

Photocatalytic oxidation of thiophene on BiVO₄ with dual co-catalysts Pt and RuO₂ under visible light irradiation using molecular oxygen as oxidant†‡

Feng Lin,^{§ab} Donge Wang,^{§ab} Zongxuan Jiang,^a Yi Ma,^{ab} Jun Li,^a Rengui Li^{ab} and Can Li^{*a}

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Thiophene is one of the main sulfur-containing compounds in gasoline and difficult to be oxidized with the conventional oxidative processes. Herein for the first time we report that thiophene can be oxidized to SO₃ on BiVO₄ co-loaded with Pt and RuO₂ co-catalysts (denoted as Pt-RuO₂/BiVO₄) under visible light irradiation with molecular oxygen as oxidant. The high activity of the catalyst can be achieved by only loading as low as 0.03 wt% of Pt and 0.01 wt% of RuO₂ as dual co-catalysts on BiVO₄. ESR measurements give the evidence that the active oxygen species (OH and O₂^{•-}) generated by photocatalytic processes are involved in the photocatalytic oxidation of thiophene. The considerable enhancement of photocatalytic activity can be attributed to the simultaneous presence of the reduction and oxidation co-catalysts which are beneficial for the efficient separation and transfer of the photo-generated electrons and holes.

1. Introduction

Since an early study on the photocatalytic oxidation of organic compounds in aqueous system by Carey in 1976,¹ there have been intensive investigations on the application of photocatalysis for the photodecomposition of hazardous wastes and photodegradation of dye molecules.^{2–5} Air pollution, caused by the

emission of SO_x, is one of the most serious environmental problems in the world,⁶ and the automobile exhaust gas is the major source of SO_x formed *via* the burning of sulfur-containing components including thiophene and its derivatives. Sulfur-containing organic compounds are harmful to the environment and are difficult to remove from fuels, especially thiophene in gasoline.^{7–10} The current hydrodesulfurization (HDS) technology requires severe conditions (*e.g.*, high temperature, high pressure, and high hydrogen consumption),^{11,12} which result in a high operating-cost and a substantial octane loss, particularly for gasoline. Therefore, several non-HDS methods have been developed to meet the demands of producing clean gasoline with an extremely low sulfur level. Oxidative desulfurization (ODS) is considered to be one of the most promising alternative processes.^{13–24} Due to its mild operating conditions and no consumption of H₂, oxidative desulfurization has received great attention from industry.

^aState Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, 457 Zhongshan Road, Dalian, 116023, China. E-mail: canli@dicp.ac.cn; Web: <http://www.canli.dicp.ac.cn>. Fax: +86-411-84694447; Tel: +86-411-84379070

^bGraduate University of Chinese Academy of Sciences, Beijing, 100049, China

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§ Both authors contributed equally to this work.

Broader context

Thiophene, one of the main sulfur-containing compounds in gasoline, is most difficult to oxidize with conventional oxidative processes. To develop green and energy-saving desulfurization processes, photocatalytic oxidation of desulfurization utilizing solar energy has received increasing attention in recent years. In this article, for the first time, we report that a visible-light responsive photocatalyst BiVO₄ co-loaded with low loadings of Pt and RuO₂ co-catalysts (denoted as Pt-RuO₂/BiVO₄) can achieve over 99% conversion in thiophene oxidation under visible light irradiation using molecular oxygen as oxidant, and the sulfur in thiophene can be photocatalytically oxidized to SO₃. The considerable enhancement of photocatalytic activity in the oxidation of thiophene is attributed to the co-loading of the reduction and oxidation co-catalysts which are helpful for the efficient separation and transfer of photo-generated electrons and holes. This strategy could be potentially extended to the oxidation of any other pollutants in the environment, as well as to photocatalysis for solar energy conversion.

Besides, sulfur-containing organic compounds are a class of pollutants in water and the removal of these pollutants is also highly desired. However, thiophene, one of the main sulfur-containing compounds in gasoline, is most difficult to oxidize with conventional processes. The inertness of thiophene in oxidative desulfurization is mainly due to its aromaticity and its low electron density on the S atom, which makes oxidation of the thiophene molecule more difficult. Therefore, the removal of thiophene from fuels, particularly gasoline, is still a challenge in oxidative desulfurization.

