

# Driving Sustainable Solutions: Exploring Supported-Polyoxometalate Catalysts for Enhanced Oxidative Desulfurization

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Sulfur oxides that originate from fuels can cause compounding damage to the environment if left unchecked. As such, deeper desulfurization methods have been researched for higher sulfur conversion for cleaner fuels. Oxidative desulfurization (ODS) is a promising substitute for hydrodesulfurization as it focuses on organosulfur compounds and has lower reaction conditions. Improving the conversion percent involves several parameters, such as reaction temperature, oxidant concentration, catalyst dosage, and catalyst nature. One of the most efficient catalysts for ODS is polyoxometalates. They are homogeneous catalysts with transition metal centers. This makes it difficult to extract from the fuel to reuse in another ODS cycle. This paper reviews the available supports for polyoxometalate catalysts which help increase recyclability and conversion efficiency. Supports create heterogeneous catalysts that are easier to extract after ODS. These include metal oxides, activated carbon, silica, and metal-organic frameworks (MOF). Metal oxides tend to be the most stable due to strong intermolecular bonds between the polyoxometalate and the metal. They can also be customized depending on the catalyst requirements. Activated carbon and silica are incredibly porous which are desirable qualities for a heterogeneous catalyst. It allows for more sulfur to adhere to the surface of the catalyst which increases the conversion percentage. MOFs have the benefit of being porous while also having adsorptive desulfurization capabilities. Increasing recyclability can increase the volume of desulfurized fuel while reducing costs.

## 1. Introduction

Increasing awareness of the hazards of sulfur emissions have led to smaller thresholds of allowable levels of this in fuels. 40 million t of SO<sub>2</sub> were released last 2019 mainly attributed to the combustion of fossil fuels due to human activity (Dahiya et al., 2020). These sulfides can cause a host of environmental issues like corrosion, haze, and acid rain if released unchecked into the atmosphere (Zhou et al., 2022). This can also poison catalysts in downstream refinement processes which would render them ineffective (Fayad et al., 2022). They also cause lung and heart disease, dementia, and fertility issues, as well as being responsible for 4.5 M premature deaths in 2019 (Dahiya et al., 2020). Inorganic sulfur compounds are easiest to remove with current methods, but organic sulfur compounds like benzothiophene (BT) and dibenzothiophene (DBT) are more difficult because of steric strain (Rajendran et al., 2020). It then becomes more important to reduce these compounds to prevent further pollutants from reaching the atmosphere.



Figure 1: Diagram of the effect of sulfur emissions on the environment.

Hydrodesulfurization (HDS) converts aliphatic hydrocarbons and hydrogen sulfide in harsh conditions. It requires a large amount of  $H_2$  and has selectivity issues with alkene hydrogenation (Rajendran et al., 2020). It also has difficulty processing organic sulfur compounds because of this which are more abundant in fuel oils and their alternatives, such as pyrolysis oil (Haruna et al., 2022). Oxidative desulfurization (ODS) occurs at much milder conditions and can tackle organic sulfur compounds. It does so through oxidation and can use a variety of reagents to do so. The most common oxidant is  $H_2O_2$  due to its nontoxic and recyclable byproduct and its abundance (Zhou et al., 2022). ODS is a slow and inefficient process without the use of a catalyst and consumes upwards of five times the stoichiometric ratio of oxygen and sulfur (Rajendran et al., 2022). As such, selecting an effective catalyst is integral in making ODS a viable desulfurization method.

ODS currently uses polyoxometalates (POM) as homogeneous catalysts. POMs have high selectivity and catalytic activity which make it the most common choice for ODS. This improves the conversion percent but has low recyclability. It is difficult to extract after the ODS and requires several toxic solvents to do so. The low surface area also negatively impacts its efficiency. One way to improve it is to provide a solid support catalyst. This can be done through embedment or encapsulation with a porous material such as silica, metal oxides, or metal-organic frameworks (MOF). This paper aims to discuss how solid supports benefit the recyclability, conversion efficiency, and conversion time of POMs.

