Application of Fumed Silica as a Support during Oxidative Desulfurization

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ABSTRACT: Here, a hydrophilic fumed silica (F-SiO₂) was used as a support, and we place phosphotungstic acid (HPW) onto the F-SiO₂ via a simple impregnation method normally used to prepare a HPW/F-SiO₂ catalyst, which is used in oxidative desulfurization processes. A number of characterization analyses were used, such as X-ray diffraction, Fourier transform infrared, and Transmission electron microscopy, to prove that the HPW catalyst was homogeneously distributed on the F-SiO₂. The structural parameters of the catalyst and the support were tested with Brunauer–Emmett–Teller, and it was confirmed that the catalyst is a mesoporous material. Energy-dispersive spectrometry was used to characterize the distribution of the active component distribution. Catalytic performance was investigated using the catalytic oxidative desulfurization process. During optimal conditions, the removal effect of dibenzothiophene (DBT) in simulated oil can reach 100%. After 13 cycles, catalytic activity is still high, and the DBT conversion can still attain 95.362%.

1. INTRODUCTION

The main components of acid rain are the sulfur oxides produced via fuel combustion. The formation of acid rain can lead to serious environmental pollution, destroy ecosystems, and endanger human health. Therefore, the deep desulfurization of fuel oil has gradually become an urgent environmental issue and requires a solution.¹ Hydrodesulfurization is a relatively developed technology that can remove the majority of sulfides. However, because of steric hindrance, the removal effect of heterocyclic sulfides and their derivatives is not effective. Therefore, previous studies have developed various desulfurization technologies, such as adsorption,² extraction,³,⁴ and oxidative desulfurization (ODS). Among these methods, the ODS process is one of the most promising because of advantages with mild reaction conditions, simple operation processes, and highly efficient desulfurization. Excellent desulfurization effect required specific catalysts. Among the various catalysts,⁵–⁸ heteropolyacids, characterized by a Keggin structure, have attracted significant attention for catalysis applications, such as in sulfur-containing compounds.⁹ In the presence of excess hydrogen peroxide, the HPW peroxided and decomposed to generate an anionic peroxide metal complex W(O₂)₆, which provides an active site for ODS.¹⁰ However, homogeneous heteropolyacid catalysts pose difficulties when attempting to separate them from the ODS process. Thus, it is difficult to use them in industrial application. In order to overcome these shortcomings, numerous previous studies have attempted to immobilize HPW onto a support to increase the recycle number.

Support selection should consider the properties and structure of the material, which includes the presence of a strong interaction between the support and HPW to ensure that HPW loads onto the support. Xiao et al.¹¹ prepared a HPW/AC (activated carbon) catalyst using activated carbon as a support. In the simulated oil system, they studied the thiophene removal effect, and a high thiophene conversion can be reached to 90% at 363 K after 2 h. Catalyst pore size is only 1.95 nm, which affects HPW loading and mass transfer during the reaction process, resulting in a relatively long reaction time. Yang et al.¹² loaded HPW using multistage porous silica as a support to the ODS of fuel oil. At 333 K and 0.1 g catalyst, O/S = 12, the reaction conversion can reach to 100%, after 2 h, but after the catalyst is recovered seven times, the desulfurization effect dropped to below 96.2%. Although the catalyst has a large specific surface area and high activity, the catalyst pore diameter is only 5.1 nm. This type of structure leads to an unevenly distributed HPW, which results in excessive loading of the active component. In addition, the reaction time was still 2 h with a large amount of hydrogen peroxide. Yue et al.¹³ also studied HPW loading onto silica with multistage pores, which not only maintains a high specific surface area but also provides pore structures with different sizes to improve catalyst performance. Under the optimal conditions, the dibenzothiophene (DBT) removal can reach to 99.8% but dropped to 95.1% after eight cycles. The results indicate an enhancement of catalyst stability. However, there are few active sites exposed on the surface are few, which does not successfully reduce the load. In order to solve this problem,
we studied the application of various supports in ODS. In our previous studies, we studied the applications of catalysts to improve the catalyst recovery capacity during ODS, such as HPW/NH₂-MCM-41 and HPW/mpg-C₃N₄ in ODS reactions. Amino modification of the MCM-41 molecular sieve enhances the interaction between HPW and the support, and this interaction reduces the loss of HPW during the reaction. The amino modification reduced the amount of catalyst and reduced the amount of HPW. The HPW/NH₂-MCM-41 catalyst did not significantly decline the catalytic performance. However, the HPW load remains as high as 20 wt %. HPW/mpg-C₃N₄ was prepared via the impregnation method using a mesoporous graphite carbonitrile material as the support. The HPW/mpg-C₃N₄ catalyst is reusable (15 cycles) without a significant change of catalytic activity, indicating a significant improvement in catalyst stability. Although catalyst pore size increases to 10.6 nm, HPW is prone to agglomeration because of their smaller specific surface areas. Therefore, large loads still remain a problem. Huang et al. prepared a HPW/NOLC catalyst by doping nitrogen into an onion-like carbon (NOLC) support. The catalyst not only has a higher specific surface area but has also a pore size of 11.38 nm, which allows the HPW to disperse more efficiently on the support. A HPW/NOLC catalyst (10 wt %) can achieve 100% desulfurization effect in simulated oil within 2 h. However, the support preparation process is complex and uses an expensive diamond carbon source. At the same time, because of the small specific surface area of the catalyst, HPW is prone to agglomeration and cannot be industrially produced.