In our previous work,^{7,9,23,24} we reported that dibenzothiophene and its derivatives in diesel can be efficiently oxidized in a catalytic emulsion system using H_2O_2 as oxidant under mild conditions. However, this does not work for the oxidation of thiophene in gasoline. Photocatalytic oxidation, with molecular oxygen, is a cleaner and more environmentally friendly way to remove the sulfur-containing compounds from gasoline and has received increasing attention in recent years. TiO_2 (with a band gap of 3.2 eV) has been used as the photocatalyst for the elimination of environmental contaminants^{25–28} and photocatalytic oxidation of sulfur-containing compounds as well.^{29,30} TiO_2 , although an excellent photocatalyst, can absorb only ultraviolet light. Unfortunately, the fuels (diesel and gasoline) also strongly absorb the UV light (as shown in Fig. 1). So the UV-light-responsive photocatalyst is practically unsuitable for the photocatalytic oxidation of sulfur-containing compounds in fuels, because the fuels can absorb most of the incident light. Therefore, it is highly desirable to develop visible-light responsive photocatalysts, because fuels are optically transparent in the visible light region. Photosensitizers together with TiO_2 have been investigated for the photocatalytic oxidation of thiophene and its derivatives under visible light irradiation.^{31–35} However, the photosensitizer itself is often oxidized and difficult to recover from the oxidation systems. Therefore, it is ideal to develop visible-light responsive and robust photocatalysts for the removal of sulfur-containing compounds in gasoline or water *via* photocatalytic oxidation.

BiVO_4 has been reported to be a visible-light-active photocatalyst for the water oxidation reaction^{36–38} and the two step overall water splitting, the so-called Z-scheme type system.^{39–41} A number of researchers also used the co-catalysts to improve the

photocatalytic activities.^{42–44} Herein we report the photocatalytic oxidation of thiophene by a visible-light responsive photocatalyst BiVO_4 co-loaded with ultra-low loadings of Pt and RuO_2 co-catalysts (denoted as $\text{Pt-RuO}_2/\text{BiVO}_4$). We find that BiVO_4 co-loaded with co-catalysts, Pt and RuO_2 , shows the strongly synergistic effect between the two co-catalysts on the photocatalytic activity of thiophene oxidation. Over 99% conversion of thiophene oxidation can be achieved under visible light irradiation ($\lambda \geq 420$ nm) using molecular oxygen as oxidant.

2. Experimental

2.1 Catalyst preparation

All chemicals used in these experiments were of analytical reagent grade without further treatment. NH_4VO_3 (36.0 mmol) and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (36.0 mmol) were dissolved in 300 mL and 60 mL of 2.0 M nitric acid solutions, respectively. Then the above solutions were mixed to form a yellow homogeneous solution. The pH value of the resulting solution was adjusted to approximately 2.0 with ammonia solution under constant stirring. An orange precipitate was obtained during the adjustment of the pH value of the solution, and the suspension was further stirred for 0.5 h. After subsiding for 2 h, the slurry of the orange precipitate at the bottom of the beaker (*ca.* 70 mL) was transferred to a Teflon-lined stainless steel autoclave and hydrothermally treated at 473 K for 24 h. After the autoclave was cooled to room temperature, a yellow powder was obtained. The powder was separated by filtration, and then washed several times with distilled water. Finally, the obtained sample was dried at 353 K for 12 h.

The loading of metal oxide (M_2O_x) on BiVO_4 was performed by the impregnation method. RuCl_3 and H_2IrCl_6 were used as precursors. BiVO_4 powder was impregnated in an aqueous solution containing a given amount of the chloride salts. The solution was then evaporated over a water bath at 50 °C followed by a calcination in air at 350 °C for 1 h. The samples co-loaded with noble metal on $\text{M}_2\text{O}_x/\text{BiVO}_4$ were obtained by the photo-deposition method. The photocatalyst, BiVO_4 co-loaded with the noble metals M_1 (Pt, Pd) and metal oxide M_2O_x (RuO_2 , IrO_2) was denoted as $\text{M}_1\text{-M}_2\text{O}_x/\text{BiVO}_4$.

2.2 Catalyst characterization

The prepared samples were characterized by X-ray powder diffraction (XRD) on a Rigaku D/Max-2500/PC powder diffractometer. Each sample was scanned using $\text{Cu-K}\alpha$ radiation with an operating voltage of 40 kV and an operating current of 200 mA. The scan rate of 5° min^{-1} was applied to record the patterns in the range of 8–80° at a step of 0.02°.

UV-Visible diffuse reflectance spectra (UV-Vis DRS) were recorded on a UV-Vis spectrophotometer (JASCO V-550) equipped with an integrating sphere. The morphologies and particle sizes were examined by scanning electron microscopy (SEM) equipped with a Quanta 200 FEG scanning electron microscope.

