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Study on performance and mechanism for aerobic oxidative desulfurization based on the dual-functional material possessing catalytic and adsorptive properties

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Abstract: Three polyoxometalates including $K_3PW_{12}O_{40} \cdot 10H_2O$, $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$, and $K_8H[P_2W_{15}V_3O_{62}] \cdot 9H_2O$ were successfully prepared and used in the air/n-octanaloxidative desulfurization (ODS) system. In which, Dawson-type polyoxometalate $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$ exhibited the best performance with 99.63% of desulfurization ratio. Then, $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$ was supported on graphene oxide (GO) to obtain $K_6P_2W_{18}O_{62}/GO$. The prepared catalysts were characterized by Fourier transform infrared spectra (FT-IR), ^{31}P Nuclear Magnetic Resonance (^{31}P NMR), X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive X-ray spectra (EDX), transmission electron microscopy (TEM), and Boehm titration. Using $K_6P_2W_{18}O_{62}/GO$ as catalyst, the final sulfur removal ratio could achieve 96.10% without extraction post-treatment due to its inherent adsorption capacity. In addition, the influencing factors on the desulfurization were investigated. The recovery experiment showed that the supported catalyst could be reused for 5 times with little catalysis deactivation. Finally, the reaction mechanism was proposed with the aid of the gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) and contrast test.

1. Introduction

Facing the increasingly serious global environmental problems, governments have promulgated a series of regulations to prevent and control pollution in city.^{1, 2} More recently, sulfur emission of vehicle has been limited to 10 ppmw in many countries.^{3, 4} For one thing, the combustion of sulfur compounds in fuel oil will bring various health and environmental hazards to human such as the formation of acid rain, promotion of hazardous particulates, and inducement of respiratory disease. For another, the residual sulfur compounds in fuel oil will poison the diesel oxidation catalyst, thus reducing the removal efficiency of other harmful emissions including unburned hydrocarbon (HC), nitrogen oxides (NO_x), and other odour gases to take multiple harmful consequences.^{5, 6} In short, the sulfur emission is a pressing environmental problem of this moment, especially in the developing counties.^{7, 8} Under this background, the ultra-deep desulfurization of fuel oil is becoming an important subject in both academia and industry, and deeply studied by the relevant scholars. In earlier research, the sulfur compounds in fuel oil were mainly removed by hydrodesulfurization (HDS) method. In the process, the sulfur compounds reacted with hydrogen to obtain the

hydrocarbons and hydrogen sulfide gas, and then the desulfurization was achieved through the removal of the hydrogen sulfide by adsorption or other methods.⁹ Through years of study, HDS has already become a mature technology and widely used in industry.¹⁰⁻¹² However, the HDS was always carried out under high temperature and high hydrogen pressure, as well as its low efficiency in the heteroaromatic sulfur compounds removal, making it large capital investment and energy consumption in need to meet the new sulfur emission regulations. Concerning this undeniable problem, the researchers have been trying to explore more effective desulfurization methods over the last decades, and the oxidative desulfurization (ODS) and adsorption desulfurization (ADS) are widely sought after with their mild reaction conditions and high efficiency for heteroaromatic sulfur compounds removal, such as benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT).¹³⁻¹⁵

In the ODS process, stubborn organosulfur compounds in non-polar fuel oil were oxidized to their strong polar products such as sulfones or sulfoxides, and the oxidation products were removed through polar solvent extraction or adsorption. The frequently-used oxidants for ODS include H₂O₂,¹⁶ organic peroxide,¹⁷ molecular oxygen,¹⁸ and solid peroxide.¹⁹ As a great potential one, the molecular oxygen (or air) exhibited incomparable advantages with its inexpensiveness, wide resource, environmental friendliness and safety for storage. Therefore, many researchers have begun to explore the ODS system using molecular oxygen or air as oxidant.^{20, 21}

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However, due to its low reactivity, some extra conditions must be provided to activate the molecular oxygen when used for ODS. The common methods to activate the molecular oxygen in ODS include high temperature treatment,^{22, 23} photocatalysis,^{24, 25} and so on. As early as 2004, Murata *et al.* have proposed an interesting strategy to reach the ultra-deep desulfurization under mild conditions with the aid of aldehyde co-assistant.²⁶ However, the studies in this field have been relatively few since then, and one of the important reasons to limit the application of this technology is the carboxylic acid produced through the oxidation of aldehyde will be residual, thus affecting the quality of the fuel oil.

The polyoxometalates have been widely used for ODS process due to its remarkable catalytic performance, and the most frequently used polyoxometalates are the Keggin-type ones.²⁷⁻²⁹ A universally accepted mechanism for these researches is as follows: the polyoxometalates reacted with the oxidant H₂O₂ to obtain peroxy-polyoxometalates which possessed high catalytic activity. Then, DBT would be oxidized to DBTO₂ by the peroxy-polyoxometalates and removed through polar solvent extraction. Therefore, the polyoxometalates (catalyst)/H₂O₂ (oxidant)/polar solvent (extractant) system is the most mature ODS technology in this respect, and widely studied by the relevant scholars. More recently, some researchers began to explore the catalytic performance of Dawson-type polyoxometalates for ODS, which are another common polyoxometalates widely used in many fields.³⁰⁻³² For instance, Banisharif *et al.* used [cetrimonium]₁₁P₂W₁₃V₅O₆₂ as the catalyst for ODS, and they proposed that the prepared polyoxometalates could also react with H₂O₂ to obtain peroxy-polyoxometalates to oxidize the thiophene derivatives to their corresponding sulfones in the fuel oil/extractant biphasic systems, thus achieving the ultra-deep desulfurization by the extraction for the high-polar sulfones.³³⁻³⁵ Gao *et al.* supported H₈P₂Mo₁₆V₂O₆₂ on carbon nanotubes to prepare a composite catalyst for ODS using molecular oxygen as oxidant, and 99.4% of DBT removal efficiency could be achieved.³⁶

The sulfur compounds in fuel oil were removed by the adsorption function in the ADS process. Therefore, to prepare the adsorbents with excellent adsorptivity and high selectivity for the target pollutants is the most critical step in the process. After many scholars research in this field, varieties of superior adsorbents were designed and used.³⁷⁻³⁹ As a new kind of cheap adsorption materials, the carbon-based materials are widely used for ADS recently. For instance, Danmalikiet *al.* used the nickel/activated carbon (AC) as the adsorbent for DBT, and 96% of sulfur removal ratio could be achieved in the model oil with an initial sulfur content of 59 ppm.⁴⁰ Saleh explored the ADS performance of AC loaded with cobalt and copper, the result showed that the adsorbent was not only applicable for the DBT removal, but also for other kinds of thiophene derivatives.⁴¹ Menzel *et al.* supported layered double hydroxides onto exfoliated GO, and the composite exhibited excellent adsorption capacity, pronounced selectivity and fine recycling property in the ADS process.⁴²