Therefore, we must choose a support that has a large specific surface area and a strong binding force with HPW. Hydrosilicic F-SiO₂ is an inert carrier characterized by a low bulk density, large specific surface area, and suitable wetting properties. F-SiO₂ can form a stable suspension in water, and the addition of F-SiO₂ can improve solution properties, thereby a solution wettability and surface energy increase. HPW/F-SiO₂ is also very soluble in water. These special properties allow the effective dispersion of HPW onto the surface of the F-SiO₂ during the impregnation process with a strong bonding force. A simple impregnation method allows the loading of HPW onto the F-SiO₂. The HPW/F-SiO₂ catalyst not only has a high activity at low loading but also has high stability.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. Figure 1 displays the X-ray diffraction (XRD) patterns for the F-SiO₂, HPW, and HPW/F-SiO₂ samples with different HPW contents (10–50 wt %). In Figure 1, the diffraction peak of F-SiO₂ was observed at 2θ = 21.7°, which proves that the support is amorphous silica. This diffraction peak also exists in the four other HPW/F-SiO₂ catalysts. The characteristic diffraction peak of HPW was not observed for 10–30 wt % catalysts with different loads, which indicates that the amount of active component HPW loaded onto the F-SiO₂ support is relatively small. However, the characteristic diffraction peaks of HPW at 25.72, 35.18, 38.24, 53.59, and 60.21° were clearly observed in the 50 wt % HPW/F-SiO₂ catalyst, indicating that HPW was successfully supported on the F-SiO₂ support.

Figure 2 shows the Fourier transform infrared (FTIR) spectra of the HPW, F-SiO₂, and HPW/F-SiO₂ samples. The characteristic peaks of the HPW were observed with the Keggin structure at 1077, 983, 896, and 810 cm⁻¹, which are attributed to the stretching vibrations of the P–O, W–O, W–O bonds in WO₆ octahedron) still exists in the FTIR spectrum of the 50 wt % HPW/SiO₂ catalyst. At 896 cm⁻¹ (W–Oc–W Bridge oxygen bond vibration) and 810 cm⁻¹ (W–Oc–W Bridge oxygen bond vibration), the absorption peak gradually increases with the increase of the load, which suggests that the HPW Keggin structures were loaded onto the F-SiO₂ support successfully. At the same time, a force was generated between HPW and the carrier, consistent with the XRD characterization results.

The N₂ adsorption/desorption isotherms for the F-SiO₂ and HPW/F-SiO₂ samples with varying HPW contents are shown in Figure 3A. Together, the five samples represent a type-IV adsorption isotherm characteristic of a type-H1 hysteresis loop with a relative pressure ranging from 0.8 to 1.0. These characteristics indicate that the F-SiO₂ support has a mesoporous structure, and the mesoporous structure still exists after loading the HPW. Figure 3B shows the pore size

Figure 1. XRD patterns of (a) HPW, (b) F-SiO₂, (c) 10 wt % HPW/F-SiO₂, (d) 20 wt % HPW/F-SiO₂, (e) 30 wt % HPW/F-SiO₂, and (f) 50 wt % HPW/F-SiO₂.