UV Raman spectra were recorded on a home-assembled UV Raman spectrograph using a Jobin-Yvon T64000 triple-stage spectrograph with a spectral resolution of 2 cm^{-1} . The laser line at 325 nm of an He-Cd laser was used as excitation source with

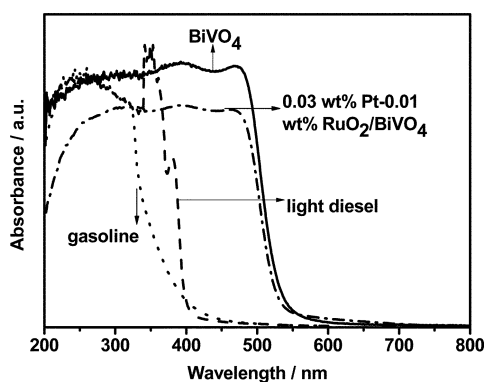


Fig. 1 UV-Vis DRS of BiVO_4 prepared by the hydrothermal method and of $\text{Pt-RuO}_2/\text{BiVO}_4$ photocatalyst with 0.03 wt% Pt and 0.01 wt% RuO_2 co-catalysts, gasoline and light diesel.

an output of 50 mW. The power of the laser at samples was about 1.0 mW.

ESR signals of radicals trapped by DMPO were recorded at ambient temperature on a Bruker ESR A200 spectrometer. After bubbling O₂ for 10 min, the samples were introduced into the home-made quartz cup inside the microwave cavity and illuminated with a 300 W Xe lamp (CERAMAX LX-300). The settings for the ESR spectrometer were as follows: center field, 3486.70 G; sweep width, 100 G; microwave frequency, 9.82 GHz; modulation frequency, 200 kHz; power, 10.00 mW. Magnetic parameters of the radicals detected were obtained from direct measurements of magnetic field and microwave frequency.

2.3 Photocatalytic reaction

The photocatalytic reactions were carried out in a Pyrex reaction cell with O₂ (air can also be used as oxidant) bubbled in a constant flow as oxidant. Photocatalyst, 50 mg, was dispersed in 50 mL of acetonitrile solution containing thiophene ([sulfur content]_{initial} = 100 ppm; 200 ppm; 400 ppm; 600 ppm; 800 ppm; 1200 ppm). The suspension was irradiated by a 300 W Xe lamp (CERAMAX LX-300) which is equipped with an optical filter ($\lambda \geq 420$ nm) to cut off the light in the ultraviolet region. The temperature of the reaction solution was maintained at 6 ± 2 °C by a flow of cooling water. The products and byproducts were analyzed by GC-FPD (Agilent 7890, FFAP column) and GC-MS after separation of the catalyst from the reaction system by centrifugation.

3. Results and discussion

3.1 The absorption edges of BiVO₄ samples, gasoline and light diesel

BiVO₄, prepared by hydrothermal treatment at 200 °C for 24 h, is a monoclinic scheelite according to the standard card of No. 14-0688 (Fig. S1, ESI†). Fig. 1 shows the UV-vis diffuse reflectance spectra of BiVO₄ and 0.03 wt% Pt-0.01 wt% RuO₂/BiVO₄. BiVO₄ shows strong absorption in the visible light region until 535 nm in addition to that in the UV light region. The band gap of BiVO₄ was estimated to be 2.3 eV from the absorption edge of the UV-vis diffuse reflectance spectrum. After loading co-catalysts on BiVO₄, no obvious shift of the absorption edge is observed for Pt-RuO₂/BiVO₄. Fig. 1 also shows the UV-vis diffuse reflectance spectra of gasoline and light diesel. The absorption edges of gasoline and light diesel were estimated to be about 400 nm, namely in the UV light region. Therefore, both gasoline and light diesel are not optically transparent to UV light, and compete with the UV-light responsive photocatalyst to absorb the incident light. Consequently, the photocatalytic activity of TiO₂ is quite low. The problem can be solved by utilizing the visible-light responsive photocatalyst (e.g. BiVO₄), which can absorb the light ($\lambda \geq 400$ nm) beyond the absorption edges of gasoline and light diesel.

