Development of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ /Montmorillonite nanocomposite as efficient catalyst for photocatalytic desulfurization

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Abstract

A novel $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ /Montmorillonite (MMT) nanocomposite was prepared by one-pot hydrothermal method. XRD, TEM, Raman, UV-vis, FT-IR, PL and XPS were employed to characterize the nanocomposites. The photocatalytic desulfurization properties of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ /MMT nanocomposites were performed by oxidizing dibenzothiophene (DBT) in the model oil under visible light irradiation. Results indicate that the molar fraction of Mo doping has critical impact on the desulfurization rate. Adequate Mo doping may form well-defined “solid solution/co-precipitation” heterostructure of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{Bi}_2\text{MoO}_6$, which enhances the visible light absorption efficiency and promotes the

separation rate of photogenerated electron-hole pairs, thus leads to the improved photocatalytic desulfurization performance. The desulfurization rate of the model oil can reach 95% when the molar fraction x is 0.7 under visible light irradiation for 3 h.

Keywords: Clay; Bi_2WO_6 ; Heterostructure; Nanocomposite; Photocatalysis; Desulfurization

1. Introduction

Atmospheric haze, acid rain and other environmental issues have strong association with SO_x , a product of combustion of sulfur compounds existing in fuels. It is therefore essential to develop technologies for deep desulfurization of fuels [1, 2]. As a conventional method, hydrodesulfurization (HDS) has been extensively applied to remove sulfur-containing substances. However, high temperature and pressure as well as expensive hydrogen are needed in the process of HDS [3-5]. Meanwhile, it is difficult for HDS to satisfy the demands of deep desulfurization because of the stability of DBT and derivatives [6]. For instance, 4, 6-dimethyl dibenzothiophene (4, 6-DMDBT) is hard to be abated under hydrogenation [7-9]. To save energy and cost, extractive desulfurization [10], biodesulfurization [11], adsorptive desulfurization [12] and oxidative desulfurization [13, 14] have been employed to remove sulfur compounds from model oil in the last few years. In

particular as one of the most cheap and efficient desulfurization strategy, photocatalytic oxidative desulfurization has drawn much attention. Lu et al. [15] prepared $\text{CeO}_2/\text{TiO}_2$ nanotube arrays by anodization combined with microwave synthesis and found that over 90% of benzothiophene could be removed under visible light irradiation. Mandizadeh et al. [16] obtained BaFe_2O_4 by hydrothermal method demonstrating that the removal of dibenzothiophene by photocatalytic oxidative desulfurization reached as high as 96.6%.

Nevertheless, developing cost-effective and more efficient visible light photocatalytic material for the abatement of sulfur compounds remains as an imperative challenge. Layered Bi_2WO_6 has excellent chemical and thermal stability [17, 18]. However, its low absorption rate of sunlight and high recombination of photogenerated carriers greatly impede its photocatalytic performance [19]. In most cases, Bi_2WO_6 is used in combination with other semiconductors in order to solve the above drawbacks. For instance, Zhang et al. [20] synthesized $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ composites which were in favor of accelerating the separation of photogenerated carriers thus enhancing the photocatalytic activity. Liu et al. [21] fabricated $\text{ZnO}/\text{Bi}_2\text{WO}_6$ composites which prevented the recombination of electron-holes. Bi_2MoO_6 is a layer-structured material which possesses narrower band gap than its analogous counterpart Bi_2WO_6 [22]. It is reported that Bi_2WO_6 and

Bi_2MoO_6 may form coherent nanocomposite to improve the photocatalytic performance due to the fact that the $\text{Bi}_2\text{Mo}_x\text{W}_{1-x}\text{O}_6$ heterojunction structure formed by two-step heating treatment improves the separation of photogenerated carriers, and narrows the band gap [23]. This paper reports, for the first time to the best of our knowledge, the photocatalytic oxidative enhancement of the resulting compound through the incorporation of Mo into Bi_2WO_6 .

Moreover, the agglomeration of nanoparticles often occurs during the synthetic progress. The adsorption property of support may largely address the above problem. For instance, we have previously prepared attapulgite- $\text{CeO}_2/\text{MoS}_2$ ternary composite for photocatalytic oxidative desulfurization of model oil [24]. Except for attapulgite, plenty of other supports have been researched, including graphene, clay minerals, zeolites [25-27] etc. As a typical layered clay minerals, MMT possesses large surface area and chemical stability, which are adopted to control particle size and avoid particle agglomeration [28, 29]. Wu et al. [30] prepared CaO_2 -MMT nanocomposites and found that the CaO_2 particles were well dispersed on the surface of MMT with the average size around 10 nm.