Figure 2. FTIR spectra of (a) F-SiO₂, (b) 5 wt % HPW/SiO₂, (c) 10 wt % HPW/F-SiO₂, (d) 20 wt % HPW/F-SiO₂, (e) 30 wt % HPW/F-SiO₂, and (f) HPW.
distribution curves for the 10 wt % HPW/F-SiO₂ sample. The average pore size is approximately 36 nm, which is consistent with the pore size of Brunauer–Emmett–Teller (BET). Figure 3C displays the F-SiO₂ particle size distribution. The wide particle size distribution is because of the clustering of the silica particles, which reduces the bulk density of the support forming fluffy large particles, such that HPW is more dispersed and fixed on the surface of the F-SiO₂. Table 1 lists the sample physio-chemical structure parameters. Based on the data in the table, the catalyst specific surface area decreased gradually with an increasing load. As the loading increases, the specific surface area of the catalyst decreases slightly mainly because the HPW-loaded support surface occupies a certain surface, but it has a specific surface area, so the decrease is small. The pore volume and size of the HPW/F-SiO₂ catalyst are more than twice those of the pure carrier. This is mainly because the fumed silica has strong cohesiveness, a gel is formed during the preparation of the catalyst, and the silica particles are bonded to each other. The particle deposits cause a sharp increase in pore volume and pore size and also increase the specific surface area, which is one of the reasons why the loading amount increases and the specific surface area of the catalyst does not change much. The larger specific surface area permits a high dispersion of HPW on the support surface, and the larger mesoporous pore size accelerates mass transfer in the reaction process. Thus, catalysts with low loading can attain a high activity in the ODS process.

To demonstrate the high HPW active component dispersion on the F-SiO₂ surface, we tested HPW dispersion on the support. As Figure 4 shows, transmission electron microscopy (TEM) analyses indicate that the HPW did not agglomerate on the F-SiO₂ surface, which suggests that HPW is highly dispersed along the F-SiO₂ support surface. To verify these results, the dispersion of P and W element in the HPW is uniform on the F-SiO₂ surface using high-resolution energy-dispersive spectrometry (EDS) elemental maps. These analyses further illustrate the uniform dispersion of HPW on the F-SiO₂ support.

### Table 1. Catalyst Structure Parameters

| sample         | \( S_{\text{BET}} \) (\( \text{m}^2/\text{g} \)) | \( V_p \) (\( \text{cm}^3/\text{g} \)) | \( d \) (nm) |
|----------------|-----------------|-----------------|---------|
| F-SiO₂         | 205.08           | 0.6288           | 15.21   |
| HPW            | 10.03            | 0.0208           | 10.87   |
| 5 wt % HPW/F-SiO₂ | 203.94           | 1.3834           | 35.25   |
| 10 wt % HPW/F-SiO₂ | 195.08           | 1.3335           | 35.36   |
| 20 wt % HPW/F-SiO₂ | 193.14           | 1.4464           | 36.91   |
| 30 wt % HPW/F-SiO₂ | 179.76           | 1.3316           | 36.01   |

Figure 3. (A) Nitrogen adsorption/desorption isotherms for: (a) F-SiO₂, (b) 5 wt % HPW/F-SiO₂, (c) 10 wt % HPW/F-SiO₂, (d) 20 wt % HPW/F-SiO₂, and (e) 30 wt % HPW/F-SiO₂. (B) Pore size distribution curves for 10 wt % HPW/F-SiO₂. (C) Particle diameter distribution curves for F-SiO₂.

Figure 4. TEM and elemental mapping images of the 10 wt % HPW/F-SiO₂ sample and EDS mapping of O (red), Si (green), P (yellow), and W (blue).
HPW/F-SiO₂, and 30 wt % HPW/F-SiO₂ is nearly 100%. The DBT removal effect for the 5 wt % HPW/F-SiO₂ catalyst is not complete because of a low level of loading, which did not provide a sufficient amount of active sites for the reaction. For a larger load in the 30 wt % HPW/F-SiO₂ catalyst, the load amount induces active component agglomeration and reduces the catalyst specific surface area, resulting in a lower desulfurization effect. The optimal HPW load is 10 wt %, which is lower than previously reported in the literature. 12,13