3.2 The effect of co-catalysts on photocatalytic oxidation of thiophene

Fig. 2 shows the conversion for photocatalytic oxidation of thiophene on BiVO₄, Pt/BiVO₄, RuO₂/BiVO₄, Pt-RuO₂/BiVO₄,

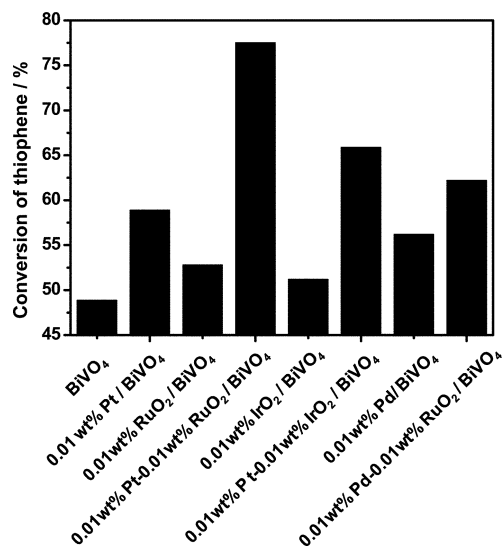


Fig. 2 Photocatalytic activity of thiophene oxidation on BiVO₄ and BiVO₄ loaded with various co-catalysts under visible light irradiation ($\lambda \geq 420$ nm). Reaction conditions: [sulfur content]_{initial} = 600 ppm; the concentration of photocatalyst: 1 g L⁻¹; O₂ (bubbled into the system); reaction time: 3 h.

IrO₂/BiVO₄, Pt-IrO₂/BiVO₄, Pd/BiVO₄ and Pd-RuO₂/BiVO₄ photocatalysts. To study the intrinsic effect of the co-catalyst, an ultra-low loading of co-catalyst, 0.01 wt%, was adopted for all the co-catalysts. BiVO₄ without loaded co-catalyst exhibited low conversion for photocatalytic oxidation of thiophene (ca. 48%), and the conversion was enhanced by loading only 0.01 wt% Pt co-catalyst (ca. 59%) or 0.01 wt% RuO₂ co-catalyst (ca. 53%). By loading only individual co-catalysts, either Pt or RuO₂, the conversion can at best be enhanced by about 10%. Most interestingly, when 0.01 wt% Pt and 0.01 wt% RuO₂ were co-loaded on BiVO₄, the conversion was markedly enhanced to ca. 78%, much higher than those of Pt/BiVO₄ and RuO₂/BiVO₄. The conversion was also improved greatly when Pt and IrO₂ were co-loaded on BiVO₄, compared with Pt/BiVO₄ and IrO₂/BiVO₄ alone. A similar trend was observed for Pd-RuO₂/BiVO₄ catalyst in comparison with Pd/BiVO₄ and RuO₂/BiVO₄ alone. According to the above results, Pt-RuO₂/BiVO₄ is a most effective photocatalyst for the photocatalytic oxidation of thiophene. The synergistic effect of co-catalysts on BiVO₄ is very favorable for the improvement of the photocatalytic activity of thiophene oxidation.

The dependence of the conversion for photocatalytic oxidation of thiophene on the loadings of Pt and RuO₂ on BiVO₄ are shown in Fig. 3a. For Pt/BiVO₄ catalyst, as the loading of Pt increased from 0 to 0.2 wt%, the conversion for photocatalytic oxidation of thiophene reaches a maximum, 69% when the loading of Pt is increased to 0.1 wt%. However, the conversion for photocatalytic oxidation of thiophene on RuO₂/BiVO₄ shows an obviously different trend. The conversion is slightly increased from 48% to 56% when the loading of RuO₂ varied from 0 to 0.05 wt%. It is noteworthy that when only 0.01 wt% RuO₂ was loaded, the conversion can reach as high as 53%. The conversion for photocatalyst with higher loading of RuO₂ does not increase obviously, that is, the extra amount of RuO₂ loaded on BiVO₄ is not necessary. So the loading of RuO₂ (0.01 wt%) is chosen to

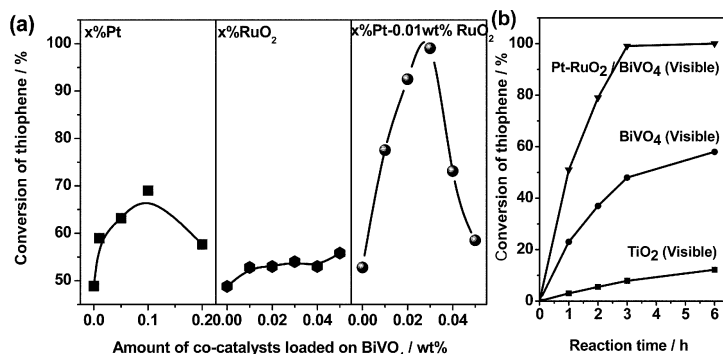


Fig. 3 (a) Photocatalytic activity of thiophene oxidation as a function of the loading amount of Pt alone, RuO₂ alone, and Pt, RuO₂ co-loaded on BiVO₄. x denotes the loading amount of co-catalyst. Reaction conditions: [sulfur content]_{initial} = 600 ppm; concentration of photocatalyst: 1 g L⁻¹; O₂ (bubbled into the system); reaction time: 3 h. (b) Photocatalytic activity of thiophene oxidation on different photocatalysts under visible light irradiation ($\lambda \geq 420$ nm), 0.03 wt% Pt-0.01 wt% RuO₂/BiVO₄, BiVO₄ and TiO₂ (P25). Reaction conditions: [sulfur content]_{initial} = 600 ppm; the concentration of photocatalyst: 1 g L⁻¹; O₂ (bubbled into the system); reaction time: 6 h.

