Immobilization of K\textsubscript{7}PW\textsubscript{11}O\textsubscript{39} on ZrO\textsubscript{2} Nanofiber: Ultra-deep Desulfurization Based in Extraction Catalytic Oxidation Desulfurization System

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Abstract: In this work, K\textsubscript{7}PW\textsubscript{11}O\textsubscript{39} (abbreviated as PW11) was immobilized on ZrO\textsubscript{2} nanofibers and used as an efficient recyclable catalyst in extraction catalytic oxidation desulfurization system (ECODS). The 500 ppm DBT model oil (5mL) can desulfurize completely within 20 min with the catalytic conditions of 50 °C, 0.010 g 50 wt% CTAB– PW11–ZrO\textsubscript{2} nanofibers and O/S molar ratio \(\text{H}_2\text{O}_2/\text{DBT molar ratio} \) was 2:1. The synthesized catalyst was characterized by Fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS) and thermo gravimetric analyzer (TGA). The results indicated the PW11–ZrO\textsubscript{2} nanofibers were synthesized successfully and the possible catalytic mechanism is also revealed.

Keywords: desulfurization, polyoxometalate, nanofibres, ZrO\textsubscript{2}, PW11

1. Introduction

The use of fuel is increasing year by year [1]. The combustion of organosulfur in fuel had already caused a series of environmental problems, such as the air pollution and the acid rain [2, 3]. Some countries introduced regulations to limit the sulfur content to below 10 ppm in fuel [4]. Ultra-deep desulfurization is in urgent demand.

Hydrodesulfurization (HDS) is a traditional technique for desulfurizing, which has been widely used in removing thiols, sulfides and disulfides. However, high cost, strict operation condition and long reaction time are main drawbacks of the HDS [1, 5]. Thus, several of other techniques emerged in recent years, such as oxidative desulfurization system (ODS) [6], adsorption [7] and bio-desulfurization [8-10]. Extraction catalytic oxidation desulfurization system (ECODS) has received extensive attention because of its excellent desulfurization efficiency under mild condition. So we conducted a series of explorations based on the ECDOS.

The Keggin structure polyoxometallates (POMs) has applied to be the catalyst of the oxidation desulfurization, because it has unique properties and efficient catalytic performance. It was reported that monovalent Keggin-type phosphotungstate ([PW\textsubscript{11}O\textsubscript{39}]\textsuperscript{7−}) as heterogeneous catalysts in solvent-free ODS processes has an excellent catalytic performance [11]. However, pure POMs is hard to apply to industrial applications owing to high solubility and low surface area [12]. Therefore, our experimental work is mainly focus on improving its catalytic surface area and recycling capacity.

In our previous work, nanofiber materials performed well in the conversion of sulfide in ECODS [13, 14]. The surface of nanofibers has lots of loading sites and large specific surface area, which makes it easy to immobilize POMs. Besides, nanofibers can obtain easily via electrospinning [15]. ZrO\textsubscript{2} has been reported to enhance the removal reactivity of sulfides and the regeneration of catalysts with its acid resistance, high strength, large surface area and thermal chemical stability [16]. We also found that Zr-Based Metal-Organic Frameworks can accelerate the desulfurization process. So we immobilized PW\textsubscript{11} on ZrO\textsubscript{2} nanofibers and synthesized a series of PW\textsubscript{11}–ZrO\textsubscript{2} nanofibrous materials.

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Through the combination of ZrO$_2$ and PW$_{11}$, it may overcome the deficiency of high solubility and low surface area to suitable for industry scale desulfurization.

Herein, we explored the morphology, structure, optimal conditions of the desulfurization system, reusability and possible mechanism of PW$_{11}$-ZrO$_2$ nanofibers in this work. We found the PW$_{11}$-ZrO$_2$ nanofibers can desulphurize (5mL model oil contains 500 ppm DBT) completely in 20min with its optimal conditions: temperature is 50°C, H$_2$O$_2$/DBT molar ratio is 2, the dosage of catalysts is 0.01g and the loading amount of PW$_{11}$ on ZrO$_2$ is 50wt%. In addition, the catalyst can be reused over 6 times which prove immobilized PW$_{11}$ on ZrO$_2$ nanofibers do increase the recycling capacity of PW$_{11}$.