We optimized the various reaction conditions, which include reaction temperature, reaction time, catalyst dosage, and O/S, as shown in Figure 6. Figure 6A shows the relationship between the DBT removal effect in simulated oil and the reaction temperature. With an increase in temperature, the DBT conversion increases. The sulfur removal increases rapidly between 303 and 313 K with no significant changes after 313 K. When temperature reached 343 K, the DBT removal effect decreased slightly because of the excessive temperature, which caused the decomposition of H₂O₂ and a decrease in the W(O₂)₆ concentration. 25 Consequently, the optimal reaction temperature for the HPW/F-SiO₂ catalyst is 313 K. The reaction temperature in this experiment is lower than previously reported catalyst experiments. Figure 6B examines the relationship between the DBT removal effect and reaction time. The DBT conversion is nearly 100%. Within 1 h, the DBT had completely oxidized to sulfone or sulfoxide, and the desulfurization effect became nearly stable with time. Therefore, the optimal reaction time is 1 h. Compared with previous studies, the reaction time required to obtain a 100% desulfurization effect is shorter. As shown in Figure 6C, the O/S ratio has a significant impact on the DBT removal. With an increase in the O/S molar ratio, the DBT desulfurization effect increased until the O/S ratio increased to 4, after which the desulfurization effect tended to remain stable. However, at an O/S ratio of 12, the DBT conversion decreased slightly. This is possibly because of an excessive amount of aqueous hydrogen peroxide attached to the surface of the catalyst, which affects DBT adsorption on the catalyst surface. 26 However, the theoretical O/S molar ratio for the oxidation of DBT to the corresponding sulfone is 2, and the actual O/S molar ratio is greater than the theoretical value because of a H₂O₂ component that has decomposed. Therefore, the optimum O/S molar ratio is 4. Figure 6D shows that the DBT conversion increases with an increase in the HPW/SiO₂ catalyst dosage. When the catalyst dosage was 0.06 g/10 mL, the desulfurization effect was nearly 100%. This result indicates that the 0.06 g/10 mL catalyst can provide a sufficient amount of active sites in the simulated oil. Under the optimal conditions, the DBT desulfurization effect is near 100%, and compared with the previous catalyst, the catalyst prepared in this experiment has higher activity. In summary, the optimal

![Figure 5](https://example.com/figure5.png)

**Figure 5.** DBT conversion in the ODS process with varying HPW contents.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** (A) Effects of reaction temperature (catalyst dosage = 0.1 g/10 mL, O/S = 10, t = 1 h). (B) Effects of reaction time (T = 313 K, O/S = 10, catalyst dosage = 0.1 g/10 mL). (C) Effects of O/S molar ratio (T = 313 K, t = 1 h, catalyst dosage = 0.1 g/10 mL), and (D) effects of catalyst dosage (t = 1 h, T = 313 K, O/S = 4).
conditions for this experiment are $T = 313$ K, $t = 60$ min, O/S = 4, and catalyst dosage = 0.06 g/10 mL.

Figure 7 compares the catalytic activity for the various sulfides. The experimental results show that the DBT conversion can attain 100% in 1 h, and the benzothiophene (BT) conversion after 1 h of reaction is 73.91%, which is because of the different sulfur atom electron density in various sulfides. The sulfur atom electron density in DBT is 5.758, whereas it is 5.739 in BT.27 Higher electron densities more easily induce the oxidation of the sulfur atom. The electron density of a sulfur atom in 4,6-dimethyldibenzothiophene (4,6-DMDBT) is higher than the electron density of a sulfur atom in DBT. However, the 4,6-DMDBT desulfurization effect in this experiment is lower than the DBT removal. This deviation is possibly due to the fact that the functional groups around the S atom hinder contact between the sulfur atom and the catalytically active site. The electron density of the sulfur atom of Th is 5.696, so the conversion of Th is the lowest. Figure 7 shows that the sulfur removal for the sulfur-containing compounds, under the optimal reaction conditions, follows the order DBT > 4,6-DMDBT > BT > Th. Therefore, the sulfur removal for the sulfur-containing compounds is not only affected by the sulfur atom electron density but also by steric hindrance.

