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Photocatalytic aerobic oxidation of toluene and its derivatives to aldehydes on Pd/Bi₂WO₆

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ABSTRACT

The selective oxidation of toluene and its derivatives is extremely important in the chemical industry. The use of photocatalysis in organic synthesis has attracted considerable attention among synthetic chemists because of its “green” environmental characteristics. In this study, nanoscale Bi₂WO₆ with a flower-like morphology was found to be a highly efficient photocatalyst in the catalytic oxidation of toluene and its derivatives using O₂ as the oxidant. The loading of Pd nanoparticles as a co-catalyst onto the flower-like Bi₂WO₆ was found to produce a significant enhancement in the catalytic activity. Mechanistic investigation showed that the superior performance of Pd/Bi₂WO₆ could be attributed to the improvement of both the reductive and oxidative abilities of Bi₂WO₆ by the loading of the cocatalyst.

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1. Introduction

The use of heterogeneous photocatalysis for organic synthesis has attracted considerable attention among synthetic chemists because of its “green” environmental characteristics [1–4]. The development of new catalytic systems with high efficiency has been the subject of numerous studies [5–8]. Metal oxides [9–18], plasmonic photocatalysts [19–29] and polymeric graphitic carbon nitride [30–33] have been demonstrated to be efficient heterogeneous photocatalysts in certain valuable selective redox organic transformations. Despite the significant progress made so far, the development of new strategies to discover additional heterogeneous photocatalysts for challenging organic transformations remains an important goal.

The selective oxidation of toluene and its derivatives is

extremely important in the chemical industry, because the oxidized products are commercially versatile intermediates in the manufacture of pharmaceuticals, dyestuffs, preservatives, perfumes, plasticizers and flame retardants [34]. Industrial processes for the selective oxidation of toluene rely on metal catalysts under harsh conditions, including high temperature, high oxygen pressure and the use of acid as the solvent [35]. Recently, heterogeneous photocatalysis was demonstrated to be an efficient way to realize the oxidation of toluene and its derivatives under very mild conditions [36,37]. In 2012, Yuan et al. [38] applied surface-chlorinated BiOBr/TiO₂ as the photocatalyst in the selective oxidation of toluene, achieving the highest reactivity reported to date. The group of Xu [39,40] reported that cubic-phase CdS could achieve the oxidation of toluene and its derivatives with high activity and selectivity as a visible-light-driven photocatalyst, using

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molecular oxygen as the oxidant. Recently, Yin's group [41] found that the use of Bi_2WO_6 as a photocatalyst allowed the conversion of saturated C–H bonds into aldehydes. In spite of these notable achievements, however, industry still requires the development of a stable, non-toxic and more efficient photocatalyst for this important transformation.

Very recently, our group has found BiVO_4 to be an efficient photocatalyst under visible-light irradiation for the selective oxidation of amines to imines [42]. Subsequently, we described the first colloidal synthesis of single-crystalline, ultrathin nanosheets of BiOCl with strong absorption in the visible range, which displayed higher reactivity in the selective oxidation of amines than previously reported catalytic systems [43]. As part of our ongoing interest in developing more efficient Bi-based heterogeneous photocatalysts for organic transformations, we found that a flower-like morphology of Bi_2WO_6 loaded with 0.1 wt% Pd could dramatically increase the activity of toluene oxidation. In this paper, we report the detailed optimization of the conditions for this reaction, the substrate scope and the results of control experiments to elucidate the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

The procedures for the synthesis of Bi_2WO_6 in the present work were based on a hydrothermal approach as described previously [44]. In a typical procedure, 0.98 g (2 mmol) of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was ultrasonicated in 30 mL of an HNO_3 solution with a pH value of 5.61, 3.33, 2.75, or 0.49 until complete dissolution; the resulting solutions were denoted Bi_2WO_6 -1, 2, 3, 4, respectively. Separately, 0.33 g (1 mmol) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 30 mL of water. Then, the solution of Na_2WO_4 was added dropwise into the above solution with vigorous stirring, and a white precipitate was formed. After another 24 h vigorous stirring, the mixture was transferred into a 100 mL Teflon-sealed autoclave, which was heated at 160 °C for 12 h in the oven and cooled naturally to room temperature. The resulting solid powder was obtained by filtration, washed with deionized water to remove the residual ions and dried at 60 °C in the oven for further use.