The carbon-based materials exhibited excellent adsorption performance for the sulfur compounds in fuel oil, and directly

used for ADS process. However, some recent researches showed that a few carbon materials could adsorb the ODS products sulfones/sulfoxides more easily than the untreated sulfur compounds in fuel oil. For instance, Chenet *al.* used activated clay as the adsorbent for the sulfone compounds produced in the ODS process catalyzed by phosphotungstic acid, and the sulfur content in the treated fuel oil was below 10 ppm.⁴³ Yang *et al.* used modified activated carbon to adsorb the sulfones obtained through the pre-oxidation of sulfur compounds in fuel oil, and impressive sulfur removal efficiency had been achieved in both of model oil and real oil.⁴⁴ Zhang *et al.* used GO as the adsorbent for the sulfones produced in the octanal-air ODS system, and a notable desulfurization result was achieved in model oil.⁴⁵

Due to the high desulfurization efficiency of ODS and ADS, this work aimed at designing a dual-functional material possessing catalytic and adsorptive properties to realize the in-situ removal of sulfur compounds in oil. Inspired by previous work,⁴⁵ we found that GO had a high adsorption capacity for sulfones produced in the octanal-air ODS system, corresponding to 45.1 mg-S/g-sorb. However, 89.21% of the final desulfurization ratio still could not meet the current ultra-deep desulfurization requirement. Also, a large number of n-octanal must be provided (molar ratio of octanal/S was 24) to oxidize the sulfur compounds. Hence, we designed the composite catalyst K₆P₂W₁₈O₆₂/GO through hydrothermal method. Due to the excellent catalytic performance of K₆[α-P₂W₁₈O₆₂]₁₄H₂O in the octanal-air ODS system and the high adsorption capacity of GO for sulfones, 96.10% of the final desulfurization ratio could be achieved through the in-situ adsorption of the catalyst, and less n-octanal was needed (molar ratio of octanal/S was 4) to oxidize the sulfur compounds. To remove the produced carboxylic acid, the extraction treatment was added into the process. The result showed that no carboxylic acid was residual in the fuel oil through the multi-function of adsorption and extraction, and the sulfur compounds in fuel oil could be completely removed in a very short time. An efficient and novel desulfurization was proposed based on the prepared dual-functional material.

2. Experimental

2.1. Materials.

All the chemicals were directly purchased from the suppliers and used as received without further purification. Detailedly, dibenzothiophene (99%) and benzothiophene (99%) were obtained from Acros Organics (USA); 4,6-dimethyldibenzothiophene (97%) were obtained from J&K Chemicals (China); acetonitrile (99%), n-octane (95%), potassium chloride (99.5%), sodium perchlorate monohydrate (99%), xylene (98%) and sodium nitrate (99%) were obtained from Tianjin Kermel Chemicals (China); sodium tungstate (97%), ethanol absolute (99.9%) and sodium metavanadate (98%) were purchased from Tianjin Fuchen Chemicals (China); phosphoric acid (85wt%) and hydrogen peroxide (30wt%) were purchased from Laiyang Kant Chemicals (China); n-octanal

(97%), octanoic acid (97%) and n-octylene (97%) were available from Aladdin Chemicals (China); potassium carbonate (99%) was available from Tianjin Dengke Chemicals (China); sodium chloride (99%) was obtained from Tianjin Guangcheng Chemicals (China); sodium carbonate anhydrous (99%) and Phosphotungstic acid (97%) were purchased from Sinopharm (China); natural graphite (99.9%) was purchased from Qingdao Huataitech Company (China); and potassium permanganate (99.5%) was available from Guangzhou Liqiang Chemicals (China). All the used reagents were analytically pure.

2.2. Characterization

FT-IR spectra of the samples were collected using ALPHA-T Fourier Transform Infrared Spectrometer (BRUKER Corp., Germany), with a range of 400–4000 cm^{-1} . KBr pellet was used in the measurement. ^{31}P NMR spectra were recorded on ADVANCE 400 MHz NMR spectrometer (BRUKER Corp., Germany). XRD patterns were recorded by D8 ADVANCE instrument (BRUKER Corp., Germany) using Cu-K α radiation ($\lambda = 0.15405 \text{ nm}$, 40 KV \times 60 mA). SEM micrographs were obtained by JSM-6700F field emission scanning electron microscopy (JEOL Corp., Japan), equipped with an Oxford INCA X sight energy spectrum analyzer using the acceleration voltage of 2 kV. TEM micrographs were taken by JEM-1011 transmission electron microscope (JEOL Corp., Japan).

2.3. Preparation of the Catalysts.

$\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ and $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}] \cdot 9\text{H}_2\text{O}$ were prepared according to the literature methods.^{46, 47} The Keggin-type polyoxometalates $\text{K}_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$ was prepared according to the literature method with some modifications.⁴⁸ In a typical synthesis, 9.792 g (0.0034 mol) $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot \text{xH}_2\text{O}$ was fully dissolved in 100 ml deionized water to obtain a clear solution A, and 0.7823 g (0.011 mol) KCl was dissolved in 50 ml deionized water to obtain solution B. The solution B was slowly added into solution A over 30 min under vigorous stirring, and the white precipitant was gradually formed. After stirred for another 8 h, the white precipitant was collected by centrifugation, and washed with deionized water for several times to remove chloride ion. The wet precipitation was treated by vacuum freeze-drying to obtain $\text{K}_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$. The element compositions of the prepared polyoxometalates were analyzed by inductively Coupled Plasma-atomic Emission Spectrometry (ICP-AES) as follows: Anal. Calcd for $\text{K}_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$: K, 3.70; W, 69.49. Found: K, 3.75; W, 69.52. Anal. Calcd for $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$: K, 4.84; W, 68.23. Found: K, 4.87; W, 68.29. Anal. Calcd for $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}] \cdot 9\text{H}_2\text{O}$: K, 7.05; W, 62.10; V, 3.44. Found: K, 7.11; W, 62.14; V, 3.42.

GO was prepared through the modified Hummer's method.⁴⁵ Briefly, 3 g natural graphite powder, 1.5 g sodium nitrate and 70 ml concentrated sulfuric acid were added in the flask, and cooled down in the ice bath. Then, 9 g potassium permanganate was slowly added into the mixtures over 1 h. After the addition, the resultant mixtures were stirred for 2 h and the temperature was kept below 20 °C. After that, the mixtures were stirred for 30 min at 35 °C. When the mixtures were cooled to room temperature, 150 ml deionized water was added and stirred for 3 h at 98 °C. 15 minutes later, the

mixtures were treated by 400 ml deionized water and 30 ml hydrogen peroxide, and the obtained suspension was filtered and washed with 10% hydrochloric acid solution. The solid was collected and washed with deionized water and absolute ethanol until the filtrate was neutral. Finally, GO product was obtained through vacuum freeze-drying.