## 2. Oxidative Desulfurization

ODS converts sulfides into sulfoxides and then sulfones in a two-step oxidation process. The product can then be treated to extract the sulfoxides which creates sulfur-free fuel. ODS is particularly good at extracting organic sulfur compounds which HDS finds difficult to extract. This is due to a competing alkene hydrogenation reaction that interferes with the selectivity of HDS. ODS also occurs in milder conditions compared to HDS with  $< 70\text{ }^\circ\text{C}$  and 101.325 KPa compared to HDS with 200-325  $^\circ\text{C}$  and 1034-1723 KPa (Doble and Kumar, 2005). This would make it easier, safer, and more energetically efficient to maintain than HDS while tackling a persistent source of sulfur emissions. It may also use catalysts, phase transfer agents (PTA), and extractants to further maximize efficiency. Other modifications can be introduced to improve interfacial contact between the oxidant and the fuel or to simplify the process. One of them is mixing-assisted oxidative desulfurization (MAOD) stirs the ODS system with enough force to create an emulsion which increases the contact area between the oxidant and the fuel phase (Lu et al., 2014). This improves the effectiveness of the PTAs as they facilitate the transfer of the sulfur compounds between them. Ultrasound-assisted oxidative desulfurization (UAOD) acts similarly through irradiation and the combination of other separation processes (Choi et al., 2021). Extractive ODS (EODS) uses continuous extraction of the sulfones via polar solvents such as acetonitrile or methanol to maximize sulfur conversion (Zhou et al., 2022). This eliminates the need for a secondary extraction stage to remove the sulfones. Photocatalytic ODS (PODS) integrates light as a source of energy through the use of photocatalysts which allows the reaction increased efficiency in lower temperatures (Chitgar et al., 2024). ODS can be performed without catalysts but often reports low conversion due to poor selectivity and requires harsher conditions similar to HDS. Ribeiro et al. (2018) compared the performance of ODS with and without a catalyst and found that only 27 % desulfurization occurred without it under the same conditions. As such, modifications to the catalyst would greatly increase the efficiency of the process.

### 2.1 Current ODS Catalysts

There are several ODS catalysts currently under study. Some are heterogeneous, such as metal oxides, MOFs, and silicates, while others are homogeneous, like common acids and POMs (Rajendran et al., 2020). They can also utilize different reaction paths with different oxidants, which leads to a wide variety of catalysts suitable for different situations. Formic acid, sulfuric acid, and acetic acid are some examples of acids used as catalysts, as seen in studies by Choi et al. (2016 a) and Te et al. (2001). They are rather inefficient without modification though as Rajendran et al. (2020) reports that these have an estimated conversion percent of 64.59, 57.41, and 52.87 % when studied under the same conditions.

Recent studies have also focused on creating photocatalysts for ODS through composite materials. These heterogeneous catalysts can be easily extracted and operate better at milder temperatures, usually around 25  $^\circ\text{C}$  (Jabbari et al., 2024). A novel composite catalyst of Cu-doped  $TiO_2$  with  $BiVO_4$  has a desulfurization percentage of 93 % when used in a DBT model fuel oil with  $H_2O_2$  as an oxidant. It does have a low recyclability rate with only 3 cycles above 90 % conversion, but it utilizes light as an easy and renewable source of energy (Jabbari et al., 2024). Another photocatalyst proposed by Chitgar et al. (2024) consisting of  $BiOI$ ,  $CeO_2$ , and NaY zeolite can be used in 5 ODS cycles with a conversion percent above 90 %. It also has a better sulfur conversion of 98.4 % in a DBT model fuel oil with air as an oxidant (Chitgar et al., 2024). It does take more power to operate as it used a 400 W bulb compared to the 100 W bulb of the previous study. This could explain the higher catalyst efficiency as the performance of the catalyst improves under more intense light.