Photodeposition was used to load the Pd cocatalyst onto the Bi_2WO_6 . 861 μL PdCl_2 aqueous solution (0.581 mg (Pd)/mL) and 500 mg Bi_2WO_6 were added to a mixture of 50 mL H_2O and 25 mL CH_3OH . After stirring under Ar flow to extract the air, the suspension was irradiated by a 300 W Xe lamp under Ar atmosphere for 1 h. The Pd-loaded Bi_2WO_6 was recovered by filtration, washed with water and dried at 60 °C in the oven. The as-obtained powder was used for characterization of the product and testing of its catalytic activity.

2.2. Characterization

All reagents and solvents were obtained commercially and toluene was distilled prior to use. Gas chromatography (GC) measurements were made with a GC7890 equipped with an FID detector and β -DEX 225 column, using Ar as the carrier gas.

Ultraviolet-visible (UV-vis) diffuse reflectance spectra were collected on a JASCO V-550 spectrometer. X-ray diffraction (XRD) patterns of these samples were obtained at room temperature on an X-ray diffractometer (Rigaku) using $\text{Cu K}\alpha$ as the X-ray radiation source at 40 kV and 30 mA. Scanning electron microscopy (SEM) images were taken on a Quanta 200 FEG scanning electron microscope. N_2 adsorption-desorption isotherms to quantify the Brunauer-Emmett-Teller (BET) surface areas were measured at –196 °C using a Micromeritics ASAP 2000 analyzer.

2.3. Electrochemical measurements

Photoelectrochemical measurements were conducted in a three-electrode quartz cell using a CH Instruments 760D potentiostat. A Pt plate was used as the counter electrode, and saturated calomel electrode (SCE) was used as the reference electrode, while the working electrode was prepared on fluoride-tin oxide (FTO) conductor glass. The sample powder (50 mg) was ground with water and triton X-100 to obtain an even slurry. The slurry was spread onto FTO glass. The working electrode was dried in the oven at 550 °C for 1 h. The electrolyte was a saturated aqueous solution of K_2SO_4 . The light irradiation source was a 300 W Xe arc lamp system with a current of 20 A, and the light was directed through the conductor glass to the interface of the substrate and the catalyst.

2.4. Evaluation of photocatalytic activity

The photocatalytic reactions were carried out under irradiation by a 300 W Xe lamp with continuous stirring in a 15 mL Pyrex glass bottle (light with wavelengths below 400 nm was excluded using 1 mol/L NaNO_2 solution as a filter). The Pyrex glass bottle was sealed with a glass stopper, connected to an O_2 balloon and surrounded with water to maintain the temperature between 14 and 17 °C. A typical reaction system contained 1 mL substrate and 50 mg Bi_2WO_6 with a stirring bar. The products were analyzed by GC and characterized using standard samples and GC-MS.

3. Results and discussion

3.1. Catalyst preparation and characterization

The XRD patterns of the Bi_2WO_6 -1,2,3,4 samples are shown in Fig. 1. The predominant phase of Bi_2WO_6 detected in the prepared samples was orthorhombic (JCPDS 73-2020), with (113) as the preferred orientation, along with (006), (200), (020), (206), (026), (220), (018), (119), (313), (208), (226) and (0110) reflections. No other likely impurities, such as Bi_2O_3 or WO_3 , were detected. The XRD data reveal that the structure of Bi_2WO_6 was unaffected by changing the pH during synthesis.

SEM images of the samples are presented in Fig. 2. Their morphologies were strongly dependent on the pH values. Fig. 2(b)–(d) shows that the products consisted of a large quantity of nanoplates. Fig. 2(a) shows an SEM micrograph of the Bi_2WO_6 sample prepared at pH 0.49, which was evidently

Fig. 1. XRD patterns of different Bi_2WO_6 samples.