2.Materials and methods

2.1 Chemicals

Zirconium(IV) butoxide solution (TNBZ, AR, Beijing Chemical Works), N,N-dimethylformamide (DMF, AR, Tianjin Tiantai Chemical Co. Ltd.), Ethanol (AR, Beijing Chemical Works), Polyvinyl pyrrolidone (PVP, MW = 1300000, Aladdin), Concentrated nitric acid (AR, Beijing Chemical Works), Cetyltrimethyl Ammonium Bromide (CTAB 99%, Energy Chemical), octadecyl trimethyl ammonium bromide (OTACI, 99%, Energy Chemical), dodecyl trimethyl ammonium bromide (DTACI, 99%, Energy Chemical), hydrogen peroxide (H$_2$O$_2$, 30 wt%, Beijing Chemical Works), dibenzothiophene (DBT, 99%, China Pingmei Shenma Energy & Chemical Group Co., Ltd.), dichloromethane (AR, Tianjin Tiantai Chemical Co. Ltd.), n-octane, biphenyl (AR, Tianjin Tiantai Chemical Co. Ltd.), phosphotungstic acid (AR, Beijing Chemical Works), potassium chloride (AR, Beijing Chemical Works), sodium hydrogen phosphate dihydrate, sodium tungstate dihydrate (AR, Beijing Chemical Works),1-Butyl-3-methylimidazolium hexafluorophosphate([Bmim]PF6, AR, Beijing Chemical Works). All chemicals are purchased directly without purification and treatment.

2.2 Synthesis and preparation of the materials

The synthesis process of ZrO$_2$ nanofibers: DMF (1.6 mL), absolute ethanol (1.6 mL), HNO$_3$ (1.0mL) and PVP (0.56g) added in a beaker. Stirring for half an hour. After that, TNBZ (0.52g) was added, and then the solution was stirred 30min to produce the spinning precursor. Then the obtained solution was put into a 5mL plastic syringe. We put one of electrode in the plastic syringe (immersed in solution), and then fix the other electrode on the iron net which 15.3cm away from the plastic syringe, electrospinning with a voltage of 15-16 kV. The droplets at the exit of the syringe are subjected to Coulombic and gravitational forces to form a continuous jet, which refines and stretches as the solvent volatilizes, and finally attaches to the receiver (iron net). After electrospinning, the ZrO$_2$ nanofibers were calcined at 600°C to remove the PVP.

Immobilization of PW$_{11}$ on ZrO$_2$ nanofibers: Potassium salts of [PW$_{11}$O$_{39}$]$^-$ (PW$_{11}$) was synthesized according to the literature [17]. ZrO$_2$ nanofibers (0.060g) were dissolved in deionized water (10 mL) and ethanol (10 mL), stirring for 10h; PW$_{11}$ (0.060g) and surfactants (0.060g) were dissolved in deionized water (10 mL) and ethanol (10 mL), stirring for 10h. Then mixing them and stirring for 24h. After that, washing the precipitations with water and ethanol. Ultimately, drying at 50°C for 24h. The 50-CTAB-PW$_{11}$-ZrO$_2$ nanofibers were synthesized. A series of PW$_{11}$-ZrO$_2$ nanofibers prepared with similar way.

2.3 Desulfurization experiments

DBT (0.1g) and biphenyl (0.2g, as the standard substance) dissolved in n-octane(100mL), and the model oil with sulfur content of 500ppm was prepared. Then, putting model oil (5mL), IL ([Bmim]PF6), H$_2$O$_2$(definitive amount) and catalysts (definitive amount) into a flask. The upper oil sample was analyzed on gas chromatography (Agilent 7820A) after reacting for a while.
2.4 Characteristics

The infrared (FT-IR) absorption spectra were examined with KBr Pelles on a Mattson Alpha-Centauri Fourier transform infrared spectrometer, and the range was fixed in 4000–400 cm\(^{-1}\) with the number of scan 64 and the resolution 4 cm\(^{-1}\). Thermogravimetric analysis (TG) was implemented on a Perkin-Elmer Thermal Analyzer under nitrogen atmosphere at a heating rate of 10°C/min. XRD analysis used a Powder Rigaku D/max-RA XRD which 20 range from 10° to 80° with Cu Kα radiation. Transmission electron microscope (TEM) analysis was carried out using a JEM-2010 transmission electron microscope. The elemental analysis and mapping of product were employed using OXFORD ISIS-300 energy-dispersive spectrometer. The Agilent 7820A-GC System using DB-5 chromatographic column with 30m×0.32mm×0.25μm was used to GC analysis, and injection port temperature was 200°C, detector temperature was 250°C, and 150°C was immobilized as oven temperature.