POMs are also rather popular since they are a new green acid solid with interesting properties. They consist of a transition metal center, usually molybdenum or tungsten, connected to several oxygen atoms. There are multiple shapes that the polyoxometalate can take. The Keggin-type POM is the most used catalyst because of its high redox potential (Hu et al., 2024). Tungsten is also a popular transition metal choice with several studies stating that it has a higher sulfur conversion compared to other metal centers. Phosphotungstic acid (PW) and its salt NaPW are the most reactive forms of tungsten polyoxometalates with an average conversion percent above 82 % (Haboc et al., 2023). This outperforms common acids as a homogeneous catalyst. Wang et al. (2021), Choi et al. (2016) and, Ding and Wang (2016) all employ HPWs in their research with high sulfur conversions in both model and real fuel oil. Choi et al. (2016 b) also compared the rate constants of catalysts PW, SiW, and PMo to determine how much the ODS reaction improves depending on the species of the POM. They found that PW had the highest rate constant for both DBT at  $0.37 \text{ min}^{-1}$  and BT at  $0.16 \text{ min}^{-1}$ . The higher rate constant shows that the PW-catalyzed reaction proceeds faster than with any other POM catalyst. As such, POMs are frequently used because of their high selectivity, reproducibility, catalyst activity, and easy synthesis procedure. They are also homogeneous which allows for increased contact between the sulfur compounds and the catalyst. This does also make it difficult for the polyoxometalate to regenerate. The price of creating the catalysts makes it unsustainable without recycling and may also require toxic extraction solvents to recover (Ribeiro et al., 2013). Increasing both the recyclability and the surface area of POMs without affecting its activity may help improve ODS by creating more accessible and cheaper catalysts.

## 2.2 Heterogeneous Catalyst Supports

A way to mitigate the disadvantages of homogeneous catalysts is to add a solid support. This prevents dissolution and increases surface area. It may also be separated easily through physical processes, which does not require toxic solvents for extraction. The supports can usually act as catalysts themselves, but through the combination of POMs a higher conversion efficiency and recyclability can be achieved.

Metal oxides are porous supports that may utilize Lewis centers to facilitate further adsorption of the sulfur compound onto the catalyst (Wang et al., 2021). They are one of the more commonly found supports for catalysts since they can be customized according to the oxidized molecule to improve selectivity. These supports are synthesized through precipitation then calcination. The POM is added during the precipitation stage, and the bonds are strengthened during calcination. This allows the metal oxide to firmly attach to the POM which reduces leaching and loss in catalytic activity. Wang et al. (2021) observed that catalyst could be recycled 5 times while maintaining DBT conversion above 95 % when using  $\text{ZrO}_2$  as the support. The catalyst shows no obvious differences in the FT-IR spectrum and Raman spectrum before and after the process which further implies its stability. Other supports such as  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  can be used, but  $\text{ZrO}_2$  exhibits the best selectivity and stronger chemical bonds compared to other metal oxides. The concentration of Lewis centers can determine how well a metal oxide can assist in the ODS process. This is because a higher density facilitates the adsorption of DBT onto the catalyst surface which leads to further decomposition of the molecule. As such, a support like  $\gamma\text{-Al}_2\text{O}_3$  with a Lewis acidity of  $140.9 \mu\text{mol/g}$  may also be considered in the future (Avramidou et al., 2017).

Silica and activated carbon also feature highly porous surfaces that are ideal as catalyst support. The polyoxometalates for these supports are usually embedded onto the surface of the material. This allows the sulfur compounds and the oxidant to react as the fuel oil diffuses through it. The synthesis procedure using this support is easier versus encapsulation since the support can be premade and is more readily available, but it does have a chance to wash away the POM due to fewer bonds surrounding it. SBA-15 and  $\text{SiO}_2$  are the main forms of silicon used as support. SBA-15 has achieved a conversion percent of 100 % for a model fuel oil in 37 min at  $70 \text{ }^\circ\text{C}$  with  $\text{H}_2\text{O}_2$  as an oxidant and  $[\text{BMIM}]\text{PF}_6$  as solvent. Repeated use showed little change in catalytic activity with similar XRD and FT-Raman bands found before and after use (Ribeiro et al., 2018). Activated carbon is more readily abundant but can be difficult to use as support. A study by Barilla et al. (2022) shows that a POM@AC catalyst has a conversion percentage of 61.73 % in 90 min and at  $65 \text{ }^\circ\text{C}$  using MAOD. This may be due to the use of a simulated diesel rather than a model fuel oil, but PW achieved a conversion of 85.90 % with real diesel fuel under similar conditions (de Luna et al., 2018).