Herein, in this work, we synthesize $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ composite photocatalysts via a one-pot hydrothermal method in an attempt to form $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{Bi}_2\text{MoO}_6$ heterostructure by rational tuning the doping

fraction of Mo. The visible light absorption range is anticipated to be extended, and the recombination of photogenerated carriers is expected to be prohibited. The molar fraction of Mo doping influencing the photocatalytic oxidative desulfurization performance is investigated by degrading DBT in the model oil.

2. Experimental section

2.1 Materials

Bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was obtained from Medicine Group Chemical Reagent Co., Ltd. Sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), Sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) and hydrogen peroxide (H_2O_2) were afforded by Lingfeng Chemical Co., Ltd. DBT($\text{C}_{12}\text{H}_8\text{S}$) was purchased from Aladdin Bio-Chem Technology Co., Ltd. N-N dimethyl formamide (DMF, $\text{HCON}(\text{CH}_3)_2$) and octane (C_8H_{18}) were obtained from Shengqiang Chemical Co., Ltd.

2.2 Synthesis of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$

$\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ samples were prepared via a one-pot hydrothermal method. In a representative reaction, 2 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 2 mmol $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ with W/Mo molar fractions of 9/1, 8/2, 7/3, 6/4, 5/5, 4/6, 3/7, 2/8 and 1/9 were dissolved into 15 mL deionized water with magnetic stirring. 1 g MMT was dissolved into 20 mL deionized water. Whereafter, the above

solutions were transferred into a 100 mL Teflon-lined stainless steel autoclave, and held at 180°C for 24 h. Then the products were washed several times by deionized water and ethanol, and subsequently dried at 80°C for 12 h.

2.3 Materials characterization

The powder X-ray diffraction (XRD) was characterized with a D/max 2500PC diffractometer radiated by Cu K α under room temperature. Tube voltage and current were 40 kV and 100 mA, continuous scanning speed was 6°/min, scanning speed was 0.02°/s, and scan range was 5-80°. The morphology and size of grain were observed by a JEM-2100 transmission electron microscope (TEM) equipped with Gatan 832 CCD operating at a voltage of 200 kV. Ultraviolet visible diffuse reflectance spectra (UV-vis DRS) were obtained using a UV-2500 Shimadzu UV-vis spectrophotometer with scanning range from 200 nm-800 nm. Raman spectra were measured with a Renishaw spectrometer, and the excitation wavelength was 514 nm. FT-IR spectra were obtained with a Nicolet vatar370 with scanning wavelength range from 500 cm⁻¹ to 4000 cm⁻¹. The photoluminescence (PL) spectra were collected with a PerkinElmer LS45 at room temperature. The X-ray photoelectron spectroscopy (XPS) characterization was performed with a PerkinElmer PHI 5300 XPS spectrometer equipped with Mg K α under a position of 284.6 eV for C 1s.

2.4 Photocatalytic desulfurization

The desulfurization process of model oil was carried out by a visible light catalytic reaction apparatus equipped with a 300 W xenon lamp as simulative sunlight source to verify that only irradiated by visible light without any wavelengths shorter than 420 nm. The model oil with sulfur content of 200 ppm was prepared by dissolving 0.4031 g DBT into 500 mL of octane. Then adequate amount of catalyst were added to the above solution, and then transferred into the apparatus. The photocatalytic desulfurization reaction was performed in the dark with constant magnetic stirring for 30 min firstly. 30 wt% H₂O₂ was added to the mixture (the optimal S/O molar ratio was 1:4). Subsequently, the reaction system was irradiated by 300 W xenon lamp. The degraded samples were collected twice an hour, then DMF was added into the samples to extract the supernatant liquid. Eventually, the top layer model oil was collected, which was used to detect sulfur content with a sulfur determinator (THA2000S), and the desulfurization rate D was measured in accordance with the following formula:

$$D = (1 - C/C_0) \times 100\%$$

where C₀ and C are the initial and the final sulfur content, respectively.

3. Results and discussion

3.1 XRD analysis

Fig.1 states the XRD patterns of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ and MMT. The diffraction peaks at 5.64° and 22.3° are assigned to (001) and (110) (JCPDS 50-1496) of pure MMT. As can be seen, reflection observed at 28.3° , 32.5° , 47.5° and 56.1° corresponds to the natural diffraction of the (131), (200), (026) and (313) planes of the pure Bi_2WO_6 (JCPDS 79-2381) [31]. The high and sharp diffraction peak shows well-defined crystallinity. It is worth mentioning that the product may form solid solution phase when x is less than 0.5, however with further increasing content of Mo doping, four diffraction peaks assigned to (131), (002), (060), (331) of the plane of Bi_2MoO_6 in the composite appear at 28.6° , 32.3° , 33.1° , 47.2° . It is noticed that the (131) peak of Bi_2WO_6 at 28.3° shifts to lower angle with increasing of Mo doping, which may be due to the substitution of Mo for Bi_2WO_6 , leading to the lattice distortion and more structural defects.