3. Results and discussion

3.1 Catalysts characterization

We used PXRD analysis (2θ, 10°-80°) to research the structure of 50-CTAB-PW\(_{11}\)-ZrO\(_2\) nanofibers. Figure S1 showed the PXRD spectra of 50-CTAB-PW\(_{11}\)-ZrO\(_2\) nanofibers after six cycles which are pure t-phase ZrO\(_2\) (PDF#50-1089). It proves that the structure of the catalyst is unchanged after six cycles. We also explored the phase structure of PW\(_{11}\)-ZrO\(_2\) materials with various cations. From Figure 1, 50-DTA-PW\(_{11}\)-ZrO\(_2\) nanofibers and 50-OTA-PW\(_{11}\)-ZrO\(_2\) nanofibers appeared the characteristic peaks of mixture t-phase (PDF#50-1089) and monoclinic phase ZrO\(_2\) (PDF#37-1484), implying the structure of the ZrO\(_2\) will change with different cations.

We find the characteristic peaks of PW\(_{11}\) in Figure 2a are changed to 957, 902 and 712 cm\(^{-1}\); it's maybe due to the strong interaction between PW\(_{11}\) and CTAB [21]. In addition, the Figure S2 showed FT-IR spectra of different loading amounts.

![Figure 1. PXRD spectra of 50-CTAB-PW\(_{11}\)-ZrO\(_2\) nanofibers(a), 50-DTA-PW\(_{11}\)-ZrO\(_2\) nanofibers(b) and 50-OTA-PW\(_{11}\)-ZrO\(_2\) nanofibers(c)](image-url)
FE-SEM showed the surface morphologies of 50-CTAB-PW\textsubscript{11}-ZrO\textsubscript{2} and 50-CTAB-PW\textsubscript{11}-ZrO\textsubscript{2} after six cycles. In Figure 3a, fibrous ZrO\textsubscript{2} evenly distributed on the image, which showed uniform diameters. After cycling, these fibers gathered together due to agitation during the reaction (Figure 3b), which may reduce the catalytic efficiency. From Figure 3c, many obvious black spots were prominent on the ZrO\textsubscript{2} nanofibers [22]. It proved that PW\textsubscript{11} are loaded on the nanofibers. As the elemental mapping showed in Figure 3(d), P, W, Zr had excellent dispersibility on the ZrO\textsubscript{2} nanofibers. It also illustrated these elements are present in the catalyst. The energy dispersive spectrum (EDS) was also investigated. Zr, O, W, C, N and P elements were observed in Figure 4 and Figure 5. The results proved that 50-CTAB-PW\textsubscript{11}-ZrO\textsubscript{2} nanofiber was highly pure and the element of the catalyst is unchanged after six cycles.

In addition, we treated the catalyst at high temperature, the thermogravimetric (TG) image showed that the catalyst remains stable in mass below 100°C (Figure S3).
3.2 Catalytic performances

3.2.1 The impact of Different systems and different catalysts

Figure 6 exhibits desulfurization efficiency of 50-CTAB-PW$_{11}$-ZrO$_2$ nanofibers, POMs and bare ZrO$_2$ nanofibers. The PW$_{11}$ showed a high catalytic activity, which removed sulfur completely under 60min. But the desulfurization efficiency is still lower than the 50-CTAB-PW$_{11}$-ZrO$_2$ nanofibers. A possible reason is PW$_{11}$ has the water solubility. DBT removal efficiency is 7.2% for bare ZrO$_2$ nanofibers in 60min; it may be due to the physical adsorptive capacity of bare ZrO$_2$ nanofibers. However, when PW$_{11}$ loaded on the ZrO$_2$ nanofibers, the desulfurization time reduced to 20min. It proved that there is an interaction between PW$_{11}$ and ZrO$_2$ nanofibers in the 50-CTAB-PW$_{11}$-ZrO$_2$ nanofibers to improve the catalytic performance.