The supported catalyst was prepared by the following method: The given amount of GO was dispersed in 80 ml deionized water under ultrasonic treatment for 3 h to obtain suspension A, and corresponding amount of $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 14\text{H}_2\text{O}$ was dissolved in 15 ml deionized water to obtain solution B. Then, solution B was drop by drop added in suspension A and stirred for 2 h at room temperature to obtain mixture C. Mixture C was treated by hydrothermal method at 100 °C for 24 h, and washed with deionized water and absolute ethanol. Finally, the supported catalyst $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}/\text{GO}$ was obtained through vacuum freeze-drying.

2.4 Oxidative Desulfurization Experiment.

The experiment was carried out in a three-necked flask immersed in constant temperature bath. When the setting temperature was reached, 60 ml model oil was added in the flask, and the model oil was prepared by fully dissolving DBT in n-octane (corresponding S concentration was calculated as 250 ppmw). Then, the catalyst (0.5 wt%) and n-octanal (molar ration of octanal/S was 4) were successively added into the model oil. The air with the flow rate of 200 ml/min was bubbled into the reaction mixture, and the stirring was started. At set intervals, the model oil (1 μl) was sampled and extracted by MeCN, if necessary. The sulfur content in the samples was determined by a micro-coulomb comprehensive analysis meter (WK-2E). The desulfurization ratio was calculated by the following equation:

$$\text{Desulfurization ratio (\%)} = (C_0 - C_t) / C_0 * 100$$

Where, C_0 represented the initial sulfur content in the model oil, C_t represented the sulfur content after treated for t time.

2.5. Recovery Experiment.

When the oxidative desulfurization experiment was completed, the reaction mixture was filtered to remove the liquid phase. The obtained solid was washed with MeCN for 3 times, and dried at 60 °C overnight. After these treatments, the recovered catalyst was obtained and used in the desulfurization experiment again.

3. Results and discussion

3.1. Characterization of the Polyoxometalates.

As shown in Figure. 1, the IR peaks of $\text{K}_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$ appear at 1080 cm^{-1} (P-O_a), 983 cm^{-1} (W=O_d), 891 cm^{-1} (W-O_b), 800 cm^{-1} (W-O_c-W) and 526 cm^{-1} (W-P-W), which are the typical characteristic peaks of Keggin-type polyoxometalates.⁵⁰ The IR peaks of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ appear at 1089 cm^{-1} (P-O), 961 cm^{-1} (W=O), 911 cm^{-1} (W-O_b-W) and 780 cm^{-1} (W-O_c-W), which are the typical characteristic peaks of Dawson-type polyoxometalates.⁴⁶ The IR peak positions of $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}] \cdot 9\text{H}_2\text{O}$ mainly located at 1077 cm^{-1} (P-O), 935 cm^{-1} (V=O), 875 cm^{-1} (W-O_b-W), and 765 cm^{-1} (W-O_c-W), which

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are the characteristic peaks of Vanadium-substituted Dawson-type polyoxometalates. ⁴⁷The IR results prove the successful preparation of three polyoxometalates.

Furthermore, the ³¹P NMR spectra of the prepared polyoxometalates are given in Figure. 2. As shown in the figure, a major peak appears at around -15.07 ppm in the spectrum of $K_3PW_{12}O_{40} \cdot 10H_2O$, as reported in the reference. ⁵¹ A major peak appears at around -12.7 ppm in the spectrum of $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$, which was determined as α -isomer peak in reference. ⁴⁶ Two obvious peaks appear at around -6.7 and -14.3 in the spectrum of $K_8H[P_2W_{15}V_3O_{62}] \cdot 9H_2O$, which is in agreement with that reported in the reference. ⁴⁷ The NMR results further indicate the successful synthesis.

3. 2. ODS Experiment Catalyzed by Polyoxometalates.

The ODS experiment was carried out as described in section 2.4. Furthermore, then-octane solution containing 500 ppm sulfur content of DBT was used as model oil, and MeCN was used as extractant to remove the oxidation products. As shown in Figure. 3, the final desulfurization ratios in model oil catalyzed by $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$ and $K_3PW_{12}O_{40} \cdot 10H_2O$ were 99.63% and 69.10% in 2 h, respectively. Obviously, the Dawson-type polyoxometalates exhibited much higher catalytic activity than Keggin-type ones in the aldehyde/O₂ ODS system. The Vanadium-substituted Dawson-type polyoxometalates $K_8H[P_2W_{15}V_3O_{62}] \cdot 9H_2O$ was also synthesized and its catalytic performance was investigated in the ODS process. As shown in Figure. 3, the final desulfurization ratio in model oil catalyzed by $K_8H[P_2W_{15}V_3O_{62}] \cdot 9H_2O$ were 92.99% in 2 h and 98.49% in 4h, respectively. Both of the desulfurization ratio and reaction rate were inferior to $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$. Overall, $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$ with the highest activity was chosen as the optimum catalyst to be further studied in the follow-up experiment.

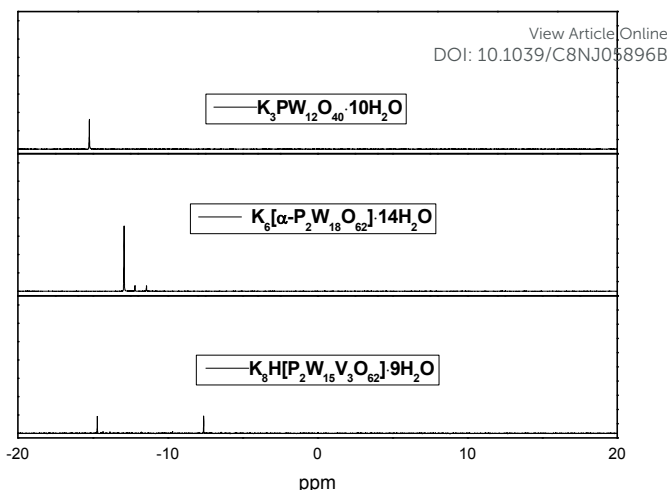


Fig. 2. ³¹P NMR spectra of the prepared polyoxometalates

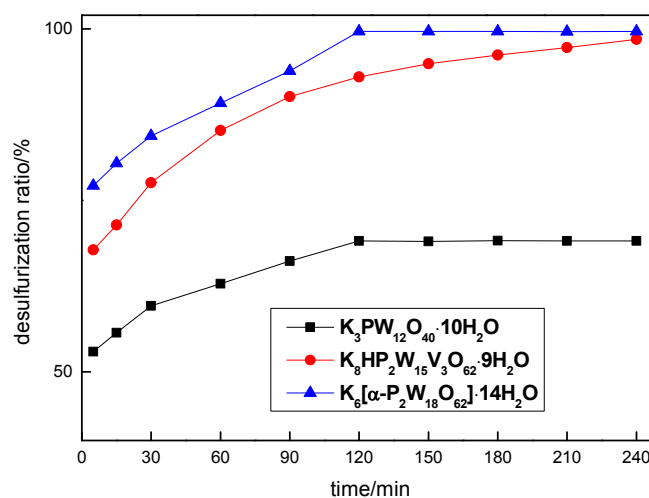


Fig. 3. The ODS curves over reaction time catalyzed by different polyoxometalates. (Condition: T=60 °C; w_{cat}=0.5%; m_s=500 ppmw; molar ratio of octanal/S is 4).

