOX photocatalysts and the effects of SO_2 and NO under fluorescent light were evaluated. We also characterized BiOX (X = Cl, Br, I)

* Corresponding authors.
E-mail addresses: anchaozhang@126.com (A. Zhang), xiangjun@mail.hust.edu.cn (J. Xiang).

http://dx.doi.org/10.1016/j.catcom.2016.09.003
1566-7367/

photocatalysts by various techniques. Moreover, the possible mechanism for higher Hg^0 removal and the influences of SO_2 and NO over BiOBr and BiOI were discussed.

2. Experimental

For the photocatalyst synthesis, photocatalytic test, and characterization see the experimental section in the Supplementary information.

3. Result and discussion

3.1. Experimental results and characterization analysis

Fig. 1 shows the Hg^0 removal efficiencies of BiOCl, BiOBr, and BiOI under baseline (BL) gas condition. It was observed that the Hg^0 removal efficiencies of the three samples increased to their maximums in just 5 min (Fig. 1(a)). In comparison with BiOCl, BiOBr and BiOI exhibited much excellent Hg^0 removal performance.

The presences of SO_2 and NO often displayed strong influences on Hg^0 removal during the wet scrubbing processes [22,23]. Thus, it is important to investigate the effects of SO_2 and NO on Hg^0 removal. As shown in Fig. 1(b), the Hg^0 removal efficiency of BiOI slightly decreased from 99% to 94% in 90 min when 400 ppm SO_2 was added. However, the Hg^0 removal efficiency over BiOBr photocatalyst greatly decreased from 92% to about 30% in 60 min in the presence of SO_2. When SO_2 gas was turned off, the Hg^0 removal efficiency quickly returned to about its original level in 15 min. The result obviously suggested an excellent performance of BiOI and a poor nature of the BiOBr photocatalyst on SO_2 resistance. Moreover, it also indicated a different mechanism of Hg^0 removal over BiOBr and BiOI photocatalysts.

Fig. 1(c) shows the effect of NO on Hg^0 removal efficiency. Hg^0 removal efficiency of BiOBr gradually decreased from 92% to 78% in 60 min after the addition of 300 ppm NO. Once the NO gas was turned off, the Hg^0 removal efficiency over BiOBr slowly rose to about its initial value. A similar result was also observed when BiOI was used in the presence of NO. Obviously, NO had an inhibitory influence on Hg^0 removal.

Moreover, the recycling tests about photocatalytic oxidation of Hg^0 over BiOBr and BiOI under visible light were carried out for four times. As shown from Fig. S2, after four consecutive cycles, the Hg^0 removal efficiencies over BiOBr and BiOI still maintained above 80%, indicating that BiOBr and BiOI exhibited remarkable and stable photocatalytic activity of Hg^0 removal under visible light.

Fig. S3 gives the SEM images of as-prepared samples with three dimensions (20 μm, 5 μm, and 1 μm) as well as TEM and HRTEM. BiOCl and BiOBr samples were microspherical structures with 5–15 μm in diameter, and they were consisted of many flakes. By comparison, the sizes of BiOBr were relative bigger than that of BiOCl. BiOI photocatalyst was comprised of irregular plate-like composites with smooth surfaces. This implied that for different bismuth oxyhalides, different morphologies of materials can be obtained by the same preparation method. Moreover, in the Fig. S3(d)–(f), the HRTEM images demonstrated that three types of lattice images are obtained with d-spacing of 0.275 nm, 0.278 nm and 0.282 nm, corresponding to the (110) plane of BiOCl, the (110) plane of BiOBr, and the (110) plane of BiOI, respectively. The XRD and TG analyses (Fig. S4 and Fig. S5) are given in Supplementary information.

The DRS may reflect the ability to harvest visible light, the energy level and band gap of a photocatalyst, which would play a crucial role in determining its photocatalytic activity [24]. BiOCl and BiOBr presented the photoabsorption properties from the UV light region to the visible light shorter than 400 nm and 470 nm, respectively (Fig. 2(a)). The steep shape of the spectra indicated that the visible-light absorption was not due to the transition from the impurity level but was due to the band-gap transition [24]. BiOI showed an extended absorption region than that of BiOCl and BiOBr though its absorption intensity was much lower. Furthermore, according to the literature [25], the band gap energies of the three photocatalysts were determined (Fig. S6). Detailed calculated method can be found in Supplementary information. The valence band (VB) and conduction band (CB) potentials of BiOCl were calculated to be 3.48 eV and 0.20 eV, respectively, and the VB and CB potentials of BiOBr were estimated to be 3.04 eV and 0.33 eV, respectively, and the VB and CB potentials of BiOI were obtained to be 2.32 eV and 0.66 eV, respectively. It was clear that the band gap of

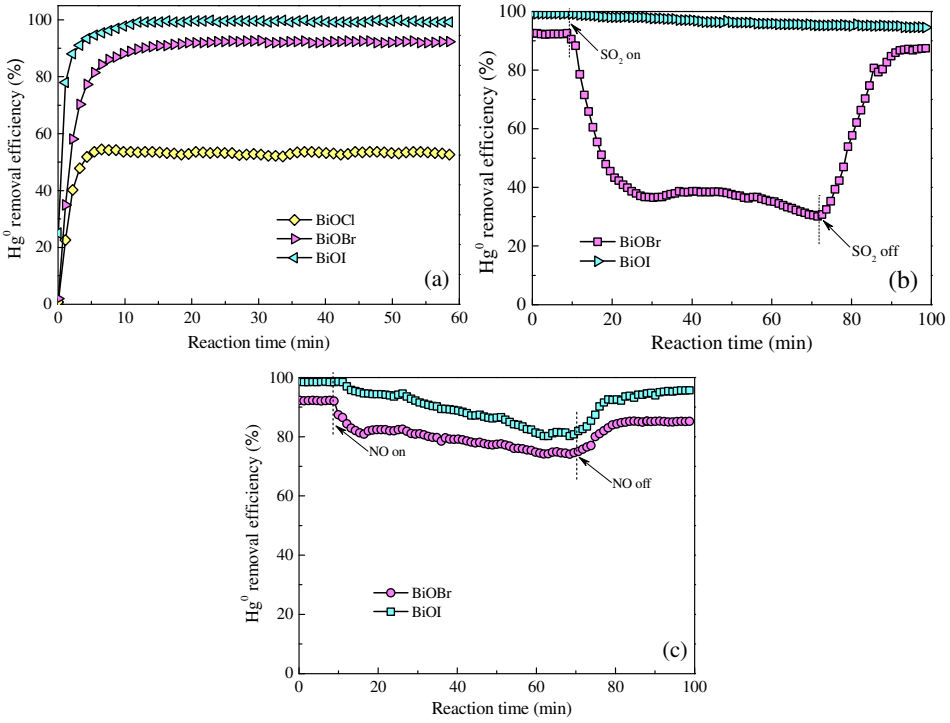

Fig. 1. (a) Hg^0 removal efficiencies of BiOX (X = Cl, Br, I) under FSL irradiation, (b) the effect of SO_2 on Hg^0 removal efficiency, and (c) the effect of NO on Hg^0 removal efficiency.