Journal of Catalysis 332 (2015) 95-100

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Contents lists available at ScienceDirect

Journal of Catalysis

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

Selective oxidation of sulfides on Pt/BiVO₄ photocatalyst under visible light irradiation using water as the oxygen source and dioxygen as the electron acceptor



JOURNAL OF CATALYSIS

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ARTICLE INFO

Article history: Received 16 July 2015 Revised 28 August 2015 Accepted 29 August 2015

Keywords: Photocatalysis Bismuth vanadate Selective oxidation Isotopic labeling Peroxy species Sulfide oxidation

1. Introduction

Photocatalytic oxidation reactions have attracted significant interest because of their potential ability to provide a sustainable pathway for green synthesis [1–7]. Among the semiconductorbased photocatalysts, TiO₂ is frequently used as a model photocatalyst to explore various oxidation reactions and to understand the fundamental processes of photocatalysis [8-10]. However, the main obstacle lies in the unsatisfactory selectivity of the desired product for TiO₂ photocatalytic oxidation reactions, which involve many parallel oxidation pathways, such as direct oxidation by holes and indirect oxidation by various reactive oxyradicals (O_2^{-}) , 'OOH, 'OH, etc.), derived from photogenerated electrons and holes, respectively [8,10–12]. Even when the reactions are performed in inert organic solvent to prevent the generation of 'OH radicals [13], the selectivity is usually very low due to the nonselective auto-oxidation of the photogenerated radicals [1]. Hence, the rational control of reactive species derived from photogenerated electrons and holes is an essential prerequisite for highly selective oxidation reactions.

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ABSTRACT

Photocatalytic selective oxidation represents an environment-friendly strategy for chemical transformation. Herein, we report the oxidation of sulfides into sulfoxides with high selectivity (up to 99%) on Pt/BiVO₄ photocatalyst in water under visible light illumination. The system exhibited excellent performance for the oxidation of sulfides in water compared with organic solvents. Isotopic oxygen (H_2 ¹⁸O) experiments clearly revealed that the oxygen atoms in the sulfoxide were mainly from water. Electron paramagnetic resonance demonstrated that the reactive oxygen species were the peroxy species, which were generated from water oxidation on BiVO₄ via the two-electron pathway. Dioxygen was reduced to water through proton-coupled electron transfer.

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Recently, metal-complex catalysts using water as an oxygen source have flourished via charge-transfer catalysis mediated by photosensitizers, such as organometallic complexes (Ru(bipy)²⁺, etc.) [14–19] and semiconductors [20]. Several oxygenation reactions of substrates containing sulfur [17-20] or alkene [16] have shown substantial yields and excellent selectivity. The oxygenation reactions have been carried on with water as the sole source of oxygen atoms through the photogeneration of high-valence metal-oxo species such as iron [19], ruthenium [14,15,17,18,20], and manganese [16] molecular complexes. These highly oxidized metal-oxo species derived from water oxidation pave a mild and controllable pathway for photocatalytic oxidation reactions. However, such molecular systems are intrinsically limited because they require a stoichiometric metal complex as a sacrificial acceptor of electrons, which considerably reduces the sustainability of the processes. Therefore, the development of systems that can directly use dioxygen as an electron acceptor source is highly desirable. Unfortunately, dioxygen is easily reduced to a variety of reactive oxyradicals $(0^{-}_{2}, 00H, etc.)$, which are difficult to control and lead to poor selectivity of the desired products [8,10–12].

Here, we present the oxidation of sulfides using a Pt/BiVO₄ photocatalyst under visible light irradiation in aqueous solution. Water, as the major oxygen source, is activated to generate reactive peroxy species via a two-electron pathway, while dioxygen, as the

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sacrificial electron acceptor, is thoroughly reduced to water via a four-electron pathway (see Scheme 1). The system does not involve oxyradicals derived from photogenerated holes and electrons, effectively avoiding unselective radical oxidation pathways. Meanwhile, the experimental evidence strongly suggests that the active oxygen species derived from water oxidation on $BiVO_4$ are responsible for the selective oxidation of organic substrates.