Note: T: reaction temperature; w_{cat}: catalyst dosage; m_s: initial sulfur content.

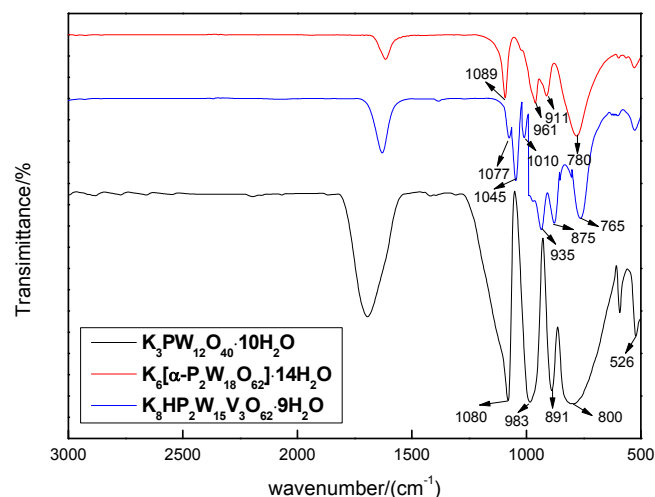


Fig. 1. FT-IR spectra of the prepared polyoxometalates

3.3. Characterization of $K_6P_2W_{18}O_{62}/GO$.

GO and $K_6P_2W_{18}O_{62}/GO$ were prepared as described in section 2.3 and characterized by FT-IR, XRD, SEM, EDX and TEM. As shown in Figure. 4, IR peak positions of GO are mainly located at 3427 cm⁻¹, 1728 cm⁻¹, 1628 cm⁻¹, 1230 cm⁻¹ and 1067 cm⁻¹, corresponding to the characteristic peaks of oxygen-containing functional groups as -OH, C=O, COOH, C-O-C and C-O, respectively. The introduction of these functional groups prove the successful preparation of GO. Furthermore, these peaks can be also observed in the spectrum of $K_6P_2W_{18}O_{62}/GO$ and the Dawson-type characteristic peaks are also maintained, indicating that $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$ was successfully supported on GO, and both of them kept their original structures. Besides, it could be deduced that $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$ was supported on GO only by physical adsorption and no chemical reactions between them occurred, since no new peaks were observed.

The successful preparation of the materials is also confirmed by XRD method. As shown in Figure. 5, the crystal surface

characteristic diffraction peak of GO (002) at around 11° is clearly observed in the XRD pattern of GO, proving its successful preparation.⁴⁵ For $K_6P_2W_{18}O_{62}/GO$, the sharp peak at around 11° disappears, and a broad peak at $20\sim 30^\circ$ is observed. This is in agreement with the literature work.⁵² Besides, no diffraction peaks which appear in the XRD pattern of $K_6[\alpha-P_2W_{18}O_{62}]\cdot 14H_2O$ can be observed in the pattern of supported catalyst, which may be caused by the well dispersion of the polyoxometalate on GO.

As shown in Figure. 6, the layered structure as well as bending in the edge is observed in the SEM image of GO, which is similar with the traditional GO structure.^{45, 49} The same structure is maintained in the SEM image of $K_6P_2W_{18}O_{62}/GO$, indicating the structure of GO was not destroyed in the preparation process. Besides, $K_6[\alpha-P_2W_{18}O_{62}]\cdot 14H_2O$ was not observed on the supported catalyst, confirming the well dispersion of polyoxometalate on GO. As shown in the EDX spectra, the element carbon, oxygen, potassium, phosphorus, and tungsten can be observed in the spectra of supported catalyst, indicating the successful preparation of the supported catalyst. The similar result is also observed in Figure. 7. For one thing, clear wrinkle could be observed in the TEM image of GO, which was consistent with previous report.⁴⁵ For another, the TEM image of $K_6P_2W_{18}O_{62}/GO$ also illustrated the wrinkle structure, and the uniform dispersion of polyoxometalate on GO makes the supported catalyst darker than pure GO. According to the analysis, it could be concluded that $K_6P_2W_{18}O_{62}$ was successfully supported on GO, and the supported catalyst still maintained the original morphology of GO.

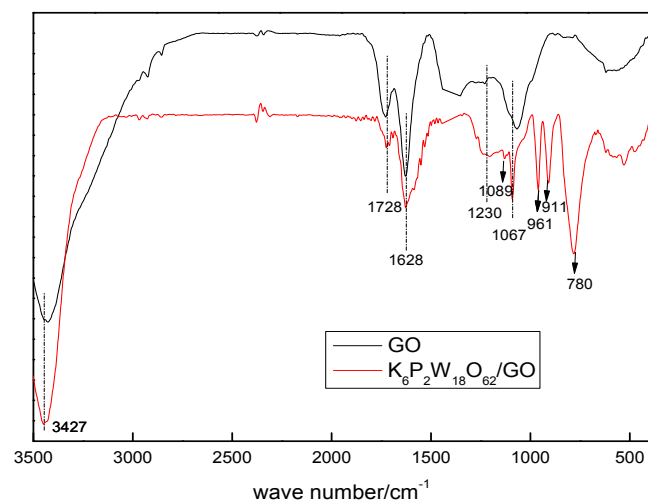


Fig. 4. FT-IR spectra of GO and $K_6P_2W_{18}O_{62}/GO$.

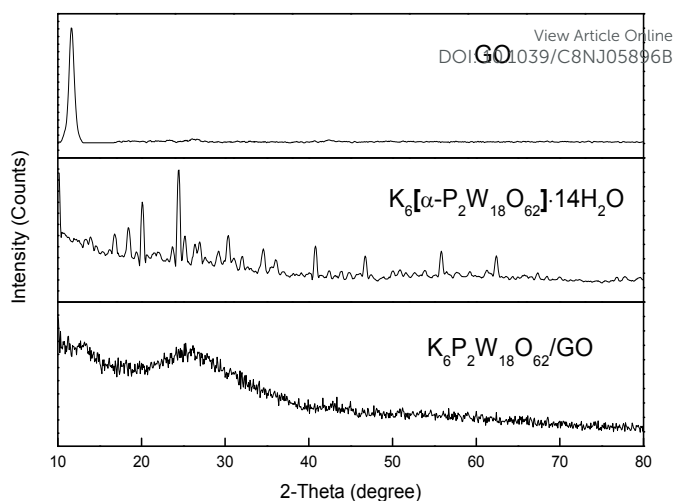


Fig. 5. XRD patterns of GO and $K_6P_2W_{18}O_{62}/GO$.