Metal-organic frameworks (MOFs) are a molecular structure that utilizes lipids and metals to create a porous material that hybridizes organic and inorganic components. The POMs are added during the synthesis of the MOF to encapsulate the molecules in an in-situ method. The POMs remain heterogeneous as the MOF does not dissolve in the ODS mixture. It can then be extracted through centrifugal force after ODS. MOFs are non-reactive and easily customizable. This allows for the support to be viable in a variety of situations and to improve the selectivity by creating pores with a size conducive for the diffusion of the sulfur compounds. It can also take on the optimal shape for a solid catalyst that encourages quick mass transfer. The ability of MOFs to perform adsorptive desulfurization can compound with the desulfurization efficiency of POMs. For instance, the performance of PMo and PMo@MOF-199 is different. The former can achieve 100 % 4,6 – DMBT model fuel

oil conversion at 120 °C using O<sub>2</sub> as an oxidant in 85 mins, while the latter only achieves 40 % given the same conditions (Zhou et al., 2022). Rafiee and Nobakht (2015) shows that the catalytic activity of PMo improves when encapsulated in HKUST-1. This is higher than PW encapsulated similarly for ODS involving methyl pentyl sulfide (MPS) with 100 % conversion in 45 min compared to 65 min for PW at 45 °C with H<sub>2</sub>O<sub>2</sub> as the oxidant. This implies that certain MOFs and POMs combinations have better synergy than others. The amount of POM encapsulated in a MOF also affects the conversion percentage and durability of the catalyst. Hu et al. (2013) tested HPW@MIL-101 with increasing concentrations of HPW. The conversion rate increases from 72 % to 90 % as the weight percent of HPW increases from 17 % to 40 %. The increase diminishes as the weight becomes 50 % with only a 1 % improvement. This catalyst can withstand 3 ODS cycles before the conversion percent falls below 90 %. The main issue seems to come from catalyst recovery as only 71 % is recovered at this stage. The strength of the encapsulation is like embedment with only an overall change of 9 % wt of HPW. A better recyclability for HPW is found using UiO-67 as the MOF with 7 cycles above 90 % (Gao et al., 2024). It shows that encapsulation is another viable method of creating a heterogeneous catalyst. Unfortunately, the support has low thermal and mechanical stability. Increasing the temperature of ODS could degrade the catalyst (Alcaraz et al., 2023). This directly contrasts the benefits of increasing the temperature as doing so decreases the reaction time of the fuel by increasing the sulfur conversion rate. A low mechanical stability may also prevent usage of ultrasound or shear forces to further optimize the process as it may break during the process. This may also contribute the loss of catalytic mass previously discussed. Table 1 shows a summary of the catalysts, their conversion percentage of various sulfur compounds, and their recyclability.

*Table 1: Summary of Pertinent Solid Support Catalyst Studies*

Authors (Year)	Catalyst	Oxidant	Operating Parameters	Maximum Sulfur Conversion (%)	Number of Cycles
Hu et al. (2013)	PW@ML-101	H <sub>2</sub> O <sub>2</sub>	75 mg catalyst, 1-5 h, 40-50°C	DBT: 91	4
Rafiee and Nobakht (2015)	PMo@HKUST-1	H <sub>2</sub> O <sub>2</sub>	0.06 g catalyst, 3 h, 65°C	95 (DBT) 90 (TH) 98 (MPS)	4
Zhou et al. (2022)	HPMo@MOF-199	O <sub>2</sub>	0.02 g catalyst, 2 h, 120°C	100 (4,6-DMDBT)	10
Ortiz-Bustos et al. (2021)	PMo(2)-Chol-MSN	H <sub>2</sub> O <sub>2</sub>	50 mg catalyst, 2 h, 40°C	99.7 (DBT)	3
Wang et al. (2021)	PW@ZrO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	10 mg catalyst, 25 min, 60°C	98 (DBT)	5
Ribeiro et al. (2018)	PW12@TM-SBA-15	H <sub>2</sub> O <sub>2</sub>	3 μmol catalyst, 35 min, 70°C	97 (overall)	3
Gao et al. (2024)	(TBA) <sub>3</sub> PW <sub>4</sub> @UiO-67	H <sub>2</sub> O <sub>2</sub>	6 μmol catalyst, 30 min, 70°C	99 (BT) 100 (DBT) 68.7 (4,6-DMDBT)	7
Bi et al. (2022)	HPV <sub>2</sub> Mo <sub>10</sub> /TS-1-TPAOH@SiO <sub>2</sub> -in situ	H <sub>2</sub> O <sub>2</sub>	0.06 g catalyst, 3 h, 70°C	99.3 (TH) 45.9 (BT) 84.1 (DBT)	4
Wu et al. (2024)	20-PMo <sub>10</sub> V <sub>2</sub> /APTES-HMSNS	H <sub>2</sub> O <sub>2</sub>	2.5 g catalyst, 1 h, 60°C	86.84 (BT) 99.99 (DBT) 97.84 (4-MDBT) 91.35 (4,6-DMDBT)	8
Salem and Abdelrahman (2023)	Fe <sub>6</sub> W <sub>18</sub> O <sub>70</sub> @ZrFe <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O <sub>2</sub>	0.075 g catalyst, 40 min, 50°C	98.2 (overall)	5

