Decomposition of Carbon Disulfide Using Dielectric Barrier Discharge Plasma Coupled with Limonite and Siderite Supported Bismuth Vanadate Catalysts

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ABSTRACT

This paper presents the catalytic decomposition of CS₂ using dielectric barrier discharge plasma coupled with novel limonite or siderite supported BiVO₄ composite material (limonite/BiVO₄ or siderite/BiVO₄) prepared via a hydrothermal method. The crystalline structure, surface morphology, gas adsorption properties, and surface chemistry of the catalysts are characterized. The results show that BiVO₄ supported on the limonite or siderite is highly dispersible, which increases its active site. In addition, CS₂ decomposition efficiencies obtained using catalysts fabricated with various Fe/Bi ratios and calcination temperatures are experimentally evaluated. The result show that the maximum CS₂ decomposition efficiencies are obtained using catalysts calcined at 350°C with limonite/BiVO₄ and siderite/BiVO₄ mass ratios of 3:7, which respectively yield CS₂ decomposition efficiencies that are 11.9% and 13.2% greater than that obtained with dielectric barrier discharge treatment alone. The differences in the CS₂ decomposition efficiencies of the two types of supported catalysts may be due to the chemical and physical differences between limonite and siderite, including the oxidation states of iron and the surface morphology of the iron ores.

Keywords: Dielectric barrier discharge; Supported bismuth vanadate; Carbon disulfide; Catalytic decomposition.

INTRODUCTION

Carbon disulfide (CS₂) is an odorous sulfur compound that has been widely used as important feedstock in the rubber, metallurgy, and viscose fiber industries. However, CS₂ emissions promote photochemical reactions in the stratosphere that represent the primary source of acid rain, which can have harmful effects on the environment and public health (Bates et al., 1992; Tabari et al., 2017). Moreover, CS₂ exposure has been attributed to accelerated atherosclerosis and coronary artery disease (Price et al., 1997; Jia et al., 2017). Common methods of treating CS₂ emissions include adsorption, liquid absorption, condensation, thermo-decomposition, and plasma-based decomposition (Rojo et al., 2010; Pham et al., 2016; Laing et al., 2017). In recent years, plasma-based decomposition technology employing dielectric barrier discharge (DBD) has received considerable attention in the field of hazardous gas treatment due to its significant advantages over conventional CS₂ treatments, such as low cost and milder operation conditions, and reduced energy and material consumption (Rojo et al., 2010; Zhu et al., 2013; Albertos et al., 2017; Yang et al., 2017a). However, the decomposition processes in DBD plasma treatment often involve incomplete oxidation reactions, leading to the potential generation of toxic byproducts (Holzer et al., 2002; Li et al., 2017b). This can be addressed by combining plasma decomposition treatment with catalytic processes, which can also significantly improve the energy efficiencies and decomposition performances of the treatments (Krawczyk and Mlotek, 2001; Futamura, 2005; Liu and Liu, 2011; Vandenbroucke et al., 2011; Kirkpatrick et al., 2012). At present, bismuth vanadate (BiVO₄) supported catalysts have been widely used as excellent photocatalysts for waste gas degradation applications. However, the synergistic catalytic treatment of waste gases by combined BiVO₄-supported catalysts and DBD processes has not been widely studied. As such, it warrants additional attention.

BiVO₄ is a new type of photocatalyst that possesses a narrow band gap, good visible light absorption, and stable photo-corrosion resistance (Singh et al., 2016). In addition, BiVO₄ can be converted between three different crystal phases, including tetragonal zircon (z-t), monoclinic scheelite (s-m), and tetragonal scheelite (s-t). The z-t and s-m phases of BiVO₄ possess band gaps of 2.9 eV and 2.4 eV, respectively. As such, the z-t phase of BiVO₄ exhibits optical absorption bands in the ultraviolet (UV) region, while the s-m
phase exhibits strong optical absorption bands in both the UV and visible regions. This is consistent with the observation that the s-m phase exhibits the highest photocatalytic activity of the three crystalline phases of BiVO₄ (Liu et al., 2016). However, the photocatalytic activity of the s-m phase is limited by the relatively high recombination rate of electron-hole pairs generated in the photolytic process. This has been addressed in many studies by integrating BiVO₄ with supporting materials. For example, Li et al. (2015) and Cheng et al. (2018) prepared novel hetero-structured FeVO₄/BiVO₄ composites via a hydrothermal method, and revealed that the photocatalytic activities of the composites are significantly greater than those of either material alone. Chen et al. (2017a), Wang et al. (2017) and Xiao et al. (2018) developed a Cu/BiVO₄ composite photocatalyst that provided an increased photocatalytic activity relative to that of BiVO₄ alone under visible light irradiation. This was speculated to be due to the efficient separation of electron-hole pairs in Cu/BiVO₄. The previous studies have established that the photocatalytic activity of BiVO₄ is advantageously affected by various properties of the supporting materials, such as nanostructures, high surface area, and high chemical activity (Wang et al., 2017; Wang et al., 2019a, b). These properties are possessed by a number of naturally occurring mineral materials, particularly iron ores, that are widely available and inexpensive (Li et al., 2017a), and are therefore ideal supporting materials for enhancing the photocatalytic activity BiVO₄ for use in large-scale hazardous gas treatment applications.