2. Experimental section

2.1. General information

Chemicals without special descriptions were purchased from commercial sources and were used without further purification. $Bi(NO_3)_3 \cdot 5H_2O_1$, NH_4VO_3 , $(NH_4)_6MO_7O_{24} \cdot 4H_2O_1$, CH_3CN_1 , and NaClO₄·H₂O were supplied by Tianjin Kermel Chemical Reagent Co., Ltd. Na₂WO₄·2H₂O, C₂H₅OH, and AgNO₃ were obtained from Sinopharm Chemical Reagent Co., Ltd. H₂¹⁸O, C₆H₅CF₃, and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were purchased from J&K Scientific. The isotopic enrichment of H₂¹⁸O was 98%. Various sulfides were obtained from Aladdin Industrial Corporation. H₂PtCl₆·6H₂O was purchased from Reagent No. 1 Factory of Shanghai Chemical Reagent Co., Ltd. Sulfoxides were synthesized as reported [21]. ¹H NMR spectra were recorded on a Bruker 400 spectrometer. Chemical shifts were reported in parts per million (δ) relative to TMS (0.0 ppm) for ¹H NMR data. Mass spectra were measured on an Agilent GC-MS 6890N/5973 mass spectrometer. The BET specific surface area was measured using a NOVA 4200e instrument at 77 K.

2.2. Experimental procedures

2.2.1. Preparation of photocatalysts

BiVO₄ samples were synthesized using a previously reported method [22]. The metal-loaded samples were prepared as follows: BiVO₄ powder was suspended in methanol aqueous solution (50 vol%) containing chloroplatinic acid in a photoreactor under vacuum conditions. The photoreactor was irradiated by a 300 W Xe lamp (PLS-SXE 300, Beijing Perfectlight Co., Ltd.) for 3 h, which formed Pt-loaded BiVO₄. Other metals were deposited on BiVO₄ using the same method. Bi₂MoO₆ [23] and Bi₂WO₆ [24] samples were prepared using the published method. TiO₂ (P25, ca. 80% anatase, 20% rutile) purchased from Degussa was sintered at 300 °C for 4 h.

2.2.2. Evaluation of photocatalytic activity

Photocatalytic oxidation of sulfides was carried out in mixed CH₃CN and water solvents (2:1 v/v) in suspensions of metalloaded BiVO₄ under irradiation by visible light ($\lambda > 420$ nm). A quantity of 0.1 wt.% metal-loaded BiVO₄ powder (50 mg) was suspended in 1.5 mL mixed CH₃CN and H₂¹⁶O or H₂¹⁸O solvents (2:1 v/v) including thioanisole (50 µmol). The system was connected to a balloon filled with pure molecular oxygen. The mixture was stirred for 30 min to blend evenly in the solution before visible light irradiation. The reaction temperature was controlled at 20 °C by a water-cooling system. The suspensions were irradiated by a 300 W Xe lamp equipped with a 420 nm cut filter with continuous stirring. After reaction, the mixture was centrifuged at 10,000 rpm



for 5 min to remove the catalyst particles. The remaining solution was analyzed with an Agilent Gas Chromatograph (GC6890) equipped with a flame ionization detector and an Agilent Technology HP-INNOWAX 19091N-213 capillary column using diphenyl ether as the internal standard. The chemical structures of products were confirmed by ¹H NMR. Conversion of sulfide and selectivity for sulfoxide were defined as follows:

Conversion (%) =
$$[(C_0 - C_{sulfide})/C_0] \times 100$$
,

Selectivity (%) = $[C_{\text{sulfoxide}}/(C_0 - C_{\text{sulfide}})] \times 100$,

where C_0 was the initial concentration of sulfide and C_{sulfide} and $C_{\text{sulfoxide}}$ were the concentrations of the substrate sulfide and the corresponding sulfoxide, respectively.

2.2.3. Electron paramagnetic resonance measurements

The active oxygen species generated in the photocatalytic process were probed using electron paramagnetic resonance (EPR) spectra recorded on a Bruker EPR A 200 spectrometer by trapping with DMPO. Samples containing $BiVO_4$ or 0.5 wt.% Pt/BiVO_4 (1 g/L), DMPO (0.045 M), AgNO_3 aqueous solution (0.1 M), or thioanisole (12 μ L) were vacuumized and purged with argon. Then, the mixtures were oscillated to make the catalyst blend evenly, added into an EPR quartz tube, and irradiated with a 300 W Xe lamp (CERA-MAX LX-300) with a 420 nm cutoff filter. The settings for the ESR spectrometer were as follows: center field = 3310 G, microwave frequency = 9.30 GHz, sweep width = 140 G, modulation frequency = 100 kHz, and power = 6.36 mW.