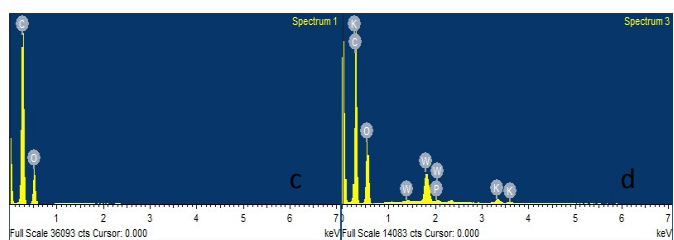
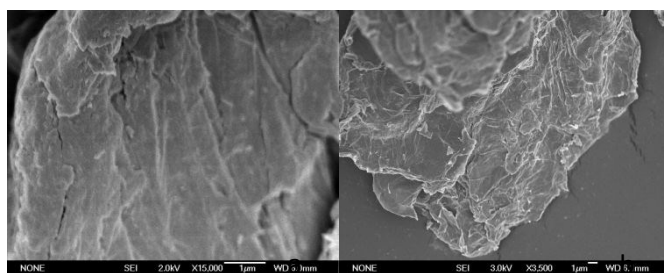


Fig. 6. SEM and EDX images of GO (a) (c) and $K_6P_2W_{18}O_{62}/GO$ (b) (d).

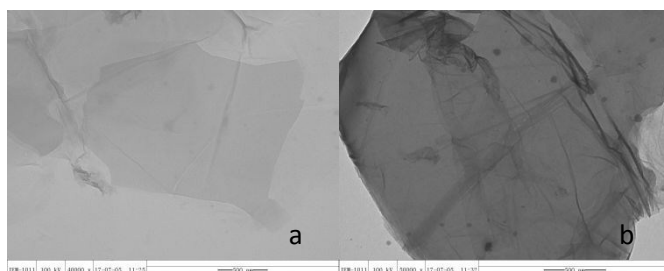


Fig. 7. TEM images of GO (a) and $K_6P_2W_{18}O_{62}/GO$ (b).

3.4. Effects of Different Parameters on ODS Catalyzed by $K_6P_2W_{18}O_{62}/GO$.

As was stated above, $K_6[\alpha-P_2W_{18}O_{62}]\cdot 14H_2O$ exhibited the best catalytic performance in aldehyde/ O_2 ODS system, corresponding to 99.63% of final desulfurization ratio. Also, it was successfully supported on GO, and both of them kept their original structures. Therefore, we supposed that the prepared $K_6P_2W_{18}O_{62}/GO$ could act as a bi-functional material possessing the catalytic activity and adsorption ability, thus making up some deficiencies existing in the previous aldehyde/ O_2 ODS system using pure GO as adsorbent, such as the large

aldehydeneed (molar ration of octanal/S was 24) and the unsatisfactory desulfurization ratio (89.21%).⁴⁵To prove our hypothesis, we carried out aldehyde/O₂ ODS experiment catalyzed by K₆P₂W₁₈O₆₂/GO, and the molar ratio of octanal/S was chosen as 4.

the supported catalysts with different K₆[α-P₂W₁₈O₆₂].14H₂O loading amounts including 10%, 15%, 17.5%, 20% and 30% were synthesized and evaluated in ODS process. The element compositions of the prepared catalysts were analyzed by inductively Coupled Plasma-atomic Emission Spectrometry (ICP-AES) as follows: Anal. Calcdfor 10%-K₆[α-P₂W₁₈O₆₂]/GO:K, 0.48; W, 6.82. Found: K, 0.43; W, 6.64. Anal.Calcdfor 15%-K₆[α-P₂W₁₈O₆₂]/GO:K, 0.73; W, 10.23. Found: K, 0.70; W, 10.01. Anal.Calcdfor 17.5%-K₆[α-P₂W₁₈O₆₂]/GO:K, 0.85; W, 11.94. Found: K, 0.83; W, 11.91. Anal.Calcdfor 20%-K₆[α-P₂W₁₈O₆₂]/GO:K, 0.97; W, 13.65. Found: K, 0.91; W, 13.31. Anal.Calcdfor 30%-K₆[α-P₂W₁₈O₆₂]/GO:K, 1.45; W, 20.47. Found: K, 1.37; W, 20.11. As shown in Figure. 8, the optimum loading amount could be determined as 17.5%, corresponding to 92.46% of final desulfurization ratio, without extraction. This could be explained in two aspects: On one hand, the active component (K₆[α-P₂W₁₈O₆₂]) was insufficient for the oxidation reaction when the loading amount was low, leading to the lower sulfur removal ratio. This can explain the increase of the desulfurization ratio when the loading amount raised form 10% to 17.5%.To confirm the assumption, the effect of K₆[α-P₂W₁₈O₆₂] dosage on the desulfurization ratio was given in Figure S1 (ESI), it could be seen that the desulfurization ratio raised from 89.21% to 98.73%, when the catalyst dosage raised from 0.05% to 0.1%, and almost kept constant subsequently, indicating the oxidation reaction would be incomplete with too low K₆[α-P₂W₁₈O₆₂] dosage. On the other hand, the excessive loading might cause the change of the specific surface area and functional group contents of the GO support, both of which were important for its adsorption capacity for the oxidation products. To analyze the influence of the surface area, the catalysts with different loading amounts were analyzed using the Brunauer-Emmett-Teller (BET) model, and the S_{BET} were 52.4 m²/g, 54.5 m²/g, 51.2 m²/g, 50.7 m²/g, 47.4 m²/g, and 45.2 m²/g,corresponding to the different loading amounts of 0% (pure GO), 10%, 15%, 17.5%, 20% and 30%. Due to the well dispersion of the polyoxometalate on GO,no obvious change of the surface area had been observed after the supporting process, indicating that the surface area was not an important influence factor for the adsorption capacity. Besides, the functional group contents of the catalysts were determined through Boehm titration, and the results were shown in Table 1.⁵³It could be seen that the functional group contents decreased with the increase of loading amount. Therefore, we deduced that the decrease of the desulfurization ratio when the loading amount raised form 17.5% to 30% might be caused by the reduction of the adsorption capacity for the oxidation products, due to the decrease of the functional group contents in the catalysts.

According the above analysis, K₆P₂W₁₈O₆₂/GO with 17.5% loading amount was chosen as the optimum catalyst and further used in the follow-up work to investigate the effects of

different parameters on ODS including temperature, initial sulfur content, different sulfur compounds and selectivity. In ODS process, temperature is an important factor to be investigated. In practical industry, large energy consumption must be provided to reach high temperature, thus causing huge capital investment and inevitable pollution. As reported in previous work,^{14, 28} high temperature is favor for the ODS process. Therefore, it is necessary to determine a suitable reaction temperature to provide the high desulfurization ratio in mild conditions. As shown in Figure. 9, the final desulfurization ratios at 40 °C, 60 °C and 80 °C were 36.84%, 96.10% and 96.77% respectively. In both regards of desulfurization efficiency and energy consumption, 60°C was chosen as the most suitable temperature. Besides, the final desulfurization ratio treated by GO adsorption at 60°C was 89.21% (the molar ratio of octanal/S is 24),⁴⁵ which was lower than 96.10% catalyzed by K₆P₂W₁₈O₆₂/GO, proving the supported polyoxometalates still exhibited catalytic activity for ODS.Furthermore, the reaction rate catalyzed by K₆P₂W₁₈O₆₂/GO was much faster at initial stage, also proving the catalytic effect of K₆P₂W₁₈O₆₂. However, the reaction rate slowed down as reaction went on. This might be caused by the covering effect of adsorbed oxidation products for the active sites.