Siderite (FeCO₃) is a traditional iron mineral resource used in steel smelting. China’s siderite resources, with reserves of 2 billion tons, are especially abundant. However, only 10% of the country’s siderite reserves have been utilized thus far (Xing et al., 2017; Huang et al., 2017). Limonite is widely present in the epigenetic oxidizing environment and one of the most important components of surface and biochemical activity in soils and sediments (Zou et al., 2013; Zhao et al., 2018).

The present study presents the catalytic decomposition of CS₂ using DBD plasma coupled with novel limonite (main component: FeO(OH)) and siderite (main component: FeCO₃) supported BiVO₄ composite catalysts prepared via a hydrothermal method. The catalysts are subjected to detailed characterization, including their crystalline structure, surface morphology, gas adsorption properties, and surface chemistry. The CS₂ decomposition efficiencies obtained using catalysts fabricated with various Bi/Fe ratios and calcination temperatures are experimentally evaluated. The results demonstrate that the optimum supported BiVO₄ catalysts obtain CS₂ decomposition efficiencies that are substantially greater than that obtained with non-catalyst DBD plasma treatment. The differences in the CS₂ decomposition efficiencies of the two types of supported catalysts are investigated based on the characterization results.

METHODS

Ores and Chemicals

We obtained limonite and siderite rock materials from Tongling mine, Anhui Province, China. The limonite mainly consists goethite, manganese oxides, and iron (III) oxide hydroxides (α-FeOOH), and bears a porous honeycomb structure generated via the weathering of crystals containing siderite and quartz (Zou et al., 2013). The siderite is formed of sedimentary hematite and metamorphic iron ore deposits, and includes a main fraction of FeCO₃ along with magnesium and manganese elements (Liang et al., 2015). After crushing, the ore was ground into a fine powder and sifted through a 200 mesh sieve. All chemicals were purchased from commercial sources, and were used without further purification. Copper acetate monohydrate, ethylenediamine, triethanolamine, hydrochloric acid, and nitric acid were purchased as analytical grade, and CS₂ and ethanol were purchased with a 99% purity.

Catalyst Preparation

Composite catalysts with limonite/BiVO₄ and siderite/BiVO₄ mass ratios of 1:9, 3:7, 5:5, 3:7, and 9:1 were synthesized via a previously reported hydrothermal method (Chen et al., 2018), filtered through 200 mesh sieves, and calcined at different temperatures of 250°C, 350°C, 450°C, and 550°C. The hydrothermal synthesis method employed can be briefly outlined as follows. Typically, Bi(NO₃)₃·5H₂O (2.43 g, 5.0 mmol) was added with stirring to an aqueous HNO₃ solution (15 mL, 2.0 mol L⁻¹). The specific iron ore material was then added in an amount based on the specific mass ratio. The mixture was stirred for 0.5 h, yielding Solution A. Solution B was obtained by dissolving NH₄VO₃ (0.58 g, 5.0 mmol) with stirring in the aqueous NaOH solution (15 mL, 2.0 mol L⁻¹). Solution B was slowly added to Solution A under vigorous stirring. The pH of the mixture was adjusted to 5 using an aqueous HCl solution (2 mol L⁻¹). The mixture was stirred for 0.5 h, and transferred to a stainless steel autoclave where it was heated at 180°C for 12 h. The mixture was filtered, and the solid component obtained was washed with distilled water and ethanol. The solid was then dried in a conventional oven at 80°C for 10 h, and calcined at different temperatures for 2 h in a muffle furnace to obtain limonite/BiVO₄ or siderite/BiVO₄ composite catalysts.

Characterization Methods

The crystallographic properties of the limonite/BiVO₄ and siderite/BiVO₄ composite catalysts were examined by X-ray diffraction (XRD) using a Shimadzu D/Max-rB automatic X-ray diffractometer in a 20 range of 3° to 70° in 3° min⁻¹. The specific surface areas, N₂ adsorption, and pore sizes of the catalysts were determined using the low temperature N₂ adsorption volumetric method conducted on a Rigaku D/max-2200/PC X-ray diffractometer with approximately 0.3 g of solid sample at a detection temperature of 30.4°C, a cold free space of 48.7 cm³, and a degas temperature of 160°C. Scanning electron microscopy (SEM) was conducted using a HITACHI SU-70 analytical ultra-high-resolution Schottky thermal field emission scanning electron microscope to analyze the surface microstructure of catalysts after calcination. The surface elements, oxidation states, and bonding environments of the calcined catalysts were analyzed using X-ray photoelectron spectroscopy (XPS).
conducted on a CasaXPS, and XPSPEAK41 was used to conduct peak analysis.