Note: Twice deionized water must be carefully redistilled in the presence of 4×10^{-5} M KMnO₄ and NaOH at pH > 12 for 36 h, and then stored in conventional plastic bottles.

2.2.4. Electrochemical measurements

Electrochemical measurements were made using a computercontrolled electrochemical station (CHI Model 730D) with a conventional three-electrode cell at room temperature. A saturated calomel electrode (SCE) was used as the reference electrode, while a platinum foil was used as the counter electrode. The working electrode was prepared as follows: BiVO₄ or 0.5 wt.% Pt/BiVO₄ catalyst (5 mg) and Nafion (5 wt.%, Du Pont Corp.) (50 μ L) were dispersed in absolute ethanol (1 mL) using sonication. The slurry (20 μ L) was spread on the glassy carbon disk, which was dried in air at room temperature. Linear sweep voltammetry (LSV) was carried out in Ar- or O₂-saturated NaClO₄ (0.1 M) solution and the electrode potential was scanned between -1.2 and 0.2 V vs. SCE with a scan rate of 0.1 V/s.

3. Results and discussion

3.1. Photocatalytic conversion of thioanisole on BiVO₄-based photocatalysts under various conditions

BiVO₄ photocatalysts possess a suitable valence band (VB) (+2.53 V vs. standard hydrogen electrode (SHE)) [25] for photocatalytic water oxidation [22] and a conduction band (CB) (+0.13 V vs. SHE) [25], and their optical absorption edge is 530 nm. The oxidation of thioanisole is chosen as a model reaction because of the following merits: (1) thioanisole is a substrate that does not contain any oxygen atoms and both the sulfoxide and sulfone products are oxygenated; and (2) the functional group that contains oxygen atoms in its products does not exchange with water or dioxygen (Fig. S1, ESI), so it is possible to trace whether the oxygen atoms in the functional group originate from water or dioxygen. The reactions were investigated under continuous illumination with visible light from a Xe lamp with power 300 W equipped with a 420 nm cutoff filter. Metal nanoparticles as reduction cocatalysts were loaded onto BiVO₄ by the photodeposition method.

The reaction conditions are screened and the results are summarized in Table 1. The preliminary results show that no reaction took place in the absence of a photocatalyst, light, or dioxygen. In dry CH₃CN, BiVO₄ gave very low conversion, ca. 3%, in an aerobic atmosphere under visible light illumination. No reaction took place in dry benzotrifluoride, which had high solubility for dioxygen [26]. Nor did a reaction take place in the protic solvent ethanol, although this solvent was favorable in some cases where dyes were used as photosensitizers [27,28]. To improve the photogenerated charge separation, BiVO₄ loaded with 0.1 wt.% Pt was tested in CH₃CN. However, the activity was still very poor, ca. 4% conversion. This result indicates that the reaction is not driven distinctly through the active singlet oxygen $({}^{1}O_{2})$ pathway, which in certain cases is dominant when dves are used as photosensitizers [27,28]. The activity in organic solvents, although very poor, may be attributable to this pathway, in which the photogenerated holes react with the substrate directly.

When H₂O was added to the reaction system, BiVO₄ gave somewhat higher conversion, \sim 7%. Unexpectedly, Pt/BiVO₄ gave up to 70% conversion in the CH₃CN/H₂O (2:1 v/v) mixture, about 10fold higher than BiVO₄. Virtually no overoxidation compounds were produced. The result strongly suggests the important role of water in the reaction.

To differentiate the roles of photogenerated holes and electrons in the reaction, the dioxygen reduction was further optimized before the effect of H₂O was studied. Various metal nanoparticles, including Au, Ag, and Pd, were investigated as cocatalysts. The nanoparticles Ag and Au as cocatalysts exhibited slightly promoting effects, and Pd gave a moderate promoting effect (Table S1, ESI). BiVO₄ with 0.5 wt.% Pt exhibited the highest activity, at least 30-fold enhanced compared with that of BiVO₄ (Fig. S2, ESI).

3.2. The dioxygen reduction species in the reaction

A linear sweep voltammetry test was performed to investigate the dioxygen reduction properties of BiVO₄, as shown in Fig. 1. In the Ar-saturated solution, only a very weak current was obtained for both BiVO₄ and Pt/BiVO₄. In the O₂-saturated solution, the linear sweep voltammetry (LSV) scan showed two peaks centered at $E_1 = 0.271$ V and $E_2 = -0.079$ V vs. SHE on the cathodic sweep of BiVO₄, indicating that dioxygen reduction occurred through at least two electrochemical pathways. When Pt/BiVO₄ was used,

Table 1

The results of photocatalytic oxidation of thioanisole under various conditions:





Notes: Reaction conditions: catalyst 50 mg, thioanisole 50 µmol, total volume 1.5 mL, O₂ 0.1 MPa, reaction temperature 20 °C, λ > 420 nm, reaction time 5 h. Based on GC.