optimize the conversion for photocatalytic oxidation of thiophene by varying the amount of the co-loaded Pt. Surprisingly, we found that the conversion can be greatly improved when the loading of Pt varied from 0 to 0.05 wt%. As the loading of co-loaded Pt is increased, the conversion is markedly enhanced to a maximum, over 99% when the loading of Pt is only 0.03 wt%. As shown in Fig. 3b, thiophene (600 ppm) can be completely converted (*ca.* 100%) in 3 h for the optimized 0.03 wt% Pt-0.01 wt% RuO₂/BiVO₄ catalyst. BiVO₄ without co-catalyst loading exhibited low conversion for photocatalytic oxidation of thiophene (*ca.* 58%) in 6 h. For comparison, the performance of the photocatalyst TiO₂ (P25) with the same initial sulfur content, 600 ppm, under visible light was also investigated. TiO₂ (P25) gave a conversion of only 12% in 6 h under visible light irradiation. Comparably, the 0.03 wt% Pt-0.01 wt% RuO₂/BiVO₄ photocatalyst exhibits the highest photocatalytic activity for thiophene oxidation under visible light irradiation.

Considering the requirements for application to ultra-low-sulfur-containing fuels, the influence of the initial sulfur content on the conversion for photocatalytic oxidation of thiophene was investigated. Photocatalytic reaction tests with different initial sulfur contents ([sulfur content]_{initial} = 100 ppm; 200 ppm; 400 ppm; 800 ppm; 1200 ppm) were carried out (Fig. 4). When the initial sulfur content is 100 ppm, thiophene can be completely oxidized in less than 3 h under visible light irradiation. When the initial sulfur content is below 400 ppm, the conversions of thiophene can be also over 99% in 3 h. The time for the complete conversion in the photocatalytic oxidation of thiophene is a little longer when the initial sulfur content was increased to 800 ppm or 1200 ppm. It took about 10 h to completely remove the thiophene. Meanwhile, blank experiments were conducted to clarify the roles of light irradiation and catalyst in the photocatalytic reaction. Blank experiment 1 was carried out without the photocatalyst. As a result the conversion of thiophene was only 7% in 3 h. Blank experiment 2 was carried out without the light irradiation. As a result, the conversion of thiophene was just 9% in 3 h.

3.3 Photocatalytic oxidation of different sulfur-containing compounds

Fig. 5 shows the photocatalytic oxidation activity of different sulfur-containing compounds, which are mostly present in

gasoline, using Pt-RuO₂/BiVO₄ catalyst. Thiophene (Denoted as "T"), 2-methylthiophene (2-MT), 2,5-dimethylthiophene (2,5-DMT), benzothiophene (BT), and dibenzothiophene (DBT) were tested. For these sulfur-containing compounds studied, although photocatalytic oxidation activity is different, they can be completely oxidized using the 0.03 wt% Pt-0.01 wt% RuO₂/BiVO₄ catalyst under visible light irradiation. To study the photoproducts, GC-FPD analyzed all of the samples and the air out of outlet was introduced to NaOH aqueous solution (0.2 M) for the further analysis. After the reaction, a white precipitate was produced when Ba(NO₃)₂ aqueous solution (0.2 M) was added into the NaOH (0.2 M) solution. It was denoted as precipitate 1.

Fig. 6a shows the XRD pattern of the precipitate 1. The XRD pattern was assigned to BaCO₃ which is in good agreement with the standard card of No. 05-0378 (space group: *Pmnc*(62), $a = 5.314$, $b = 8.904$, $c = 6.430$). This result indicated that thiophene was photocatalytically oxidized to CO₂ and escaped from the