**Dielectric Barrier Discharge Plasma**

The plasma reactor employed in this study was the standard cylindrical type DBD reactor illustrated in Fig. 1(a). The DBD reactor was customized by the research team. The reactor included two coaxial fused quartz barriers. The outer barrier was a fused quartz tube with an outer diameter of 25 mm and a wall thickness of 1 mm. The inner barrier was a fused quartz tube with an outer diameter of 7 mm and a wall thickness of 1.5 mm. The length of the reactor was 180 mm. The inner electrode was a solid copper rod with a diameter of 3 mm. The outer electrode was composed of a 10 mm band of copper foil wrapped around the external side of the quartz glass tube forming the outer barrier, as shown in Fig. 1(a). The catalyst was first ground and filtered through a 100 mesh sieve, and 1.2 g of the sieved catalyst was mixed with absolute ethanol. The resulting slurry was then applied to the inner surface of an encasing tube and dried at 85°C in a conventional oven. The encasing tube had an outer diameter of 22 mm and a wall thickness of 1 mm, and was positioned coaxially between the inner and outer barriers of the DBD reactor, as illustrated in Fig. 1(b). Simulated flue gas containing a 2000 mg m^{-3} concentration of CS_{2} in air as a carrier gas was input at a rate of 0.54 m^{3} h^{-1} in the space between the outer and inner barriers in contact with the tubes containing the packed catalyst. The contact area between the catalyst and the flue gas was increased by fabricating the encasing tube with 6 rows of parallel needle-like pyramids placed inside the inner surface of the encasing tube, as shown in Fig. 1(b).

**Analysis of CS_{2} Treatment**

The performance of the proposed CS_{2} treatment was evaluated via the decomposition efficiency \( \eta \), which is the percentage change in the initial concentration of CS_{2} (\( C_0 \); mg m^{-3}) in the simulated flue gas and the concentration of CS_{2} in the simulated flue gas after treatment (\( C_1 \); mg m^{-3}), and is given as follows:

\[
\eta = \frac{C_0 - C_1}{C_0} \times 100\%
\]  

where \( C \) is the concentration of CS_{2} in the gas to be measured (mg m^{-3}), \( m \) is the mass of CS_{2} dissolved in the sample solution (mg), \( v_1 \) is the total volume of sample solution (mL), \( v_2 \) is the volume of sample solution used in analysis (mL), and \( v_n \) is the volume of the gas sample under standard conditions (m^{3}), which refers to the China GBT 14680-1993 standard: Air quality - Determination of carbon disulfide - Diethylamine spectrophotometric method.

**Effect of Catalyst Adsorption of CS_{2} on Catalytic Performance**

The value of \( C_1 \) can be decreased without decomposition by the adsorption of CS_{2} on the catalyst. Therefore, we first conducted control experiments to determine the amount of CS_{2} adsorbed on the catalyst over time, and thereby evaluate its effect on the overall catalytic performance. To this end, limonite/BiVO_{4} (1.2 g, 5:5) and siderite/BiVO_{4} (1.2 g, 5:5) composite catalysts calcined at 350°C were individually loaded into the reactor, and the values of \( C_1 \) were measured without DBD plasma at different buffer times of 5, 10, 20, 30, 40, and 50 min, and the results compared with \( C_0 \).

**Effect of Mass Ratio on the Decomposition Efficiency of CS_{2}**

The values of \( \eta \) obtained for the different limonite/BiVO_{4} and siderite/BiVO_{4} mass ratios of both limonite/BiVO_{4} and siderite/BiVO_{4} were evaluated at the different calcination temperatures. Each catalyst was prepared with five limonite/BiVO_{4} or siderite/BiVO_{4} mass ratios and four calcination temperatures, for a total of 20 samples, and three replicates of each sample were tested. The DBD plasma power output was controlled by adjusting the DBD voltage between the outer and inner electrodes in the range of 5.0 kV to 9.0 kV.

**Effect of Calcination Temperature on the Decomposition Efficiency of CS_{2}**

The values of \( \eta \) obtained with both the limonite/BiVO_{4} and siderite/BiVO_{4} catalysts calcined at different temperatures were evaluated for limonite/BiVO_{4} and siderite/BiVO_{4} mass ratios of 3:7. The DBD voltage was controlled at 6.0 kV.