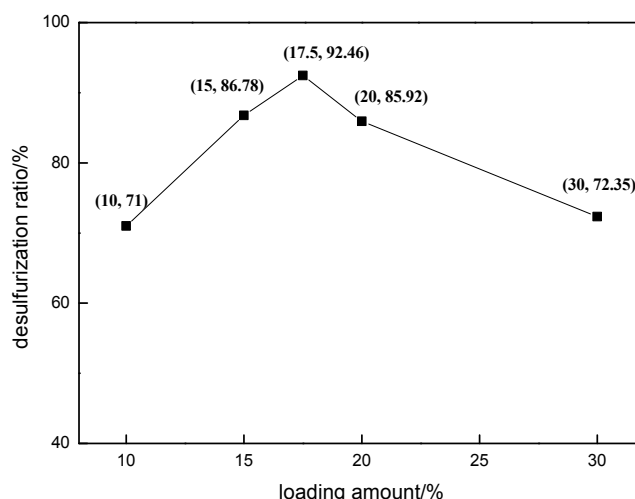


Fig. 8. The desulfurization ratio curves over loading amount of polyoxometalates in K₆P₂W₁₈O₆₂/GO. (Condition: T=60 °C;w_{cat}=0.5%;m_s=500 ppmw; molar ratio of octanal/S is 4; the reaction time was 4 h).

Table 1.Boehm titration results of the catalysts with different loading amount of K₆[α-P₂W₁₈O₆₂].14H₂O

Samples	Contents (mmol/g)		
	Carboxylic	Lactonic	Phenolic
GO	4.976	6.249	0.677
10%-K ₆ [α-P ₂ W ₁₈ O ₆₂]/GO	4.212	5.417	0.631
15%-K ₆ [α-P ₂ W ₁₈ O ₆₂]/GO	4.014	5.188	0.609
17.5%-K ₆ [α-P ₂ W ₁₈ O ₆₂]/GO	3.967	5.099	0.589
20%-K ₆ [α-P ₂ W ₁₈ O ₆₂]/GO	3.544	4.711	0.532
30%-K ₆ [α-P ₂ W ₁₈ O ₆₂]/GO	3.119	4.151	0.499

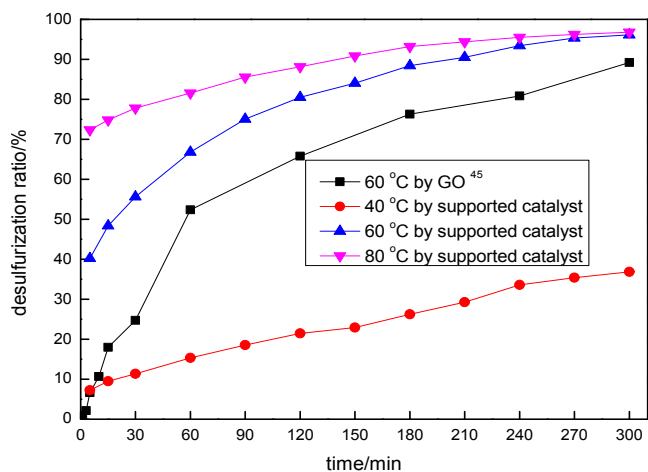


Fig. 9. The ODS curves over reaction time at different temperature. (Condition: $w_{\text{cat}}=0.5\%$; $m_s=250\text{ppmw}$; $v_{\text{air}}=200\text{ ml/min}$; molar ratio of octanal/S is 4. The condition for the reaction by pure GO was as the same as reference⁴⁵: $w_{\text{cat}}=0.5\%$; $m_s=250\text{ppmw}$; molar ratio of octanal/S is 24.)

In practical industry, the sulfur content in different liquid oil products vary greatly. Therefore, to investigate the catalytic performance in the oil with different initial sulfur content is of significance for practical application. As shown in Figure. 10, the final desulfurization ratios were 96.10%, 93.44% and 92.46%, corresponding to the initial sulfur content of 250 ppmw, 350 ppmw and 500 ppmw, respectively. It could be seen that the supported catalyst exhibited excellent performance in a broad range of initial sulfur contents.

The real oil contains various heteroaromatic sulfur compounds which are difficult to remove. Therefore, it is imperative to explore the catalytic activity of $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}/\text{GO}$ for different sulfur compounds besides DBT. As shown in Figure. 11, the final desulfurization ratios were 96.10%, 92.03% and 31.26%, corresponding to DBT, 4,6-DMDBT and BT. The reactivity were in the order of $\text{DBT} > 4,6\text{-DMDBT} > \text{BT}$. This result could be explained in previous work:^{14, 28} For one thing, higher electron density was more favor of the oxidation of sulfur compounds. For another, space steric hindrance on S atom was an obstacle to the reaction.

The real liquid oil is a complex mixture consisting of various like n-alkane, aromatics and unsaturated hydrocarbons. Therefore, it is instructive to evaluate the selectivity of catalyst for ODS. As shown in Figure. 12, n-octylene and xylene were used as the representative components to evaluate the selectivity of $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}/\text{GO}$ for ODS. The final desulfurization ratios decreased from 96.10% to 43.25% and 24.10%, when 10% n-octylene and 10% xylene were added into the model oil, respectively. Obviously, the supported catalyst exhibited poor selectivity in the process, and this could be attributed to the competitive oxidation between DBT and the added organics. To improve the desulfurization ratios, the extraction of MeCN was carried out as an after-treatment process. As shown in Table S1 (ESI), 94.31% and 84.45% of desulfurization ratios could be achieved in sample 2 and sample 3, respectively, when they were treated by ODS process as well as extraction of MeCN.

3.5. Recovery of the Supported Catalyst for ODS.

When ODS process was completed, the supported catalyst was recovered according to the method described in section 2.5, and the recovered catalyst was used in the next ODS experiment. As shown in Figure. 13, the final desulfurization ratios in the first recycle, second recycle, third recycle, fourth recycle, and fifth recycle were 95.60%, 95.25%, 94.07%, 92.16% and 90.05%, respectively, indicating that the supported catalyst could be reused at least for 5 times with little catalysis deactivation.