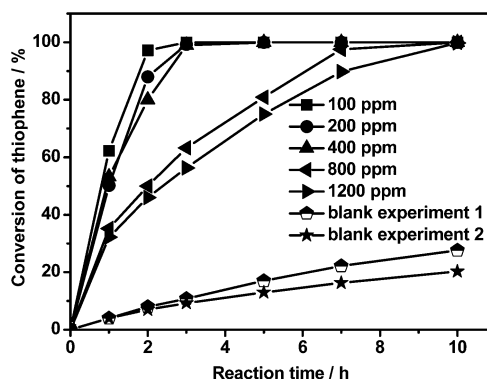


Fig. 4 Photocatalytic activity of thiophene oxidation on 0.03 wt% Pt-0.01 wt% RuO₂/BiVO₄ with different initial sulfur contents ([sulfur content]_{initial} = 100 ppm, 200 ppm, 400 ppm, 800 ppm, 1200 ppm). Blank experiment 1 was carried out under the same conditions except without the photocatalyst ([sulfur content]_{initial} = 600 ppm). Blank experiment 2 was carried out under the same conditions except without the light irradiation ([sulfur content]_{initial} = 600 ppm). Reaction conditions: the concentration of photocatalyst: 1 g L⁻¹; O₂ (bubbled into the system); reaction time: 10 h.

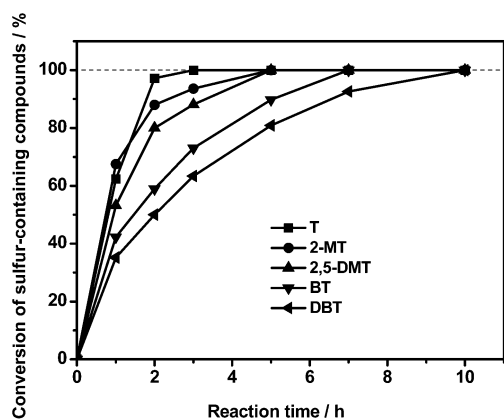


Fig. 5 Photocatalytic oxidation activity of different sulfur-containing compounds on 0.03 wt% Pt-0.01 wt% RuO₂/BiVO₄ under visible light irradiation ($\lambda \geq 420$ nm). Reaction conditions: [sulfur content]_{initial} = 600 ppm; the concentration of photocatalyst: 1 g L⁻¹; O₂ (bubbled into the system); reaction time: 10 h.

system. Most interestingly, when we added HNO₃ (aq) to precipitate 1, there was still some white precipitate remaining which couldn't be dissolved in HNO₃ (aq), this was denoted as precipitate 2. Fig. 6a shows the XRD pattern of the precipitate 2. The XRD pattern was assigned to BaSO₄ which is in good agreement with the standard card of No. 24-1035 (space group: *Pbnm*(62), $a = 7.156$, $b = 8.881$, $c = 5.454$). It indicated that the sulfur in thiophene can be photocatalytic oxidized to SO₃ after the photocatalytic reaction. Fig. 6b shows the Raman spectrum ($\lambda_{\text{ex}} = 325$ nm) of the precipitate 2. The Raman bands observed at 980 cm⁻¹, 446 cm⁻¹, 610 cm⁻¹ and 1132 cm⁻¹ are attributed to SO₄²⁻ in BaSO₄.^{45,46} The Raman bands of precipitate 2 are in good agreement with those of the BaSO₄. According to the above

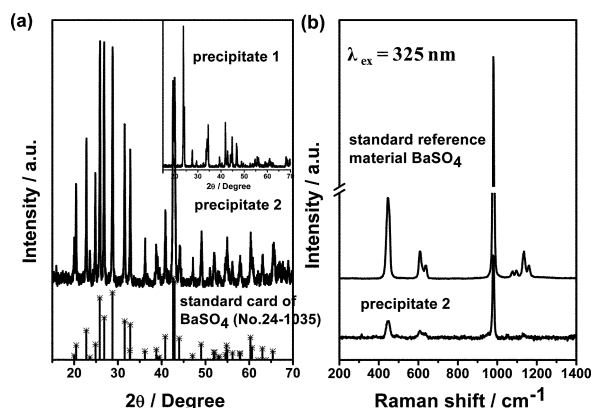


Fig. 6 (a) XRD patterns of the produced precipitates. The inset is the XRD pattern of the precipitate 1. The others are XRD pattern of the precipitate 2 and the standard card of BaSO₄ (No. 24-1035). (b) Raman spectra of the produced precipitate 2 and standard reference material BaSO₄. The gas produced in the reaction system was absorbed by NaOH aqueous solution (0.2 M), then Ba(NO₃)₂ (aq) (0.2 M) and HNO₃ (aq) was added successively to produce the precipitates 1 and 2. Reaction conditions: [sulfur content]_{initial} = 600 ppm; catalyst: 0.03 wt% Pt-0.01 wt % RuO₂/BiVO₄; concentration of photocatalyst: 1 g L⁻¹; O₂ (bubbled into the system).








results, thiophene can be oxidized to CO₂ and SO₃ in the photocatalytic oxidation system.