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**Fig. 1.** Schematic diagrams of the dielectric barrier discharge (DBD) plasma reactor setup: (a) cylindrical DBD reactor; (b) catalyst loading structure.
**Analysis of Exhaust Gas**

Qualitative analysis of the tail gas obtained from three CS2 treatment systems: DBD alone, DBD cooperating with limonite/BiVO4 (mass ratio of 3:7), and DBD cooperating with siderite/BiVO4 (mass ratio 3:7), was conducted by Fourier transform infrared (FTIR) spectroscopy using a Bruker Vertex 70 spectrometer (Germany). The three CS2 treatment systems were all implemented under the conditions of a 200 mg m–3 CS2 concentration mixed in air, a 0.54 m 3 h–1 intake flow rate, and a DBD voltage adjusted from 5000 V to 9000 V.

Formaldehyde absorption-pararosaniline spectrophotometry (China standard HJ 482-2009) was used to measure the SO2 concentration in the tail gas, and the standard curve was $y = 0.0234x - 0.0067$ and $R^2 = 0.9991$. The concentration of COS was determined indirectly by spectrophotometry, and the standard curve was $y = 0.0102x - 0.002$ and $R^2 = 0.9954$. The concentrations of CO and CO2 were determined by infrared spectroscopy.

**RESULTS AND DISCUSSION**

**XRD Analysis**

The XRD patterns of limonite/BiVO4 and siderite/BiVO4 composite catalysts calcined at 350°C with different limonite/BiVO4 and siderite/BiVO4 mass ratios are shown in Figs. 2(a) and 2(b), respectively. The primary reflections for the limonite/BiVO4 catalysts in Fig. 2(a) are at 2θ values of 19.8°, 29.2°, and 30.5°. The degree of crystallinity (i.e., the grain size) of a sample can generally be gauged according to the intensity and sharpness (i.e., the full width at half maximum; FWHM) of reflections, where the degree of crystallinity increases with increasing intensity and decreasing FWHM. Analysis of the reflections intensities indicates that the highest intensity reflections with the greater FWHM values were obtained at a limonite/BiVO4 mass ratio of 3:7, which suggests that the best crystal growth was obtained at this ratio and the BiVO4 was uniformly distributed at the surface of the limonite support (Zhao et al., 2015). The primary reflections for the siderite/BiVO4 catalysts in Fig. 2(b) are at 20 values of 19.4°, 29.8°, and 32.6°. The increase in the reflections intensity and FWHM of the XRD reflections obtained at 20 values of 19.4°, 29.8°, and 32.6° with increasing BiVO4 content indicates that the BiVO4 is uniformly distributed on the siderite support (Chala et al., 2014).

**BET Surface Area, N2 Adsorption, and Pore Size**

The N2 adsorption-desorption isotherm diagrams of the limonite/BiVO4 and siderite/BiVO4 catalysts calcined at 350°C for limonite/BiVO4 and siderite/BiVO4 mass ratios of 3:7 are given in Figs. 3(a) and 3(c), respectively, while the corresponding pore size distributions are presented in Figs. 3(b) and 3(d), respectively. These diagrams are also presented in Fig. 3 for the limonite and siderite support materials. The specific surface areas and pore sizes of the supports and catalysts are listed in Table 1. Figs. 3(a) and 3(c) indicate that all supports and catalysts exhibit type III isotherms with H3 hysteresis loops, suggesting mesoporous structures with pore diameters in the range of 2–50 nm (Chen et al., 2017b). At low relative pressures, N2 is adsorbed and concentrated on the surface, and capillary condensation occurs within the pores as the relative pressure increases, which yields curves with sharply increasing slopes and hysteresis loops in the diagrams. This indicates that the combination of BiVO4 and limonite or siderite to form composites increased the pore diameter relative to the supports alone. Figs. 3(b) and 3(d) indicate that the pore diameters of the supports and catalysts are between 2.0 nm and 10 nm, which confirms that these materials have mesoporous structures. As shown in Table 1, both limonite/BiVO4 and siderite/BiVO4 exhibited greater specific surface areas and pore volumes than the corresponding support materials. This indicates that BiVO4 loading altered the pore structure of limonite and siderite, and increased the surface area, and thus increased the concentration of active sites.

![Fig. 2. X-ray diffraction spectra of the composite catalysts calcined at 350°C with different limonite/BiVO4 and siderite/BiVO4 mass ratios: (a) limonite/BiVO4; (b) siderite/BiVO4.](image-url)
Fig. 3. N\textsubscript{2} adsorption-desorption isotherm diagrams (a) and (c), and pore size distributions (b) and (d) of limonite and siderite supports and limonite/BiVO\textsubscript{4} and siderite/BiVO\textsubscript{4} catalysts calcined at 350°C with limonite/BiVO\textsubscript{4} and siderite/BiVO\textsubscript{4} mass ratios of 3:7.