The focus of this review is to determine which support assists the POM the most in terms of recyclability, conversion efficiency, and conversion time. As such, MOFs seem to be the best support for POMs with 10 maximum cycles, near 100% conversion efficiency, and relatively short reaction time. The high durability can mainly be attributed to the method in which POMs are added to the support. Encapsulation offers more support than other ex-situ methods as it provides both a physical and chemical barrier to keep the POM in place. The discrepancy can be seen between the catalysts of Ribeiro et al. (2018) and Zhou et al. (2022). The former utilized surface bonding between the support and the catalyst through incorporating PW into the mesoporous structure of SBA-15. This leaves the POM vulnerable to detachment during the ODS process. The MOF-supported POM can withstand more than thrice the number of cycles the SBA-15-supported POM can because of this difference. The study of Bi et al. (2022) also shows a similar dilemma for silicon-based supports. It shows a low recyclability of 4 reported cycles compared to other supports. The method of encapsulation was in-situ but the size of the pores prevented the POM from going deeper than the secondary pore layer. This may have caused the low recyclability. Other forms of silicon may have higher durability by addressing this issue. A study conducted by Wu et al. (2024) found that enlarging the pores of MSN allows for deeper POM penetration. This

leads to a higher recyclability of 8 cycles with negligible changes in desulfurization rate. Metal oxides are generally more stable than silica. The catalyst in the study of Wang et al. (2021) reported 5 cycles with minimal changes to desulfurization. This may be because the POM and the metal oxide have stronger interactions due to a stronger Lewis acid-base reaction compared to silica. This is not the case for all metal oxides. Ortiz-Bustos et al. (2021) used TiO<sub>2</sub> as a support for PMo and found a 37.2 % conversion rate compared to the 90 % and above of both SBA-15 and mesoporous silica nanoparticles (MSN). Modifying the POM or the metal oxide may help improve both recyclability and conversion rate as seen in the study of Salem and Abdelrahman (2023). A sandwich-type cluster of Fe<sub>6</sub>W<sub>18</sub>O<sub>70</sub> was immobilized on a ZrFe<sub>2</sub>O<sub>5</sub> metal oxide composite. This achieved a conversion percentage of 98.2 % and 5 cycles of use at 50°C with H<sub>2</sub>O<sub>2</sub> as oxidant. It shows a similar level of durability and desulfurization capabilities to the ZrO<sub>2</sub> support but both can withstand less cycles than the modified MNS and MOFs. Overall, MOFs still have the highest durability because of their encapsulation technique and how deep the POM can reach within the MOF. The MOF is built around the POM rather than having the POM enter the support, which leads to a more holistic connection between the two structures.

### 3. Conclusion

Solid support catalysts are the next step in improving the viability of ODS as a desulfurization method specifically targeting organic sulfur compounds. There are several viable supports for POMs with their advantages and disadvantages. Metal oxides, silica, and activated carbon have simple synthesis procedures but may face difficulty with further use because of catalyst loss between ODS cycles. They may also have difficulty keeping the POM immobilized because of smaller pore sizes. MOF encapsulation is also stable and provides a high surface area but are more sensitive to other factors such as high temperatures and mechanical agitation. MOFs seem to be the most promising support overall with a high conversion efficiency, relatively short conversion time, and high durability compared to other supports.

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