0.1 wt.% Pt loading.

H₂O (0.5 mL).

d Under Ar.





Fig. 1. Dark current (J)-potential (E/V vs. SHE) curves for the BiVO₄ and 0.5 wt.% Pt/BiVO₄ electrodes in NaClO₄ (0.1 M) solutions under Ar and O₂.

the corresponding cathodic peaks E_1 and E_2 shifted to 0.164 and -0.208 V, respectively. Moreover, the cathodic current density increased significantly and the onset shifted toward a more positive potential. For instance, the cathodic current increased by about 2.5 times at -0.20 V, and the onset shifted positively to about 100 mV, indicating that the addition of Pt nanoparticles promoted the dioxygen reduction reaction. This dioxygen reduction property of Pt/BiVO₄ is similar to the result reported by Kobayashi and Tada [29], in which surface modification with $Cu(acac)_2$ endowed BiVO₄ with the ability of multielectron dioxygen reduction. The photoexcited electrons in the conduction band of BiVO₄ are theoretically incapable of the one-electron process of dioxygen reduction $(E^{\theta}(O_2/O_2^{-}) = -0.284 \text{ V} \text{ vs. SHE})$ [29], but could enable fourelectron and two-electron pathways $(E^{\theta}(O_2/H_2O_2) = +0.695 \text{ V} \text{ and}$ $E^{\theta}(O_2/H_2O) = +1.229 \text{ V vs. SHE}$ [30,31]. Therefore, the cathodic peaks E_1 and E_2 , more positive than $E^{\theta}(O_2/O_2^{-1})$, can be ascribed, respectively, to the four-electron and two-electron dioxygen reduction pathways.

We further detected H_2O_2 as the product of dioxygen reduction by iodometric titration. At low (5%) or moderate (35%) conversion, the concentration of H₂O₂ was below the detection limit of the current method (Fig. S3, ESI) [32]. These results indicate the fourelectron dioxygen reduction pathway. Hence, the Pt nanoparticles promote not only the separation of the photogenerated charge, but

also the four-electron dioxygen reduction process. However, this does not fully exclude the possibility that two-electron dioxygen reduction formed H_2O_2 and led to further rapid decomposition.

3.3. The effect of water

Next, we further investigated the effect of water. To promote the mass transfer of the substrate, the conversion of thioanisole was controlled to below 30%. Through addition of a trace amount of water (1.3% v/v) to CH₃CN, a sevenfold enhancement was observed compared with the conversion for dry CH₃CN (Fig. S4, ESI). As the water concentration increased, the increase in the amount of product was almost proportional to the water concentration. The optimal percentage of water concentration was about 33% (v/v) under the experimental conditions. The reaction was evidently suppressed by excess water because of incomplete dissolution of the substrate, even though the reaction was much faster in water than in CH₃CN.

To gain further insight into the effect of water in the reaction, ¹⁸O-labeled H_2 ¹⁸O, with an isotope abundance of 98%, was used to trace the origin of the oxygen atom of sulfoxide using 0.5 wt.% Pt/BiVO₄ in CH₃CN/H₂¹⁸O (2:1 v/v). As shown in Fig. 2, at a conversion of ca. 9%, the proportion of H_2 ¹⁸O-derived oxygen atoms incorporated into the product was 83%, of which 17% was



Fig. 2. Photocatalytic oxidation of thioanisole in the presence of $H_2^{18}O$ with 0.5 wt. % Pt/BiVO₄. Reaction conditions: catalyst 20 mg, thioanisole 100 µmol, total volume 1.5 mL, $CH_3CN/H_2^{18}O$ 2:1 v/v, O_2 0.1 MPa, reaction temperature 20 °C, λ > 420 nm.