Table 1. Specific surface areas and pore sizes of different iron ore supports and composite catalysts with limonite/BiVO\textsubscript{4} and siderite/BiVO\textsubscript{4} mass ratios of 3:7.

| Sample            | Specific surface area (m\textsuperscript{2} g\textsuperscript{-1}) | Pore volume (\times10\textsuperscript{-2} cm\textsuperscript{3} g\textsuperscript{-1}) | Pore diameter (nm) |
|-------------------|---------------------------------------------------------------|---------------------------------|-------------------|
| Limonite          | 35.25                                                         | 9.98                            | 3.818             |
| Limonite/BiVO\textsubscript{4} | 48.46                                                        | 13.28                           | 3.830             |
| Siderite          | 3.55                                                          | 0.82                            | 3.826             |
| Siderite/BiVO\textsubscript{4} | 10.67                                                        | 2.94                            | 3.818             |

TG-DTG

The differential thermogravimetric (DTG) and thermogravimetric (TG) curves of siderite in a N\textsubscript{2} atmosphere are shown in Fig. 4. Four major mass change steps between 30 and 800°C are apparent in the TG curve. Combination of the DTG and TG curve data reveals that the mass step changes can be attributed to different reasons. The mass loss occurring between 30 and 277.40°C (1.345%); as observed in the DTG curve is due to the conversion of goethite into hematite caused by dehydroxylation (Xing et al., 2017). The mass gain occurring between 277.40 and 469.12°C (2.078%) is due to the oxidation of FeO to CO\textsubscript{2} in N\textsubscript{2} prior to the decomposition of the siderite. The mass loss occurring between 469.12 and 673.96°C (14.94%) is attributed to the conversion of siderite into Fe\textsubscript{3}O\textsubscript{4} which releases a large amount of CO. Finally, the mass loss between 673.96 and 800°C (1.249%) is due to the thermal decomposition of residual structural hydroxyl groups. TG analysis indicates that goethite is present in fresh siderite samples.
**SEM**

Figs. 5 and 6 respectively present SEM images of limonite/BiVO₄ and siderite/BiVO₄ catalysts calcined at 350°C with limonite/BiVO₄ and siderite/BiVO₄ mass ratios of 3:7 (a–c) and 5:5 (d–f). It can be observed from Fig. 5(c) that the limonite surface in the limonite/BiVO₄ catalyst (mass ratio of 3:7) was covered by a smooth layer, and a partially petal shaped morphology is observed, which further suggests that BiVO₄ was uniformly distributed on the limonite surface. The SEM images of the limonite/BiVO₄ catalyst (mass ratio of 5:5) exhibit similar morphologies as those observed for the limonite/BiVO₄ (3:7) catalyst. However, a comparison of Figs. 5(a) and 5(d) suggests that the 3:7 catalyst provides a greater surface area with smoother surfaces and more irregular shapes than the 5:5 catalyst. This may promote interaction between gas precursors and BiVO₄ catalysts on iron ore supports. This can be expected to facilitate the interactions of more BiVO₄ catalyst loaded to iron ore support (Guan et al., 2010). In addition, comparison of Figs. 5(a) and 5(d) indicates that the 5:5 catalyst presents a different local stacking morphology than the 3:7 catalyst, which suggests the presence of some impurities in the limonite support material. Similar results are observed for the siderite/BiVO₄ catalysts in Fig. 6. Smooth spherical particles are again observed on the siderite surface in Fig. 6(c), suggesting that BiVO₄ was uniformly distributed on the siderite surface (Yu et al., 2014). However, aggregations of spherical particles with high intensity detected electron signals are observed in Figs. 6(d) and 6(e), which are indicative of BiVO₄ catalyst aggregations at a mass ratio of 5:5. Overall, the SEM images indicate that both limonite/BiVO₄ and siderite/BiVO₄ composite catalysts exhibit better BiVO₄ distributions for a mass ratio of 3:7.

**XPS**

The XPS survey scan spectra of the limonite and siderite supports calcined at 350°C indicate the existence of O, Fe, and C elements, while O, Fe, C, V, and Bi elements were detected in the limonite/BiVO₄ and siderite/BiVO₄ composite catalysts with mass ratios of 3:7 calcined at 350°C high

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**Fig. 4.** Thermal gravimetric analysis of siderite.