We compared the desulfurization efficiency with different PW11 catalysts in Table S1. We found that CTAB-PW$_{11}$-ZrO$_2$ nanofibers have better catalytic performance than other catalysts.
3.2.2 The impact of temperature on desulfurization

As the main factor of oxidative desulfurization efficiency, reaction temperature on DBT conversion is investigated (Figure 7). With the reaction temperature of 30°C, the sulfur removal time are 40 min. When the temperature increasing to 50 and 70°C, the required time for complete sulfur removal was reached in 20 min. The reason for the different DBT conventional speed is related to the acceleration of molecular motion. Higher temperature will accelerate the movement of molecules [23, 24]. However, high temperature can also cause the self-decomposition of H$_2$O$_2$, resulting in the reduction of efficiency [25]. Considering the economizing energy and reaction efficiency, 50°C are chosen as an optimal temperature.

3.2.3 Desulfurization efficiency of different H$_2$O$_2$/DBT (O/S) molar ratio

The amount of oxidant also profoundly affects the catalytic efficiency. In terms of stoichiometric relationship, 1 mol H$_2$O$_2$ can oxidize 2 mol sulfone [26]. We chose a series of different proportions of O/S molar ratio (1:1, 2:1, 4:1 and 8:1) to test the DBT removal efficiency. In Figure 8, the best O/S molar ratio is 2:1. When the ratio of O/S molar ratio increases to 4:1 and 8:1, the DBT removal time extends to 30 and 60 min. The reduction of catalyst efficiency is due to the nonproductive decomposition of H$_2$O$_2$ itself, and more oxidants will increase the rate of self-decomposition [27], which means more
water will be led into this reaction system. That will cause a decrease in the concentration of active sites [28]. Therefore, the 2:1 is the most appropriate O/S molar ratio.

Figure 8. Influences of different O/S molar ratio. Reaction conditions:
50°C, mcat = 0.01 g,
50-CTAB-PW_{11}-ZrO_{2} nanofibers

3.2.4 Influence of different cations on DBT removal

We compared the desulfurization efficiency with different cations. As could be observed in Figure 9, the 50-CTAB-PW_{11}-ZrO_{2} nanofibers used 20min to remove the DBT altogether, while the 50-DTA-PW_{11}-ZrO_{2} nanofibers and 50-OTA-PW_{11}-ZrO_{2} nanofibers taking 25min to achieve 100% desulfurization efficiency. The length of the carbon chain will affect the catalytic efficiency [29]. Long single-alkyl chain will provide a dual trap for both DBT and H_{2}O, but it's not conducive to the contact between sulfide and the active site of catalyst when the single-alkyl chain is too long [30]. So the CTAB was chosen as the suitable cation.

Figure 9. Influences of different cations.
Reaction conditions: 50°C,
O/S = 2, mcat = 0.01g

3.2.5 The impact of 50-CTBA-PW11 nanofibers dosage on desulfurization efficiency

Figure 10 showed the impact of catalyst dosage. The DBT was removed within 40 and 20min by using 0.005 and 0.010g catalyst, respectively. When the catalyst dosage increased to 0.020g, it also used 20min to complete desulfurization. The aggregation of nanofibers may have occurred, because of the excess catalysts. Accordingly, we concluded the best dosage of 50-CTAB-PW_{11}-ZrO_{2} nanofibers was 0.01g.
3.2.6 The effect of CTAB-PW_{11}-ZrO_{2} nanofibers loading amount on DBT removal

The CTAB-PW_{11}-ZrO_{2} nanofibers loading amount is a leading role for desulfurization, which determines the number of active species. Figure 11 shows the desulfurization efficiency of different CTAB-PW_{11}-ZrO_{2} nanofibers loading amount. It took about 20 and 30 min with 50wt% and 60wt% of CTAB-PW_{11}-ZrO_{2} nanofibers loading amount to remove sulfur completely. The probable cause was the excess catalysts cover of active sites [31]. Therefore we chose 50wt% as the best loading amount for the sake of saving catalyst.