For T, 2-MT and 2,5-DMT the main product was identified to be SO₃, however, for BT and DBT the corresponding sulfones were the main products (Table 1). The photocatalytic oxidation path is different between thiophene derivatives and benzothio-phenes derivatives. The intermediate of thiophene oxidation is very unstable, and easily further oxidized to SO₃. On the contrary, the corresponding sulfones of BT and DBT are relatively stable. The oxidized products, SO₃ and sulfones, can be conveniently removed by washing and extraction processes.⁷ Besides, since olefins and aromatic hydrocarbons are the main constituents of light oils, we choose cyclohexene and toluene as the model compounds, and investigated their stabilities in the photocatalytic reaction system under visible light irradiation. Fortunately these main constituents are quite stable under visible light irradiation (Fig. S2, ESI[†]), suggesting that the photocatalytic oxidation desulfurization doesn't change the quality of gasoline. So the photocatalytic oxidation desulfurization may be a promising approach for the ultra-deep desulfurization of gasoline.

3.4 The proposed reaction mechanism

To clarify the reaction mechanism of the photocatalytic oxidation of thiophene on Pt-RuO₂/BiVO₄, we employed the ESR spin-trap technique (with DMPO) to probe the active oxygen species generated under the illumination. Fig. 7 shows the ESR signals obtained from the *in situ* photocatalytic reaction. No ESR signals were observed either when the photocatalyst was absent or the reaction was performed with BiVO₄ in the dark. The ESR signals appearing in the presence of the photocatalyst were centered at $g = 2.0065$, and can be assigned to oxygen species.⁴⁷ The sextet ESR signal observed is assigned to DMPO-O₂⁻. The hyperfine splittings are $a_N = 1.27$ mT, $a_H^\beta = 0.99$ mT and $a_H^\gamma = 0.14$ mT, where a_N , a_H^β and a_H^γ are the hyperfine splitting constants of nitroxyl nitrogen, one β -hydrogen and one γ -hydrogen, respectively.⁴⁸⁻⁵¹ Thus, these results provide evidence of O₂⁻ formed in the presence of the photocatalysts BiVO₄, Pt/BiVO₄, RuO₂/BiVO₄ and Pt-RuO₂/BiVO₄. The characteristic quartet peaks of the DMPO-OH adduct were observed after 10 min of illumination in the presence of photocatalysts Pt/BiVO₄, RuO₂/BiVO₄ and Pt-RuO₂/BiVO₄. The hyperfine splittings are $a_N = a_H = 1.48$ mT, where a_N and a_H denote hyperfine splittings of the nitroxyl nitrogen and α -hydrogen.⁴⁷ The 1 : 1.4 : 1.4 : 1 lineshape, however, is different from the typical 1 : 2 : 2 : 1 lineshape of the DMPO-OH adduct, maybe attributable to the simultaneous presence of DMPO-O₂⁻. Thus the 'OH, which has a strong oxidation ability, was generated by the illumination. The intensity of the signals was decreased after 20 min of illumination. This is due to the consumption of the dissolved O₂ and the oxidation of the DMPO-OH adduct by h⁺ generated during the illumination. Besides, the signals of O₂⁻ generated after illumination on Pt/BiVO₄ for 10 min are more obvious than those for BiVO₄ and RuO₂/BiVO₄. This might be explained by the fact that the Pt co-catalyst is efficient for transfer of the photo-generated electrons from BiVO₄ to the Pt surface, and then O₂⁻ can be readily formed. However, RuO₂/BiVO₄ is poor at producing O₂⁻, because RuO₂ does not transfer the

Table 1 Conversions and products of various sulfur-containing compounds in 3 h under visible light irradiation ($\lambda \geq 420\text{nm}$) on 0.03 wt% Pt–0.01 wt% RuO₂/BiVO₄ photocatalyst

Sulfur-containing compounds	structure	Conversion (%)	Main products detected
Thiophene		99.1	SO ₃ + CO ₂ + H ₂ O
2-Methylthiophene		92.3	SO ₃ + CO ₂ + H ₂ O
2,5-Dimethylthiophene		89.3	SO ₃ + CO ₂ + H ₂ O
Benzothiophene		72.0	
Dibenzothiophene		62.8	