Fig. 2. SEM images of Bi_2WO_6 -4 (a), Bi_2WO_6 -3 (b), Bi_2WO_6 -2 (c), Bi_2WO_6 -1 (d).

formed of aggregated nanoplates and possessed a well-dispersed flower-like structure. These nanoplates were aligned to the spherical surface at a specific angle with clearly oriented layers. More importantly, abundant pores with varying diameters were formed, which may serve as transport channels for small molecules. From Table 1 it can be seen that the Bi_2WO_6 -4 sample (Fig. 2(a)) had a much larger surface area than the other three samples.

The optical absorption of the Bi_2WO_6 samples was measured using a UV-vis spectrometer. Fig. 3 shows diffuse reflectance spectra of Bi_2WO_6 -1, 2, 3, 4. The optical absorption properties of Bi_2WO_6 -1, 2, 3 were nearly identical. The spectra show that the Bi_2WO_6 samples displayed photoabsorption from the ultraviolet region to visible light as far as wavelengths up to 450 nm. All of the samples were light yellow in color. Each spectrum features an intense absorption band with a steep edge in the visible-light region. These indicate that the visible-light absorption corresponded to the band gap

Table 1

Oxidation of toluene over various photocatalysts.

Entry	Catalyst	S_{BET} (m^2/g)	Conversion (%) ^a	2a ($\mu\text{mol}/\text{g}/\text{h}$)	Selectivity of 2a (%) ^a
1	None	—	trace	—	—
2	Bi_2WO_6 -1	11	0.42	140	90
3	Bi_2WO_6 -2	14	0.76	252	88
4	Bi_2WO_6 -3	19	0.99	320	87
5	Bi_2WO_6 -4	35	1.47	500	92

Reaction conditions: $\lambda > 400$ nm, catalyst 50 mg, toluene 1 mL, irradiation time: 5 h, oxygen balloon 1 atm.

^a Determined by gas chromatography.

transition rather than transitions from impurity levels.

We performed the model reaction in the absence of an organic solvent, because solvent-free conditions are environmentally friendly and simplify the separation of the desired product from the reaction system. The photocatalytic activity and selectivity of toluene oxidation over the various Bi_2WO_6 catalysts are summarized in Table 1. Bi_2WO_6 -1, which was prepared in the least acidic environment, proved able to catalyze the model reaction, providing benzaldehyde with 0.42% conversion and 90% selectivity. Several previous studies have shown that the crystallinity and specific surface area of Bi_2WO_6 , which can be controlled by the pH value during its hydrothermal preparation [45,46], strongly influence its catalytic activity in the photocatalytic degradation of contaminants [47]. Thus, four samples of Bi_2WO_6 , namely, Bi_2WO_6 -1, Bi_2WO_6 -2, Bi_2WO_6 -3 and Bi_2WO_6 -4, were prepared at different pH values and applied in the photocatalytic oxidation of toluene to compare their effectiveness. However, the flower-like Bi_2WO_6 -4 (Fig. 3(a)), which was prepared in the most acidic environment (with a pH value of 0.49), achieved both the highest activity (producing benzaldehyde at a rate of 500 $\mu\text{mol}/\text{g}/\text{h}$) and the highest selectivity (Table 1, entry 5).

In sharp contrast, the samples Bi_2WO_6 -1–3 (Fig. 3(b)–(d)), with sheet-like morphologies, supplied benzaldehyde at lower

Fig. 3. UV-vis spectra of different Bi_2WO_6 samples.

reaction rates (Table 1, entries 2–4). By careful investigation of the XRD patterns (Fig. 1), UV-vis spectra (Fig. 3) and BET surface areas (Table 1) of Bi₂WO₆-1–4, the higher activity of Bi₂WO₆-4 can be attributed to its larger BET surface area (35 m²/g), which is about 3 times that of Bi₂WO₆-1 (11 m²/g).