Fig.1. XRD patterns of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ with various molar fractions

3.2 Raman analysis

The Raman spectra of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ with various molar fractions of Mo are observed in Fig.2. The band located at 170 cm^{-1} is ascribed to Si-O stretching vibration of MMT. The band in the range of $250\text{--}500\text{ cm}^{-1}$ and $700\text{--}900\text{ cm}^{-1}$ correspond to W-O bending vibration [32]. There are no new peaks present when x is lower than 0.5. However, the band locates at 1600 cm^{-1} is assigned to Mo-O stretching vibration when x is more than 0.6 [33]. In combination with the XRD analysis, the composite forms $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ solid solution phase when x is between 0.1 and 0.5. However, the peak of Bi_2MoO_6 starts to appear when x is higher than 0.5.

Fig. 2. Raman spectra of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ with various molar fractions of Mo.

3.3 TEM analysis

The morphology of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ is shown in Fig.3. It is noticed that the raw MMT shows layered structure with the absence of other impurities on the surface (Fig. 3a). Fig. 3b represents the prepared composite without any pretreatment, which can be found that there is a severe aggregation of nanoparticles on the raw MMT surface, suggesting that the untreated MMT cannot act as an appropriate support due to its thick layer. On the contrary, Fig. 3c shows the prepared composite with exfoliated MMT as a support. The well dispersed semiconductor nanoflakes on MMT surface were observed. The layer-to-layer distance of MMT can be extended by the exfoliated process. The inset is electron diffraction pattern, which shows a clear diffraction ring demonstrating that the composite has high crystallinity. Fig. 3d shows obvious lattice fringe of (002) plane for Bi_2WO_6 corresponding to a

distance of 0.275 nm, suggesting the formation of solid solution of Mo doped Bi_2WO_6 with the absence of other compounds. The lattice spacing of 0.223 nm correspond to (131) plane of Bi_2MoO_6 in addition to (002) plane of Bi_2WO_6 appears in Fig. 3e. The close integration of Bi_2WO_6 and Bi_2MoO_6 give rise to the formation of coherent heterostructure. Energy-dispersive spectroscopy (EDS) pattern demonstrates the existence of Bi, W, Mo, Si, Mg, Al elements (Fig.3f). Among of them, Si, Mg and Al are assigned to MMT substrate.

Fig.3. TEM photographs of MMT (a), composite without pretreatment (b), composite with pretreatment (c), HRTEM of the $\text{Bi}_2\text{W}_{0.7}\text{Mo}_{0.3}\text{O}_6/\text{MMT}$ (d) and $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6/\text{MMT}$ (e), and its EDS pattern (f).

3.4 UV-vis analysis

Fig.4 displays the UV-vis spectra of $\text{Bi}_2\text{MoO}_6/\text{MMT}$, $\text{Bi}_2\text{WO}_6/\text{MMT}$, $\text{Bi}_2\text{W}_{0.7}\text{Mo}_{0.3}\text{O}_6/\text{MMT}$ and $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6/\text{MMT}$ composites. The composites exhibit enhanced visible light responsive ability with Mo doping, which alters the band gap of the nanocomposites leading to red shift of absorption edge. It should be noted that the $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6/\text{MMT}$ sample shows higher absorption edge than $\text{Bi}_2\text{W}_{0.7}\text{Mo}_{0.3}\text{O}_6/\text{MMT}$ which suggests that when x is higher than 0.5, there are substantial interaction between Bi_2MoO_6 and $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ which may enhance the separation rate of photogenerated carriers.

Fig. 4. UV-vis spectra of $\text{Bi}_2\text{MoO}_6/\text{MMT}$, $\text{Bi}_2\text{WO}_6/\text{MMT}$, $\text{Bi}_2\text{W}_{0.7}\text{Mo}_{0.3}\text{O}_6/\text{MMT}$ and $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6/\text{MMT}$.