The DBT oxidation process is a quasi-first-order reaction that conforms to the first-order reaction kinetic equation, as shown by eq 1.

$$ r = -\frac{dc_t}{dt} = kC_t $$

(1)

Based on the results shown in Figure 9A, we use eq 2 to obtain the reaction rate constant $k$.

$$ \ln \left( \frac{c_t}{c_0} \right) = -kt $$

(2)

The reaction activation energy was calculated based on the Arrhenius equation, shown in eq 3.

$$ \ln k = \ln A - \frac{E_a}{RT} $$

(3)

As is shown in Figure 8B, based on the Arrhenius equation, we calculated the apparent activation energy of the 10 wt % HPW/F-SiO$_2$ catalyst during ODS to be 36.96 kJ mol$^{-1}$. This result was slightly lower than the previously reported value,$^{13}$ which indicates that the 10 wt % HPW/F-SiO$_2$ catalyst had excellent catalytic activity during ODS.

The 10 wt % HPW/F-SiO$_2$ was recycled, and the number of cycles was determined, as shown in Figure 9. After the ODS reaction, the catalyst was separated by filtration, dried at 353 K, and subjected to the next desulfurization reaction. Figure 9 shows that, after the 11th cycle, the DBT removal remains above 99%. After the 12th cycle, the DBT removal begins to relatively small decrease. After 13 cycles, the DBT removal dropped to 95.362%, which indicates that the 10 wt % HPW/F-SiO$_2$ catalyst has excellent recyclability.

The HPW content of the 10 wt %HPW/F-SiO$_2$ catalyst during recycling was tested by inductively coupled plasma (ICP). Table 2 shows that the HPW content in the fresh 10 wt

![Figure 7](image7.png)  
**Figure 7.** Relationship between the removal of various sulfides and time for (a) DBT, (b) 4,6-DMDBT, (c) BT, and (d) Th.

![Figure 8](image8.png)  
**Figure 8.** (A) Pseudo-first-order rate model data at various temperatures for catalyst 10 wt % HPW/F-SiO$_2$. (B) Determination of reaction activation energies.

![Figure 9](image9.png)  
**Figure 9.** Effects of recycling times on DBT conversion.
%HPW/F-SiO₂ catalyst is 4.86%. The main reason is that it is impossible to completely enter the pore structure of the carrier during the loading process. The HPW molecules do not enter pores, causing the pores to block, which is also the reason for the pore size bigger of the catalyst. With the increase of the number of cycles, the content of HPW in the catalyst gradually decreased, resulting in a decrease in catalytic performance. After the 13th cycle, the content of HPW in the catalyst was 2.05%, and the removal of DBT was reduced to 95.362%. The content of HPW in the catalyst was reduced by 2.81%, indicating that the silica can effectively fix the HPW, so that the catalyst has better stability.

Catalytic performance decreases with the loss of the active component. To investigate the loss of the active component, we performed a thermal filtration experiment. When the reaction performed for 0.5 h, we filtered out the catalyst to compare the desulfurization effect with the presence of the 10 wt % HPW/F-SiO₂ catalyst. As Figure 10 shows, the desulfurization effect after filtration is significantly lower than in the case with the presence of the 10 wt % HPW/F-SiO₂ catalyst, indicating that the loss of the active components in the catalyst is very small.

In the presence of excess hydrogen peroxide, HPW peroxide decomposes to form an anionic peroxide metal complex \( W(O_2)_n^- \), which provides an active site for ODS. As shown in Scheme 1, \( W=O \) in the HPW molecule is converted from hydrogen peroxide to tungsten peroxide and participates in the ODS reaction.
tested catalyst desulphurization performance by using the above substances as raw materials and dissolved them into 100 ppm model oil. Model oil (10 mL) was poured into a 100 mL three-mouth flask, a quantitative catalyst was added, and then dispersed via ultrasonication. The flask was placed in a water bath, 36% hydrogen peroxide solution was added at a specific O/S ratio under stirring. After the reaction completion, the reaction solution was poured into a 25 mL beaker, and 10 mL of methanol was added for extraction. After extraction, the sulfur content was measured with a Coulomb instrument WK-2D.

In kinetic experiments, the reaction activation energy was calculated by measuring the change in the DBT concentration at different temperatures using the Arrhenius equation.

The activity evaluation index of the catalyst is represented by the removal of the sulfide in the model oil. The method for calculating the sulphide conversion is as follows

$$\text{Sulfur removal} (\%) = - \frac{C_0 - C_t}{C_0} \times 100\%$$  \hspace{1cm} (4)

$C_0$ refers to the sulfur concentration initially in the model oil, and $C_t$ refers to the value measured by the Coulomb instrument WK-2D analyzer after the model oil is subjected to the catalytic oxidation reaction.

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**Notes**

The authors declare no competing financial interest.

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