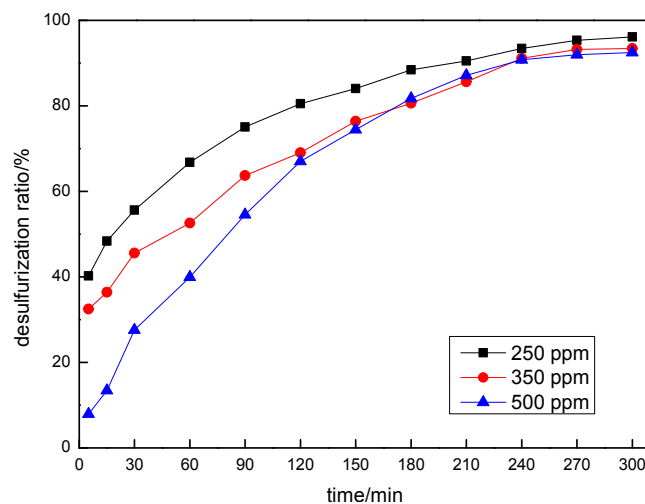


Fig. 10. The ODS curves over reaction time for different initial sulfur content. (Condition: $T=60\text{ }^\circ\text{C}$; $w_{\text{cat}}=0.5\%$; molar ratio of octanal/S is 4.)

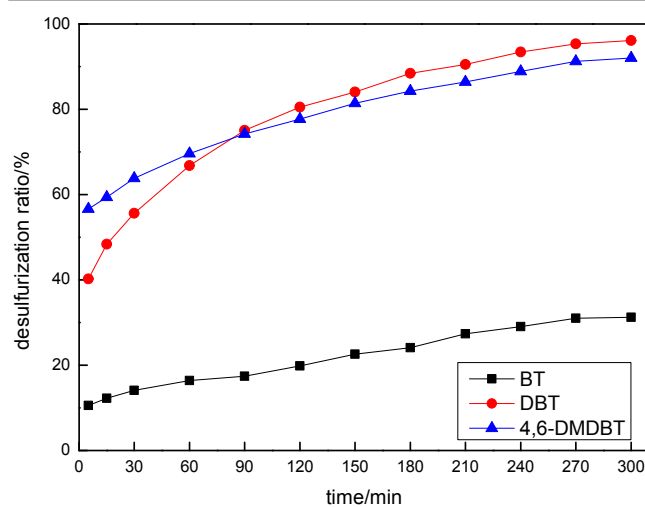


Fig. 11. The ODS curves over reaction time for different sulfur compounds. (Condition: $T=60\text{ }^\circ\text{C}$; $w_{\text{cat}}=0.5\%$; $m_s=250\text{ppmw}$; molar ratio of octanal/S is 4.)

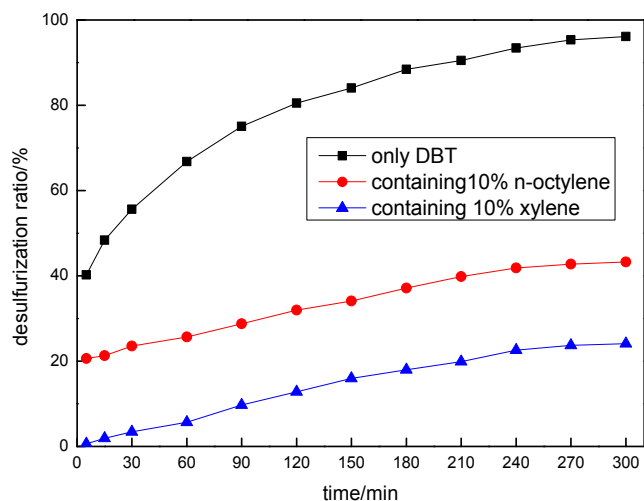


Fig. 12. The ODS curves over reaction time in model oil with different components. (Condition: T=60 °C; W_{cat.}=0.5%; m_S=250ppmw; molar ratio of octanal/S is 4).

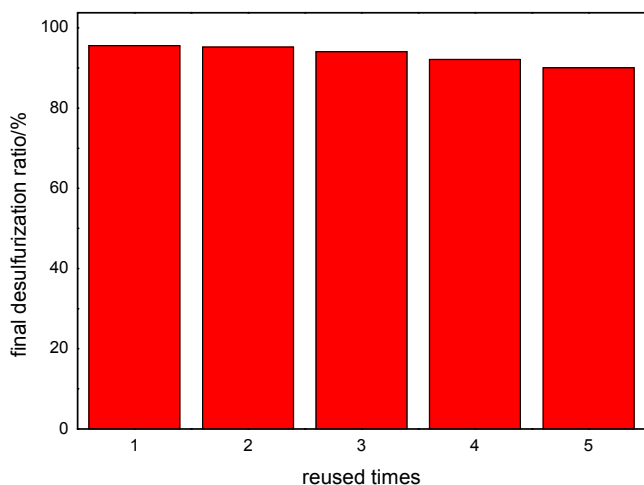


Fig. 13. The final desulfurization ratios in different recycle process. (Condition: T=60 °C; W_{cat.}=0.5%; m_S=250ppmw; reaction time is 5 h; molar ratio of octanal/S is 4).

3.6 The determination for ODS products.

The GC-MS was used to determine the products in the studied system. As shown in Figure. S2, DBT in model oil was oxidized to its corresponding sulfones DBTO₂, and n-octane was oxidized to octanoic acid. It could be seen from Figure. S2 (b) that some octanoic acid was residual in the model oil after reaction, and the residual sulfur compound was determined as DBTO₂, indicating DBT was completely oxidized, and the limitation to the desulfurization ratio was the incomplete adsorption removal for DBTO₂. As shown in figure. S2 (c), some octanoic acid and majority of DBTO₂ were observed in the MeCN eluent of the catalyst, proving K₆P₂W₁₈O₆₂/GO had an excellent adsorption capacity for the oxidation products including DBTO₂ and octanoic acid which would affect the quality of the fuel oil. To remove the residual DBTO₂ and octanoic acid in the model oil, 60 ml MeCN was added in the original model oil to form a biphasic system. The ODS reaction was still carried out as described in section 2.4. The ODS curve was given in Figure. 14.

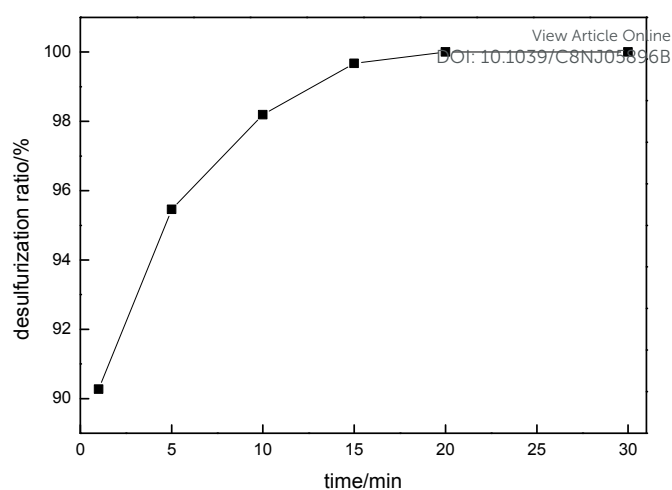


Fig. 14. The ODS curves over reaction time catalyzed by K₆P₂W₁₈O₆₂/GO combined with after-treatment of extraction by MeCN. (Condition: T=60 °C; W_{cat.}=0.5%; m_S=250ppmw; molar ratio of octanal/S is 4).