3.5 FT-IR analysis

Fig.5 demonstrates the FT-IR spectra of the composites. The band situated at 3430 cm^{-1} is corresponded to $-\text{OH}$ stretching vibration of the water on the surface of MMT. The band located at 1641 cm^{-1} is consistent with $-\text{OH}$ bending vibration in MMT [34]. Si-O stretching vibration appears in 1050 cm^{-1} and 1099 cm^{-1} [35]. The bands located in the range of $900\text{-}1700\text{ cm}^{-1}$ and $650\text{-}910\text{ cm}^{-1}$ are respectively ascribed to the stretching vibration of W-O and Mo-O [36, 37]. Comparing the spectra of $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6/\text{MMT}$ and MMT, a new band at 672 cm^{-1} is identified which can be consistent with Bi-O stretching vibration [38], implying the presence of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ on the MMT surface, which is similar to the XRD analysis.

Fig. 5. FT-IR spectra of MMT, Bi_2WO_6 , Bi_2MoO_6 , $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6/\text{MMT}$

3.6 PL analysis

The separation rate of photogenerated carriers is revealed by PL

spectra as displayed in Fig.6. It is well known that the separation efficiency of the photogenerated carriers is inversely proportional to the PL emission intensity. Therefore, the weaker PL emission intensity is, the higher separation efficiency and photocatalytic desulfurization are. The emission intensity of $\text{Bi}_2\text{WO}_6/\text{MMT}$ locates at 460 nm is the strongest, indicating high recombination rate of photogenerated carriers [39]. The separation of electron-hole pairs is relatively increased due to Mo doping which weakens the emission intensity of composites. The heterostructure constructed by $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ and Bi_2MoO_6 improves separation rate of photogenerated carriers when x reaches 0.6. In addition, the other three peaks are ascribed to surface oxygen vacancies and defects [40].

Fig. 6. PL spectra of $\text{Bi}_2\text{WO}_6/\text{MMT}$, $\text{Bi}_2\text{MoO}_6/\text{MMT}$, $\text{Bi}_2\text{W}_{0.8}\text{Mo}_{0.2}\text{O}_6/\text{MMT}$ and $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6/\text{MMT}$.

3.7 XPS analysis

The elemental compositions and chemical valence state of

$\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6/\text{MMT}$ are measured by XPS. Fig. 7a shows the survey scan of the sample indicating the existence of Al, Si, O, Bi, Mo and W elements, which is consistent with the EDS results. Bi 4f observed at 159.4 eV and 164.1 eV are ascribed to Bi^{3+} as shown in Fig. 7b. The peaks of Mo 3d at 232.5 eV and 235.4 eV and W 4f at 35.3 eV and 37.8 eV shown in Fig. 7c and Fig. 7d reveal the chemical valence state for Mo^{6+} and W^{6+} [23]. The XPS result gives that the actual concentration of Bi, W and Mo is 1.94%, 0.36% and 0.62% in the sample, which is close to the nominal concentration of each element for $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6$. The actual concentration of O is 46.36% which originates from $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6$ and MMT. As for MMT, the actual concentrations of Si, Mg and Al are 10.53%, 4.06% and 4.8%, which are similar to their corresponding nominal concentration. In addition, the concentration of C located at 284.4 eV reaches 31.33% which is ascribed to the adventitious hydrocarbon in the XPS apparatus.

Fig.7. XPS spectra of $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6/\text{MMT}$: Survey scan (a), Bi 4f (b), Mo 3d (c), W 4f (d).

3.8 Catalytic properties

The desulfurization of DBT is investigated utilizing various composites as catalyst. As shown in Fig. 8, the degradation rate is only 7% with H_2O_2 in the photocatalytic system. By adding MMT, the desulfurization rate increase up to 17.2% which may be ascribed to the adsorption of MMT with DBT molecules. The degradation rate is increased by the addition of other composites. Pure Bi_2WO_6 and Bi_2MoO_6 both have low degradation rate for DBT. Meanwhile, $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ greatly improves the degradation rate for DBT. The possible reason is that Mo doping forms the solid solution phase of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$, contributing to the red shift phenomenon compared with pure Bi_2WO_6 and Bi_2MoO_6 as seen in Fig. 4. Therefore, the visible light responsible ability of the composites is remarkably improved. Meanwhile,

the heterostructure developed by $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ and Bi_2MoO_6 improves photocatalytic properties of composites.

Fig. 9 shows the desulfurization rate with various Mo doping. It is not hard to find that the desulfurization rate of model oil is enhanced gradually along with the increase of Mo content when x is less than 0.7. According to the XRD and Raman results, $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ solid solution phase is formed when x is less than 0.5. However, the presence of Bi_2MoO_6 generates heterostructure with $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ which may accelerate separation of photogenerated electron-hole pairs when x is higher than 0.5. As a consequence, photocatalytic property is improved, and the highest desulfurization rate can reach up to 95%. Nevertheless, when x is 0.8 or higher, the abnormal aggregation of Bi_2MoO_6 may restrain the transfer of photogenerated electrons, resulting in the decreased photocatalytic ability.