**Fig. 5.** Scanning electron microscopy images of limonite/BiVO₄ catalysts calcined at 350°C for different limonite/BiVO₄ mass ratios: (a), (b), and (c) 3:7 with magnifications of 100000, 250000, and 500000 times, respectively; (d), (e), and (f) 5:5 with magnifications of 100000, 250000, and 500000 times, respectively.
Fig. 6. Scanning electron microscopy images of siderite/BiVO₄ catalysts calcined at 350°C for different siderite/BiVO₄ mass ratios: (a), (b), and (c) 3:7 with magnifications of 100000, 250000, and 500000 times, respectively; (d) and (e) 5:5 with magnifications of 500000 and 250000 times, respectively.

resolution Fe 2p spectra are presented in Fig. 7(a) for limonite/BiVO₄ (top) and limonite (bottom), and the Bi 4f spectrum for limonite/BiVO₄ is presented in Fig. 7(b). The spectra in Fig. 7(a) are fitted, and the binding energies of the Fe 2p3/2 and Fe 2p1/2 electron states are labeled. Comparison of the fitted Fe 2p spectra of limonite/BiVO₄ and limonite indicates that combining the support with BiVO₄ increases the binding energy of Fe, suggesting that the introduction of BiVO₄ altered the electron density of the Fe sites (Liu et al., 2017). Similarly, high resolution Fe 2p spectra are presented and fitted in Fig. 6(c) for siderite/BiVO₄ (top) and siderite (bottom), and the Bi 4f spectrum for siderite/BiVO₄ is presented and fitted in Fig. 6(d). The two major peaks obtained for the siderite/BiVO₄ catalyst at 708.7 eV and 722.5 eV corresponding to Fe 2p3/2 and Fe 2p1/2 electron states are consistent with the Fe³⁺ oxidation state (Ji et al., 2015). However, in this case, combining the siderite support with BiVO₄ very slightly decreased the binding energies of the Fe 2p3/2 and Fe 2p1/2 electron states. This may lead to a greater electron deficiency and a stronger reduction ability (Yang et al., 2017b). The binding energy of 156.6 eV assigned to the Bi 4f electron state of limonite/BiVO₄ in Fig. 7(b) is consistent with the Bi³⁺ oxidation state (Kong et al., 2013), while the binding energy of 162 eV assigned to the Bi 4f electron state suggests a higher oxidation state of Bi⁵⁺ (Huang et al., 2010). It can be observed that in the high resolution XPS spectrum of limonite/BiVO₄ overlap with some shoulder peaks indicative of varying chemical environments for the Bi sites (Lamdab et al., 2016). In contrast, the binding energies of the Bi 4f electron states of siderite/BiVO₄ exhibited no overlapping shoulder peaks. The appearance of overlapping shoulder peaks in Fig. 7(b) may be the result of impurities in the naturally occurring limonite. Here, we note that the collected limonite exhibited a lower purity than the siderite, and thus impurity elements may affect the binding energies of the Bi 4f electron states after forming the limonite/BiVO₄ composite catalysts.

Adsorption Equilibrium of CS₂ Absorbed by Limonite/BiVO₄ and Siderite/BiVO₄ Catalysts without DBD

The CS₂ concentration change over time obtained in the CS₂ adsorption control experiments are plotted in Fig. S1. These results indicate that the CS₂ concentration in reactions involving both the limonite/BiVO₄ and siderite/BiVO₄ catalysts reached equilibrium inside the reactor after a buffer time of 30 min. Therefore, all further research conducted in conjunction with plasma discharge was conducted after a 30 min pre-equilibrium period.

Effect of Mass Ratio on CS₂ Decomposition Efficiency

The values of η obtained as a function of DBD voltage for DBD plasma treatment alone and for coupled DBD plasma treatment with the limonite/BiVO₄ and siderite/BiVO₄ catalysts calcined at 350°C with different limonite/BiVO₄ and siderite/BiVO₄ mass ratios are shown in Figs. 8(a) and 8(b), respectively. The differences between the values of η obtained in the coupled and non-coupled treatments were
greatest for a DBD voltage of 6.0 kV. Compared with DBD plasma treatment alone, the maximum increases in $\eta$ obtained with DBD plasma coupled with the limonite/BiVO$_4$ catalysts were 8.1%, 11.9%, 5.6%, 5.7%, and 3.7% for mass ratios of 1:9, 3:7, 5:5, 3:7, and 9:1, respectively. Similarly, the maximum increases in $\eta$ obtained with DBD plasma coupled with the limonite/BiVO$_4$ catalysts were 8.6%, 13.2%, 6.1%, 4.4%, and 4.1% for mass ratios of 1:9, 3:7, 5:5, 3:7, and 9:1, respectively.