3.2. Effect of cocatalyst

In previous studies of photocatalytic water-splitting and the decomposition of environmental organic contaminants, the loading of a cocatalyst onto a semiconductor photocatalyst has been shown to be an effective means to enhance the photocatalytic performance by improving the charge separation efficiency [48]. However, this strategy has seldom been utilized to prepare photocatalysts for use in synthetic chemistry. Bi₂WO₆ has a sufficiently positive valence band level (+2.94 V) for toluene oxidation [49,50]. However, its positive conduction band (+0.24 V) hinders the efficient consumption of photoexcited electrons. Therefore, to further improve the reactivity of Bi₂WO₆, the loading of reductive cocatalysts onto its surface was explored.

Metal-nanoparticle-loaded Bi₂WO₆ samples (M-Bi₂WO₆-4) were prepared by photodeposition from metal precursors onto the as-prepared Bi₂WO₆ under visible-light irradiation in a mixture of CH₃OH and H₂O. To ensure that the intrinsic effects of the cocatalysts were measured, each cocatalyst was deposited at the ultra-low loading of 0.1 wt%. The photocatalytic activity of each M-Bi₂WO₆-4 in the model reaction was assessed and the results are listed in Table 2. Compared with neat Bi₂WO₆-4, the Bi₂WO₆-4 loaded with Ni nanoparticles showed lower reactivity (Table 2, entry 2). The introduction of Pt as the cocatalyst led to a slight increase in reactivity, with 89% selectivity for the photocatalytic oxidation of toluene (Table 2, entry 3). Pd nanoparticles proved to be the most effective cocatalyst in this reaction system, affording benzaldehyde with 3.42% conversion and 90% selectivity (Table 2, entry 4). Although the loading of nanoparticles on the Bi₂WO₆ samples may have blocked part of the active site, the higher charge separation efficiency and enhanced reduction reaction made Pd/Bi₂WO₆ a more effective catalyst than neat Bi₂WO₆ for toluene oxida-

tion [51]. It should be noted that, with a reaction rate of 1140 μmol/g/h, the catalytic activity of Pd/Bi₂WO₆-4 for the oxidation of toluene was superior to that observed for any previously reported photocatalytic system [52]. Further screening of the amount of Pd loading (Table 2, entries 5–7) showed that, among the four values compared, 0.1 wt% Pd on Bi₂WO₆-4 was the optimal cocatalyst loading in terms of reactivity and selectivity.

3.3. Oxidation products of toluene derivatives

The photocatalytic oxidation of various substituted toluenes was performed in the presence of Pd/Bi₂WO₆-4 and O₂ (Table 3). Oxidation of these toluenes proceeded efficiently to provide the corresponding substituted benzaldehydes with 85–95% selectivities and excellent functional group tolerance of both electron-donating and electron-withdrawing groups (**2a–2f**). Moreover, *o*-, *m*- and *p*-xylene were selectively oxidized to the corresponding monoaldehydes, and no dialdehydes were detected at all.

3.4. Recyclability of photocatalyst

Recycling experiments were carried out to evaluate the stability of Pd/Bi₂WO₆-4 as a catalyst for toluene oxidation under visible-light irradiation. After 5 h of photocatalytic toluene oxidation, the photocatalyst was separated from the reaction solution, washed with deionized water and dried in the oven for 12 h. As seen in Fig. 4, the solid catalyst retained almost all of its activity and selectivity through up to seven cycles of this process. XRD (Fig. 5) and SEM (Fig. 6) measurements were per-

Table 2
Effect of cocatalysts in the photocatalytic oxidation of toluene.

Entry	Catalyst	Metal loading (wt%)	Conversion ^a (%)	Yield of 2a (μmol/g/h)	Selectivity of 2a (%)
1	Bi ₂ WO ₆ -4	—	1.47	500	92
2	Ni/ Bi ₂ WO ₆ -4	0.1	0.99	337	92
3	Pt/ Bi ₂ WO ₆ -4	0.1	1.52	517	89
4	Pd/ Bi ₂ WO ₆ -4	0.1	3.42	1140	90
5	Pd/ Bi ₂ WO ₆ -4	0.001	1.17	380	88
6	Pd/ Bi ₂ WO ₆ -4	0.01	2.31	740	86
7	Pd/ Bi ₂ WO ₆ -4	0.3	1.66	580	94

Reaction conditions: λ > 400 nm, catalyst 50 mg, toluene 1 mL, irradiation time: 5 h, oxygen balloon 1 atm.