Fig. 8. Comparison of photocatalytic desulfurization of model oil by various composites.

Fig. 9. Photocatalytic desulfurization of model oil by $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ with various molar fractions of Mo.

3.9 Photocatalytic desulfurization mechanism

In order to verify the radicals of nanocomposites in the process of photocatalysis, three different kinds of captors, triethanolamine (TEOA; h^+ scavenger), tert-butyl alcohol (TBA; a $\cdot\text{OH}$ radical scavenger) and benzoquinone (BQ; a $\cdot\text{O}_2^-$ radical scavenger) are used. As shown in Fig. 10, the desulfurization rate of photocatalysts decreases slightly corresponding to the adding of TEOA and BQ. It is found that the desulfurization rate of $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6/\text{MMT}$ has a remarkable decrease to 21.8%, implying that $\cdot\text{OH}$ plays an essential role during the photocatalytic reaction. The degradation products for one, two and three hours are detected by GC-MS shown in Fig. 11 respectively. It can be

found that the obtained degradation products are almost the same compared with authentic DBTO₂ in terms of the retention time and the mass spectrum. As the degradation time goes up, the content of DBT is decreased, on the contrary, the content of DBTO₂ is increased, suggesting that DBT in model oil are almost transferred to DBTO₂ after three hours of degradation. The photocatalytic mechanism is put forward according to the above results as shown in Fig. 12. The conduction band (CB) of Bi₂WO₆ is 0.22 eV and valence band (VB) is 3.0 eV, which is higher than 1.99 eV, where -OH can be oxidized to •OH [20]. The CB and VB (-0.80 eV and 1.86 eV) of Bi₂MoO₆ are more negative than Bi₂W_{1-x}Mo_xO₆ [22]. As a consequence of this, Bi₂MoO₆ can be activated under visible light irradiation. Photogenerated electrons are rapidly transported to the surface of Bi₂W_{1-x}Mo_xO₆. The electrons may react with H₂O₂ to form •OH. Finally, those adsorbed DBT moleculars on the MMT surface will be further oxidized to DBTO₂ by the •OH radicals due to its strong oxidation ability. On account of the above statement, we presented the following reaction equations:

Fig. 10. Photocatalytic desulfurization with adding different quenching agents.

Fig. 11. GC-MS analysis of the authentic DBTO₂ and the degradation products for one two and three hours of the model oil.

Fig. 12. Photocatalytic desulfurization mechanism of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$

3.10 Analysis of recycled catalysts

The repeated desulfurization experiment of recycled catalyst is performed. After five recycle times, the desulfurization rate still remains more than 90%, indicating that the recycled catalyst has an outstanding stability. The recycling process is easy to execute, and no extra process is added. After desulfurization reaction, catalysts are separated by centrifugation to remove model oil and H_2O_2 , followed by drying to obtain the recycled catalyst. XRD and FT-IR characterizations are employed to compare the recycled catalyst and fresh catalyst. In Fig. 13,

the main peaks of W-O band and Mo-O band still can be found, suggesting that the structure of $\text{Bi}_2\text{W}_{0.3}\text{Mo}_{0.7}\text{O}_6/\text{MMT}$ has not changed. However, a new peak locates at 583.5 cm^{-1} in the recycled catalyst can be identified, which may be ascribed to the S=O band due to the fact that the DBT in the mode oil is oxidized to DBTO_2 . As shown in Fig.14, new miscellaneous peaks can be ascribed to the DBT-sulfone and trace amount of residual DBT, which further prove the conversion of DBT [41].

Fig. 13. FT-IR spectra of fresh catalyst and recycled catalyst.

Fig. 14. XRD patterns of fresh catalyst and recycled catalyst.

4. Conclusions

In this work, $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ nanocomposites have been successfully synthesized via a facile one-pot hydrothermal method. $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ demonstrates remarkable visible light catalytic performance for oxidizing DBT due to the formation of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{Bi}_2\text{MoO}_6$ coherent heterostructure which improves the visible light absorption efficiency and the separation rate of photogenerated carriers. Radicals trapping experiments identify that $\cdot\text{OH}$ radicals play an indispensable role in the photocatalytic oxidative desulfurization. The highest desulfurization rate of 95% for the model oil was achieved when x is 0.7 for 3 h. $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6/\text{MMT}$ nanocomposite is anticipated to bring promising application in deep desulfurization or other environmental abatement areas.

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