We also note from Fig. 8 that value of $\eta$ increased with increasing BiVO$_4$ content up to a maximum at the mass ratio of 3:7, which provided the best value of $\eta$ at any DBD voltage for both limonite/BiVO$_4$ and siderite/BiVO$_4$ catalysts, and then decreased for a mass ratio of 9:1. This can be explained according to the distribution of the BiVO$_4$ catalyst. An appropriate mass ratio can ensure that BiVO$_4$ is uniformly distributed over the supporting materials (Huang et al., 2015). A low BiVO$_4$ content facilitates the equal distribution of BiVO$_4$ over the available active sites, and more surface becomes covered with an equal distribution of BiVO$_4$ as the BiVO$_4$ content increases. However, with further increasing BiVO$_4$ content greater than a mass ratio of 3:7, excess BiVO$_4$ is stacked on the surfaces of the support materials, which covers the catalytic active site and decreases the decomposition efficiency (Sriwichai et al., 2014). In addition, the band gaps of the limonite and siderite supports can affect the decomposition efficiency. Here, limonite and siderite possess narrow band gaps, which can facilitate the transfer of electrons and holes from the conduction and valance bands of BiVO$_4$, and thereby inhibit the annihilation of electron-hole pairs within BiVO$_4$ (Wang et al., 2016; Wang et al., 2017; Xia et al., 2017).

The results in Fig. 8 can be included with the results shown in Figs. S2 and S3 to compare the values of $\eta$ obtained as a function of DBD voltage for DBD plasma treatment alone and for coupled DBD plasma treatment with the limonite/BiVO$_4$ and siderite/BiVO$_4$ catalysts with different mass ratios under calcination temperatures of 250°C, 350°C (Fig. 7), 450°C, and 550°C. We note that the variations in $\eta$ with respect to the DBD voltage for the
Fig. 8. CS₂ decomposition efficiency ($\eta$) for catalysts calcined at 350°C with different limonite/BiVO₄ and siderite/BiVO₄ mass ratios: (a) limonite/BiVO₄; (b) siderite/BiVO₄.

different calcination temperatures represent similar trends as those obtained at 350°C in Fig. 7.

**Effect of Calcination Temperature on CS₂ Decomposition Efficiency**

Fig. 9 presents the increases in the values of $\eta$ compared with DBD treatment alone obtained for coupled DBD plasma treatment at a DBD voltage of 6.0 kV using the limonite/BiVO₄ and siderite/BiVO₄ catalysts with a mass ratio of 3:7 under different calcination temperatures. Here, we note that the increases in the values of $\eta$ first increased with increasing calcination temperature, and then decreased after reaching peak performance at 350°C for both catalysts. This trend can be related to changes in the crystal structure of the catalysts at different calcination temperatures. The optimal calcination temperature of BiVO₄ lies between 300°C and 400°C, although the higher temperature in this range can lead to changes in the crystal morphology (Zhao et al., 2012; Yuan et al., 2015; Xia et al., 2017). The limonite and siderite support materials, as well as the composites, also suffer from disadvantageous changes in the surface area and pore size under higher calcination temperatures owing to pore space collapse and BiVO₄ catalyst aggregation, resulting in decreased catalytic performance (Liu and Zhou, 2015).

**Comparison of CS₂ Treatment Involving Limonite and Siderite Supports**

The values of $\eta$ obtained as a function of DBD voltage in Fig. 8 for DBD plasma treatment alone and for coupled DBD plasma treatment with the limonite/BiVO₄ and siderite/BiVO₄ catalysts calcined at 350°C with a mass ratio of 3:7 are presented in Fig. S4 to facilitate detailed comparison. Compared with DBD plasma treatment alone at a DBD voltage of 6.0 kV, coupled DBD plasma treatment with the siderite/BiVO₄ catalyst increased the value of $\eta$ by 13.2%, while coupled DBD plasma treatment with the limonite/BiVO₄ catalyst increased the value of $\eta$ by 11.9%. This small difference could be due to the structural and compositional differences between limonite and siderite. The results of additional experiments being conducted presently to study the effect of catalyst structure and composition on CS₂ decomposition performance will be reported in the future.

**Analysis of Exhaust Gas**

The exhaust gas FTIR spectrum is shown in Fig. 10. Here, the peak at 1373 cm⁻¹ represents S=O bond stretching vibrations (Rudakova et al., 2003), indicating that the substance is SO₂, the peak at 2345 cm⁻¹ represents C=O bond stretching vibrations, indicating that the substance is CO₂, the peak at 2100 cm⁻¹ represents C and O triple bond stretching vibrations (Chen et al., 2007), indicating that the substance is CO, the peak near 2084 cm⁻¹ represents stretching vibrations for the C=O bond of COS (Yan et al., 2013), and the peak at 1015 cm⁻¹ is an O₃ absorption peak, indicating that the intermediate products of CS₂ degradation are SO₂, CO, CO₂, and COS.