Table 2

Photocatalytic oxidation of thioanisole with catalysts in the presence of H₂¹⁸O:



Photocatalyst	Surface area (m ² /g)	The activity of thioanisole $(\text{umol } \text{m}^{-2} \text{ h}^{-1})$	Conv. (%) ^a	Product		¹⁸ O-atom from water (%)
		(µmorm m)		¹⁸ 0	¹⁶ 0	
TiO ₂ ^b	67	6	6	26	74	26
Bi ₂ WO ₆	38	0.2	4	10	90	10
Bi ₂ MoO ₆	17	0.4	3	35	65	36
BiVO ₄	2	7	7	89	11	91
Pt/BiVO4 ^c	6	150	9	81	19	83

Notes: Reaction conditions: catalyst 50 mg, thioanisole 50 μmol, total volume 1.5 mL, CH₃CN/H₂¹⁸O 2:1 v/v, O₂ 0.1 MPa, reaction temperature 20 °C, λ > 420 nm, reaction time 5 h.

^a Based on GC.

^b Degussa P25 15 mg, Xe lamp 0.5 h.

^c Catalyst 20 mg, thioanisole 100 μmol, 0.5 wt.% Pt loading, reaction time 0.5 h.

from ¹⁶O₂-derived oxygen atoms, indicating the presence of parallel pathways. The percentage of H_2^{18} O-derived oxygen atoms in the product using BiVO₄ was higher than that of the product using Pt/BiVO₄ at a similar conversion (see Table 2). The percentage of ¹⁸O in the product decreased as the conversion increased, and the final atomic ratio of ¹⁸O/¹⁶O was ca. 3.4, possibly due to the incorporation of the H_2^{16} O generated as a product of the sacrificial acceptor ¹⁶O₂. The results unambiguously suggest that both H_2 O and O₂ participate in the reaction, but the majority of the oxygen in the product is from H_2O .

3.4. Proposed mechanism

In view of the proportion of ¹⁸O originating from $H_2^{18}O$ and ¹⁶O originating from ¹⁶O₂ in the product, there are at least two pathways involved the reaction (Fig. 3). Due to the inability to reduce dioxygen to form radical species on BiVO₄, the ¹⁶O₂-derived oxygen atoms are incorporated into the product directly through the photogenerated hole-dominated oxidation pathway. The adsorbed thioanisole on the surface of BiVO₄ can be oxidized by photogenerated holes to produce sulfide radical cations, which are



Fig. 3. Two possible reaction pathways of photocatalytic oxidation of thio anisole on $\mbox{Pt/BiVO}_4.$

subsequently recombined by interacting with dioxygen. Due to the hydrophilic surface of BiVO₄ and the weak adsorption of thioanisole on the surface of BiVO₄, the hole-dominated oxidation pathway is generally suppressed. The pathway by which $H_2^{18}O$ -derived oxygen atoms are incorporated into the product is an indirect one through a water-oxidized intermediate.

To confirm whether such a mechanism is common to other semiconductor-based photocatalysts, TiO_2 (P25), Bi_2WO_6 , and Bi_2MOO_6 were also tested using $H_2^{18}O$ -labeled isotope experiments (Table 2). The percentages of $H_2^{18}O$ -derived oxygen atoms were 26%, 10%, and 36% for TiO₂, Bi_2WO_6 , and Bi_2MOO_6 , respectively, and these percentages were much lower than for BiVO₄ and Pt/BiVO₄. It is noteworthy that BiVO₄ under visible-light irradiation delivered somewhat higher activity than TiO₂ after normalization by surface area, and Pt/BiVO₄ exhibited the highest activity. The result further indicates that the excellent performance of BiVO₄ is due to its unique ability to follow both the water oxidation and four-electron dioxygen reduction pathways simultaneously.

3.5. The reactive oxygen species derived from water

A control experiment was conducted to reveal the relationship between photocatalytic water oxidation and photocatalytic oxidation of thioanisole (Table 3). Using Ag⁺ as a sacrificial electron acceptor, BiVO₄ produced about 197 µmol O₂ under irradiation. In contrast, when thioanisole was added to the same reaction solution, oxygen production was completely suppressed, resulting in about 162 µmol sulfoxide. The result clearly shows that water oxidation and oxidation of thioanisole are closely correlated. The active oxygen species that are available for thioanisole oxidation are mainly derived from the oxidation of water by photogenerated holes on BiVO₄.

To identify the active oxygen species generated in the photocatalytic process, the EPR-spin-trap technique (with DMPO as a trapping reagent) was used to detect the intermediate species in the anaerobic system using AgNO₃ aqueous solution as electron sacri-

Table 3

Photocatalytic water oxidation in the absence or presence of thioanisole on BiVO₄.