^a Determined by gas chromatography.

Table 3
Oxidation products of toluene and its derivatives.

Reactant	Product	Yield (μmol/g/h)	Selectivity (%)
		948	90
		642	90
		306	86
		432	85
		724	95

Reaction conditions: λ > 400 nm, Pd/Bi₂WO₆-4 50 mg, toluene 1 mL, irradiation time: 5 h, oxygen balloon 1 atm, loading of metal on Bi₂WO₆: 0.1 wt%; Conversions and selectivities determined by gas chromatography.

Fig. 4. Recycling experiment of Pd/Bi₂WO₆-4.

Fig. 5. XRD patterns of Pd/Bi₂WO₆-4 before (1) and after (2) one reaction cycle.

Fig. 6. SEM images of Pd/Bi₂WO₆. (a) Before reaction; (b) After one reaction cycle.

formed to discern the crystal structure and morphology of Pd/Bi₂WO₆-4 after being used as a photocatalyst. The XRD patterns revealed that the crystal structure of Pd/Bi₂WO₆-4 remained completely unchanged, with no detectable impurity phase, after one cycle. The TEM images confirmed that the flower shape of Pd/Bi₂WO₆-4 was also retained. These results clearly demonstrate that Pd/Bi₂WO₆-4 exhibits excellent stability.

3.5. Mechanistic investigation of the reaction

To further investigate the mechanism of photocatalytic toluene oxidation over the Bi₂WO₆ photocatalyst, controlled experiments were performed (Table 4). When ammonium oxalate (AO), a radical species that acts as a scavenger of holes, was

Table 4

Results of the controlled experiments.

Additive	Time (h)	Conversion (%)	Al selectivity (%)	Al activity (μmol/g/h)
None	2	0.93	93	300
AgNO ₃ (no O ₂)	0.5	0.04	—	12
AO	2	0.07	—	24

added, the oxidation reaction was terminated, indicating that the photocatalytic oxidation was driven by photogenerated holes. A similar cessation of activity was observed when AgNO₃, an electron-trapping species, was added, which suggests that the activation of O₂ by electrons was also involved in the reaction system. These results clearly show that both photogenerated electrons and holes played important roles in this reaction.

A photo-electron experiment was conducted to elucidate the effect of cocatalyst loading on the Bi₂WO₆ material. As seen in Fig. 7, when a bias of −0.2 V was applied to the catalysts, the Bi₂WO₆ by itself, with no cocatalyst, showed no photocurrent response, because its conduction band is not negative enough. In contrast, the Bi₂WO₆ catalysts loaded with Pt or Pd nanoparticles both responded with similar reductive currents, indicating that both Pt and Pd as cocatalysts were able to promote the reductive ability of Bi₂WO₆. Interestingly, when a bias of +1 V was applied to the catalysts, the Bi₂WO₆ loaded with Pd, Pt, and Ni responded with a stronger oxidative current than Bi₂WO₆ which suggests that the cocatalysts were also beneficial for the oxidation reaction. Pd/Bi₂WO₆ promoted a stronger oxidative current than Pt/Bi₂WO₆ and Ni/Bi₂WO₆, which is in accord with its activity in the photocatalytic oxidation of toluene.

Based on the above results, we propose a possible reaction mechanism, as shown in Fig. 8. Under visible-light irradiation, electron-hole pairs are generated in Pd/Bi₂WO₆. The toluene adsorbed on the surface of the catalyst is oxidized to the corresponding cationic radicals by the positive holes. Meanwhile, O₂

Fig. 7. Photocurrent transient response of the as-prepared Bi₂WO₆, Ni/Bi₂WO₆, Pt/Bi₂WO₆ and Pd/Bi₂WO₆ samples in a Na₂SO₄ aqueous solution (0.5 mol/L) with bias −0.2 and +1 V versus SCE.