Fig. 11 shows that the concentrations of SO₂, CO, CO₂, and COS in the exhaust gas for all treatments increase with increasing DBD voltage. Here, CS₂ receives energy in the process of reactor discharge, and is stimulated to produce intermediate products, such as CS*, active group O₃, OH, and O₂. These intermediate products can then form additional products, where CS* and O₂ can produce SO₂, S and O₂ can produce SO and then react with O₂ to produce SO₂, CS and O₂ can produce COS and O, and O reacts with SO₂ to
produce CO and CO₂. An increasing concentration of CS and active groups O, O₂, and O₃ are generated with increasing DBD voltage, resulting in the production of increased concentrations of SO₂, COS, and carbon oxides. The concentrations of SO₂, CO, and COS in the tail gas of the DBD combined with catalyst treatments are less than those obtained by DBD treatment alone, but the concentration of CO₂ is greater than that obtained by DBD treatment alone. Under a DBD voltage of 9000 V, the concentrations of SO₂, CO, COS, and CO₂ in the tail gas obtained for DBD treatment alone were 121.4 mg m⁻³, 106.3 mg m⁻³, 62.7 mg m⁻³, and 80.5 mg m⁻³, respectively, while these were 104.7 mg m⁻³, 89.0 mg m⁻³, 56.1 mg m⁻³, and 100.9 mg m⁻³, respectively, under the DBD cooperating with limonite/BiVO₄ (mass ratio 3:7) treatment, and 87.1 mg m⁻³, 81.9 mg m⁻³, 49.6 mg m⁻³, and 103.6 mg m⁻³, respectively, under the DBD cooperating with siderite/BiVO₄ (mass ratio of 3:7) treatment. Therefore, compared with DBD cooperating with limonite/BiVO₄, DBD cooperating with siderite/BiVO₄ produced a greater concentration of CO₂, and smaller concentrations of SO₂, CO, and COS.

Comparison with Other CS₂ Treatments

Compared with a previously reported coupled DBD plasma MnO₂ catalytic CS₂ treatment system, the proposed coupled DBD CS₂ treatment system employing limonite/BiVO₄ and
Fig. 11. Changes in SO$_2$, COS, CO$_2$, and CO concentrations in the tail gas under different DBD voltage treatments: (a) SO$_2$; (b) COS; (c) CO$_2$; (d) CO.

Siderite/BiVO$_4$ catalysts calcined at 350°C with a mass ratio of 3:7 exhibited $\eta$ values that were around 5% greater under equivalent reaction conditions. This could due to the close energy band interactions of the BiVO$_4$ photocatalyst with the supporting iron ore materials that prolonged the lifetime of the activated oxygen species by inhibiting the annihilation of electron-hole pairs within BiVO$_4$. The CS$_2$ decomposition efficiency is also enhanced relative to that of the MnO$_2$ catalytic system by the high surface area and better porous structure of the supporting materials, which facilitates the equal distribution of catalytic active sites.

CONCLUSIONS

This study developed an efficient CS$_2$ decomposition method based on DBD plasma coupled with a novel BiVO$_4$ photocatalyst supported by a limonite (FeO(OH)) or siderite (FeCO$_3$) iron ore material. The catalyst was synthesized via a hydrothermal method. The effects of the limonite/BiVO$_4$ and siderite/BiVO$_4$ mass ratios and calcination temperature on the CS$_2$ decomposition efficiency of DBD plasma coupled with the limonite/BiVO$_4$ and siderite/BiVO$_4$ composite catalysts were experimentally investigated using a standard DBD plasma reactor. The optimum composition for both composite catalysts was obtained at a calcination temperature of 350°C with limonite/BiVO$_4$ and siderite/BiVO$_4$ mass ratios of 3:7. The results of DBD plasma coupled with the optimum limonite/BiVO$_4$ and siderite/BiVO$_4$ composite catalysts demonstrated increased CS$_2$ decomposition efficiencies of 11.9% and 13.2%, respectively, relative to that of DBD plasma alone. The slightly better performance of the siderite/BiVO$_4$ composite catalyst than limonite/BiVO$_4$ could be due to the composition of the limonite and siderite iron ores. The main components of the tail gas after DBD synergistic catalytic treatment of CS$_2$ were SO$_2$, COS, CO, and CO$_2$. The catalyst can increase the oxidizing species of the discharge system, and ensure the more thorough oxidation of SO$_2$ and COS, resulting in smaller concentrations of SO$_2$, COS, and CO, and greater concentrations of CO$_2$ in the tail gas. Future study will focus on how minor elements and the
morphology of the supporting materials affect the CS₂ decomposition efficiency of the composite catalysts.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

DISCLAIMER

The authors declare no competing financial interest.

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