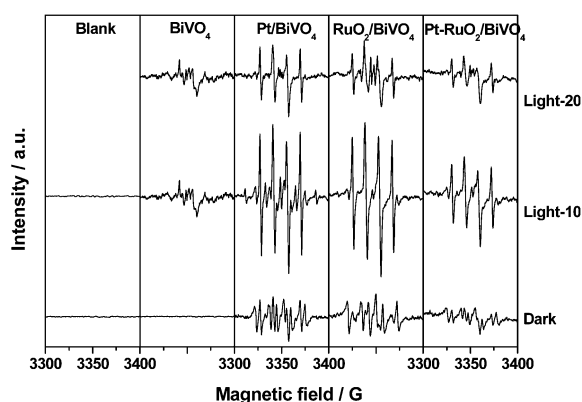
**Fig. 7** *In situ* ESR spectra of DMPO–O₂^{•-} and DMPO–OH generated in the photocatalytic oxidation reaction of thiophene with different photocatalysts. The sample tested without photocatalyst is denoted as “Blank”. The signals obtained without light irradiation are denoted as “Dark”. The signals obtained after irradiating for 10 min are denoted as “Light-10”, similarly, for 20 min named “Light-20”.

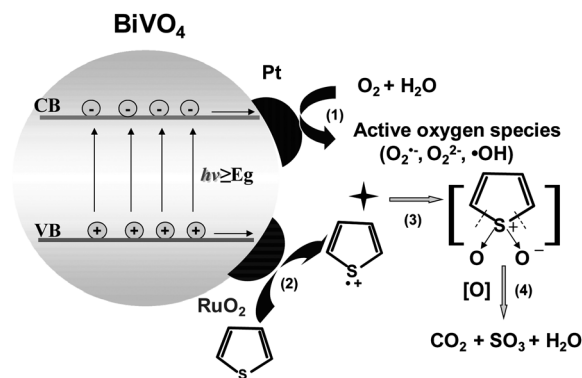
photo-generated electrons, instead transferring the holes. For Pt-RuO₂/BiVO₄, the simultaneous existence of Pt acting as a reduction co-catalyst and RuO₂ acting as an oxidation co-catalyst are beneficial for the efficient separation and transfer of the photo-excited electrons and holes respectively. The production of O₂^{•-} and photo-excited holes can be enhanced simultaneously, resulting in the high photocatalytic activity of thiophene oxidation.

A schematic description of the mechanism of photocatalytic oxidation of thiophene on Pt-RuO₂/BiVO₄ is shown in Scheme 1. After the efficient separation of the electron–hole promoted by the dual co-catalysts loaded on BiVO₄ under visible light irradiation, the adsorbed substrate (*e.g.* thiophene) can readily capture the photo-generated hole, a thermodynamically possible process, forming a radical cation C₄H₄S^{•+}.³ On the other side, a photo-generated electron transfers to O₂ via the Pt co-catalyst, where superoxide species O₂^{•-} is formed when O₂ reacts with the photo-generated electrons. O₂^{2•-}, which is the ESR-silent species, is also probably formed. Thus, the adsorbed oxygen acts as an electron trap, efficiently inhibiting electron–hole recombination.⁵² Then, OH (which has a strong oxidation ability) was

generated *via* the reaction of OH⁻ with a hole in the reaction system under illumination. Consequently, the activation of molecular oxygen and the thiophene molecule simultaneously takes place on the Pt-RuO₂/BiVO₄ catalyst. The interaction of the active oxygen species (O₂^{•-}, O₂^{2•-} and OH) with the photo-generated sulfur radical cations initiate a series of oxidation reactions. The synergistic effect of RuO₂ acting as an oxidation co-catalyst and Pt acting as a reduction co-catalyst is beneficial for the efficient separation and transfer of the photo-excited electrons and holes,^{53,54} being responsible for the high photocatalytic activity of thiophene oxidation.

4. Conclusions

The visible-light responsive photocatalyst BiVO₄ co-loaded with an ultra-low loading of Pt and RuO₂ (denoted as Pt-RuO₂/BiVO₄) can achieve over 99% conversion of thiophene oxidation under visible light irradiation using molecular oxygen as oxidant, and the dual co-catalysts Pt and RuO₂ show the strongly synergistic effect on the enhanced photocatalytic activity. The activation of molecular oxygen and thiophene molecule simultaneously takes place on the Pt-RuO₂/BiVO₄ catalyst for the thiophene oxidation reaction. The sulfur in sulfur-containing substrates can be oxidized to SO₃ for T, 2-MT and 2,5-DMT, and partially oxidized to the corresponding sulfones for BT and DBT. The results demonstrate that the co-existing oxidation and

**Scheme 1** Schematic description of the mechanism for the photocatalytic oxidation of thiophene on Pt-RuO₂/BiVO₄ photocatalyst.

reduction co-catalysts play a significant role in the photocatalytic oxidation reaction. The co-loading of oxidation and reduction co-catalysts will be crucial for developing highly active photocatalysts for photocatalytic reactions, in both solar energy conversion and environmental protection processes.

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