Fig. 8. Proposed mechanism for photocatalytic oxidation of toluene to benzaldehyde over Pd/Bi₂WO₆.

molecules, acting as electron-acceptors, are converted to reactive oxygen species by accepting electrons from the heterogeneous photocatalyst Pd/Bi₂WO₆. Finally, the toluene-derived cationic radicals are oxidized by these oxygen-containing species, thus forming the target product.

4. Conclusions

In summary, flower-like Bi₂WO₆ showed a higher efficiency than previous materials in the photocatalytic oxidation of toluene and its derivatives, using O₂ as the final oxidant, because of its large BET surface area. Palladium nanoparticles were found to be the most effective cocatalyst for this reaction system and afforded a significant enhancement in the activity. Mechanistic investigation showed that Pd as a cocatalyst improved both the reductive and oxidative abilities of Bi₂WO₆.

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Graphical Abstract

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Photocatalytic aerobic oxidation of toluene and its derivatives to aldehydes on Pd/Bi₂WO₆

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Flower-like Bi₂WO₆ loaded with Pd nanoparticles as cocatalyst is a highly efficient photocatalyst in the catalytic oxidation of toluene and its derivatives using O₂ as the oxidant.

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[52] The reported results for photocatalytic oxidation of toluene catalyzed by different inorganic semiconductors were summarized as follows: BiOBr/TiO₂ (1064 μmol/g/h, 90.6%, Ref. [38]); Graphene-CdS-TiO₂ (863 μmol/g/h, 99%, Refs. [39,40]); Bi₂WO₆ (464 μmol/g/h, 96%, Ref. [41]); Niobium hydroxide grafted with benzyl alcohol (41 μmol/g/h, 86%, Ref. [36]); V₂O₅/Al₂O₃ (32 μmol/g/h, Ref. [37]).

钨酸铋负载钯纳米粒子光催化甲苯及其衍生物到醛的氧化反应

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摘要: 甲苯及其衍生物的选择性氧化是化学工业中重要的一环. 氧化产物醛、酮和酸类化合物是各种农药、染料、防腐剂、阻燃剂、香料、塑料的合成中间体. 在传统的化工过程中, 通常在苛刻的条件下, 如高温、高压以及酸性溶剂中进行甲苯的选择性氧化. 光催化有机合成作为一种“绿色”的合成方法受到越来越多的关注. 我们发现钨酸铋作为可见光响应的光催化剂, 可以利用氧气作为氧化剂, 对甲苯及其衍生物进行催化氧化反应. 通过调节水热法合成钨酸铋的酸碱条件, 控制其成核生长过程, 改变其形貌, 发现在pH值为0.49时, 得到花状钨酸铋粉末活性最高. X射线衍射、扫描电镜、紫外可见吸收光谱和比表面测定结果发现, 花状钨酸铋粉末表现出最佳的甲苯氧化活性很可能是与它最大的比表面积有关系. 为了进一步提高催化的活性, 我们将助催化剂负载在钨酸铋粉末上, 发现Pd的负载量为0.1 wt%时甲苯氧化反应活性最高. 将邻、间、对位甲基取代以及对位甲氧基和氯取代的甲苯衍生物进行反应, 发现均可高选择性地得到目标产物. 在加入电子牺牲剂硝酸银和空穴牺牲剂草酸铵到反应体系后, 发现反应被完全禁阻, 说明在甲苯氧化反应过程中电子和空穴都起到了相应的作用. 通过电化学测试发现, 钯作为助催化剂负载在钨酸铋表面后, 产生更强的氧化和还原信号, 说明其在电子和空穴发生反应的过程中都起到了相应的促进作用. 由此推测, 在甲苯的氧化反应中, 钨酸铋材料表面吸收可见光, 产生光生电子和空穴, 而钯的负载则促进了电子和空穴进行氧气还原和甲苯氧化的过程.

关键词: 花状钨酸铋; 甲苯氧化; 苯甲醛; 助催化剂; 钯纳米粒子

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