Substrate	O ₂ (μmol)	Sulfoxide (µmol)
-	197	-
+	1	162

Notes: Reaction conditions: catalyst 150 mg, thioanisole 0.05 M, AgNO₃ 0.1 M, CH₃CN/H₂O 2:1 v/v (100 mL), reaction temperature 20 °C, λ > 420 nm, reaction time 0.5 h.



Fig. 4. EPR spectra of DMPO-spin-trapped radical species upon photocatalytic oxidation of H_2O and thioanisole on BiVO₄ and Pt/BiVO₄ under argon under visible light illumination. Reaction conditions: BiVO₄ or 0.5 wt.% Pt/BiVO₄ 1 g/L, DMPO 0.045 M, AgNO₃ aqueous solution 0.1 M, or thioanisole 12 µL. The signals obtained before irradiation are denoted as Dark, after irradiation for 5 min as Light-5, and after irradiation for 10 min as Light-10.

Table 4

Photocatalytic oxidation of various sulfides with 0.5 wt.% Pt/BiVO₄.

Substrate	Time (h)	Conv. (%) ^a	Sulfoxide sel. (%) ^b
S_	5.5	96	98
H ₂ CO S	12	96	99
S S	8	99	98
S S	17.5	95	97
	10	97	98
S S	11	97	98

Notes: Reaction conditions: catalyst 20 mg, thioanisole 100 µmol, O₂ 0.1 MPa, total volume 1.5 mL, CH₃CN/H₂O 2:1 v/v, reaction temperature 20 °C, λ > 420 nm.

^a Based on GC. ^b Based on ¹H NMR.

ficial reagent. As shown in Fig. 4, an EPR signal change was observed in the presence of $BiVO_4$ or $Pt/BiVO_4$ photocatalysts when the reaction mixture was under visible light irradiation. A sevenline paramagnetic signal was obtained for $BiVO_4$ and $Pt/BiVO_4$. This signal is a typical feature of DMPO-X [33–36] and is generated from the oxidation of DMPO by peroxide [37,38]. This indicates that the peroxy species are the most likely reactive oxygen species derived from water on $BiVO_4$. The typical four-line peak of DMPO-OH was not observed, implying that the 'OH radical may not be involved in the photocatalytic oxidation of thioanisole on $BiVO_4$ [39,40]. When thioanisole was added to the $BiVO_4/H_2O/AgNO_3$ system, the seven-line EPR signal originating from the peroxy species disappeared, further confirming that these peroxy intermediate species involved the selective oxidation of thioanisole.

3.6. Photocatalytic oxidation of various sulfides on Pt/BiVO₄

Pt/BiVO₄ was tested for the photocatalytic oxidation of a series of sulfides under the previously optimized conditions, and the results are summarized in Table 4. A number of methyl phenyl sulfides bearing electron-withdrawing or electron-donating substituents on the phenyl ring were efficiently oxidized, with both complete conversion and excellent selectivity for the corresponding sulfoxides. In addition, the location of substituents on the phenyl ring significantly affected the reaction activity. For instance, *o*-chlorophenyl methyl sulfide showed much lower oxidation activity to the corresponding sulfoxide than the *m*- and *p*-isomers because of steric hindrance effects. Thioanisole reacted faster than the methyl phenyl sulfides with substituents, possibly implying that it is difficult for hydrophobic substrates to access the surface of BiVO₄.

4. Conclusion

In summary, Pt/BiVO₄ can act as an efficient photocatalyst for the oxidation of sulfides to sulfoxides, with excellent selectivity in aqueous solution under visible light irradiation. The oxygenation of sulfides is conducted mainly with the peroxy species generated through the two-electron photocatalytic water oxidation pathway. Dioxygen as an electron acceptor is reduced to water through the four-electron pathway, avoiding the use of noble and rare complexes as sacrificial reagents. The study provides a fundamental understanding on the incorporation pathway of oxygen atoms in the oxidation of compounds on BiVO₄ photocatalysts. Importantly, the study provides a promising strategy for selective photocatalytic oxidation reactions, as the method does not involve oxyradical-induced processes. Semiconductors endowed with multielectron dioxygen reduction can significantly reduce the limitations of the thermodynamic potential for electron transfer and consumption. Consequently, a number of visible-light-respondent photocatalysts with the inability to implement single-electron dioxygen reduction could be extended to selective oxidation in organic synthesis.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (NSFC 21473190) and the DICP Fundamental Research Program for Clean Energy (DICP M201302).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.08.029.

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