3.2.7 Recycling

After each reaction was completed, the catalyst was collected by centrifugation and washed with methylene dichloride. When 50-CTAB-PW_{11}-ZrO_{2} nanofibers was put in the oven for 8h (80°C) and dried again, it was collected for desulfurization experiments. As shown in Figure 12, 50-CTAB-PW_{11}-ZrO_{2} nanofibers could maintain high DBT catalytic efficiency (higher than 95%), after going through six cycles. The results revealed that 50-CTAB-PW_{11}-ZrO_{2} nanofibers could recycle at least six times.
3.2.8 Mechanism

Figure 13 illustrated the ECODS mechanism of CTAB-PW\textsubscript{11}-ZrO\textsubscript{2} nanofiber. There are three phases in this system: oil phase (containing DBT), H\textsubscript{2}O\textsubscript{2} phase (containing oxidative agent) and IL phase (dispersive catalysts). Magnetic stirring makes the three phases in fully contact. H\textsubscript{2}O\textsubscript{2} will approach PW\textsubscript{11} [32], because of its hydrophilicity. DBT will tend to the carbon chain, because of its hydrophobicity. At the beginning of the catalytic process, [Bmim]PF\textsubscript{6} extracted DBT to IL phase, and then W=O of PW\textsubscript{11} was oxidized to peroxo species W (O\textsubscript{2}). After that, the peroxo species W (O\textsubscript{2}) oxidised DBT to DBTO\textsubscript{2} while peroxo species W (O\textsubscript{2}) reducing into W=O [33]. DBTO\textsubscript{2} has a high polarity, so it will remain at IL phase, resulting in a sustained decrease of DBT concentration in oil.

4. Conclusions

In this work, catalyst for desulfurization were successfully synthesized by electrospinning and applied to the desulfurization process. The DBT could be removed completely within 20 min with catalytic conditions of 50°C, 0.010 g 50-CTAB–PW\textsubscript{11}–ZrO\textsubscript{2} nanofibers and ratio of O/S molar was 2:1. It showed the excellent catalytic effect of PW\textsubscript{11} immobilized on ZrO\textsubscript{2} nanofibers. Besides, the catalyst could be easily reused for six consecutive cycles.
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Electronic Supporting Information (ESI)

1. XRD patterns of CTAB-PW₁₁-ZrO₂ nanofibers and CTAB-PW₁₁-ZrO₂ nanofibers after six cycles.

Figure S1 XRD patterns of CTAB-PW₁₁-ZrO₂ nanofibers(a) and CTAB-PW₁₁-ZrO₂ nanofibers after six cycles(b)

Figure S1 showed the PXRD spectra of CTAB-PW₁₁-ZrO₂ nanofibers and catalyst after circulation are pure t-phase ZrO₂ (PDF#50-1089), which has diffraction peaks of 30.270, 35.255, 50.377, 59.610, 60.205. It proves that the structure of the catalyst is unchanged after six cycles

2. FT-IR spectra of different loading amounts.

Figure S2 FT-IR spectra of 40%wt-CTAB-PW₁₁-ZrO₂ (a), 50%wt-CTAB-PW₁₁-ZrO₂ (b), 60%wt-CTAB-PW₁₁-ZrO₂ (c)

Figure S2 showed 40%wt-CTAB-PW₁₁-ZrO₂(a), 50%wt-CTAB-PW₁₁-ZrO₂(b) and 60%wt-CTAB-PW₁₁-ZrO₂(c) have similar spectra. This means the intact structure of catalysts still retain under different loading amount
3. Thermogravimetric (TG) image of CTAB-PW₁₁-ZrO₂ nanofibers.

Figure S3 TG image of CTAB-PW₁₁-ZrO₂ nanofibers

Figure S3 showed that the catalyst remains stable in mass below 100°C, which proved PW₁₁-ZrO₂ nanofibers can function as a desulfation catalyst under mild conditions.

4. Table for DBT removal efficiency of different catalysts

<table>
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<tr>
<th>Entry</th>
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<th>Desulfurization efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
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<td>1</td>
<td>Tb (PW₁₁) 2 @ MIL-101</td>
<td>120min</td>
<td>50</td>
<td>100</td>
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<tr>
<td>2</td>
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<td>40min</td>
<td>70</td>
<td>100</td>
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</tr>
<tr>
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<td>PW₁₁ / MSPM</td>
<td>120min</td>
<td>60</td>
<td>99.7</td>
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<td>60min</td>
<td>70</td>
<td>99.82</td>
<td>4[36]</td>
</tr>
<tr>
<td>5</td>
<td>PW₁₁ / SiO₂</td>
<td>90min</td>
<td>60</td>
<td>99.96</td>
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<td>6</td>
<td>CTAB-PW₁₁-ZrO₂ NF</td>
<td>20min</td>
<td>50</td>
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