As shown in the figure, a fast ODS reaction occurred, and the sulfur compounds could be completely removed in 20 min. Compared with that catalyzed by K₆[α-P₂W₁₈O₆₂]-14H₂O (shown in Figure. 3), both of the reaction rate and desulfurization ratio have been improved greatly. As shown in figure. S2 (d), no DBTO₂ and octanoic acid had been observed in the model oil, and a clean model oil was obtained. Since DBTO₂ could be dissolved into the hydrophilic MeCN phase, its covering effect for the active sites was effectively avoided, and a faster reaction occurred compared with that treated without extraction process (shown in Figure. 9).

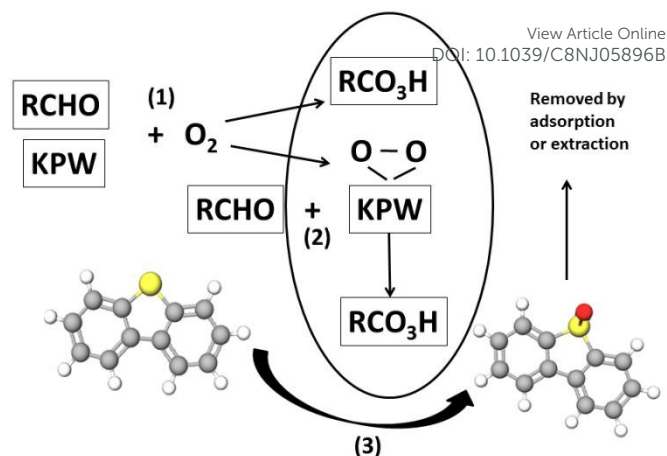
The comparison of the studied system with reported work was given in Table S2 (ESI). As shown in the table, the studied system exhibited obvious advantages with the mild reaction conditions, high desulfurization ratio and excellent recoverability.

3.7. The contrast experiment and proposed mechanism.

polyoxometalates and n-octanal were involved in the studied ODS system. Therefore, two mechanisms for ODS reported in the literatures might be referenced.^{26, 28} As reported in previous work,²⁸ polyoxometalates could react with H₂O₂ to obtain peroxy-polyoxometalates with strong oxidized characteristic, which could oxidize the sulfur compounds to their corresponding sulfones, and acted as the real active components. The mechanism in n-octanal/molecular oxygen ODS system was proposed by Murata *et al.*²⁶ In their work, molecular oxygen could be activated by cobalt catalysts, and the active oxygen would react with aldehydes to obtain peroxy acids which could oxidize the sulfur compounds to their corresponding sulfones. Therefore, peroxy acids were the real active components, and the molecular oxygen could not directly react with aldehydes to obtain peroxy acids without cobalt catalysts at 40 °C.

To analyze the mechanism of the studied system, contrast experiment was carried out and the results were given in Table S3 (ESI). As shown in Table S3, the final desulfurization ratio was 48.05% treated by extraction without ODS process. When the air was bubbled into the system but no K₆[α-P₂W₁₈O₆₂]-14H₂O or n-octanal were added, no obvious increase

in the desulfurization ratio was observed, indicating that DBT could not be directly oxidized by air without catalyst. Once $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ was added into the system, the desulfurization ratio raised from 48.12% to 62.75%. Based on the analysis in the reference,²⁸ we deduced that peroxy-polyoxometalates was obtained through the reaction of polyoxometalates and molecular oxygen, acting as the real active components for the oxidation of DBT. When n-octanal was added into the system, the desulfurization ratio raised from 48.12% to 67.13%. Differ from that reported in the reference,²⁶ the ODS reaction occurred in the n-octanal/air system without catalyst. Hence, we supposed that some of the aldehydes could directly react with molecular oxygen to obtain peroxy acids at 60°C, due to the increase of reaction temperature. When both of $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ and n-octanal were added into the system, an impressive desulfurization ratio of 99.63% was achieved. Inspired by the reference work,²⁶ we supposed that the result was not only caused by the simple superposition effect of $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ and n-octanal. $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ might also act as the catalyst for the oxidation of n-octanal to obtain more peroxy acids, thus promoting the ODS process. To validate our hypothesis, another contrast experiment was carried out and analyzed by GC method. In which, the analytical sample was prepared by dissolving 20 wt% n-octanal in the n-octane solvent. As shown in Figure S3 (ESI), some but not all n-octanal was oxidized to octanoic acid without catalyst. However, nearly all of n-octanal were oxidized, when $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ was added in the system. The result proved that $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ had the catalytic performance for the oxidation of n-octanal, thus obtaining more peroxy acids to promote the ODS process. Through the above analysis, the studied ODS system was considered as a complex system consisting of the multi-oxidation of sulfur compounds by the action of prepared catalyst and n-octanal. The proposed mechanism was illustrated in Scheme 1: first, $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ reacted with molecular oxygen to obtain peroxy-polyoxometalates, and some of n-octanal also reacted with molecular oxygen to obtain peroxy acids. Then, more peroxy acids was obtained through the catalytic effect of $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$. Finally, the peroxy-polyoxometalates and peroxy acids acted as the real active components to oxidize the sulfur compounds to their corresponding sulfones, and the sulfones were removed through the adsorption of supported catalyst or extraction.



Scheme 1. Schematic of supposed mechanism for oxidative desulfurization of model oil.

Conclusions

In this work, three polyoxometalates were successfully prepared and used as the catalysts for ODS. Among which, $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ exhibited the best performance, corresponding to 99.63% of desulfurization ratio. Furthermore, $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ was supported on GO to obtain $K_6\text{P}_2\text{W}_{18}\text{O}_{62}/\text{GO}$. Due to the high adsorption capacity of GO for ODS products, 96.10% of desulfurization ratio could be achieved using the supported catalyst 17.5% $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$, without extraction. According to the experiment catalyzed by $K_6\text{P}_2\text{W}_{18}\text{O}_{62}/\text{GO}$, 60 °C was determined as the optimum reaction temperature and the supported catalyst was suitable for the model oil with a broad range of initial sulfur contents. Besides, the reaction activity sequence of different sulfur compounds was as $\text{DBT} > 4\text{-DMDBT} > \text{BT}$, determined by the electron density and space steric hindrance on S atom. The experiment of selectivity showed that the desulfurization ratio decreased from 96.10% to 43.25% and 24.10%, when n-octylene and xylene were added into the model oil, respectively, which might be caused by the competitive oxidation. When treated by extraction of MeCN, the desulfurization ratio could increase from 43.25% and 24.10% to 94.31% and 84.45%, respectively. The recovery experiment showed that the supported catalyst could be reused at least for 5 times with little catalysis deactivation. Compared with previous study, $K_6\text{P}_2\text{W}_{18}\text{O}_{62}/\text{GO}$ exhibited much better performance than GO in the n-octanal/air ODS system due to the introduction of $K_6\text{P}_2\text{W}_{18}\text{O}_{62}$. Finally, the mechanism was proposed, and the studied ODS system was considered as a complex process consisting of the multi-oxidation of sulfur compounds by the action of prepared catalyst and n-octanal.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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