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# A Comprehensive Review on Advantages and Issues of Nanotechnology in the Oxidative Desulfurization Method for the Production of Ultra-Clean Fuels

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## ABSTRACT

Today, producing clean fuel oil is one of the major challenges in the world. One of the factors that causes environmental pollution is the sulfur compounds in crude oil. In today's world, there are strict rules for reducing the amount of sulfur in fuel. There are several ways to remove sulfur compounds from fuels, such as hydrodesulfurization (HDS), extractive distillation, biodesulfurization, adsorption desulfurization, and oxidative desulfurization (ODS). Some refractory sulfur compounds that are not removed from the fuel oil by the HDS can be easily removed by oxidation method. Nowadays, the ODS method is known as a complement to the HDS method. In the oxidation method, sulfur compounds are converted to the corresponding sulfonates by catalysts and oxidants and then separated from the feed by polar solutions or adsorbents. Various researches have been done on the Catalysts and oxidants of the ODS method. In this study, a comprehensive review has been carried out on the application of nanotechnology in the oxidative desulfurization method. Based on previous researches and available articles, nanocatalysts used in the oxidation process can be classified into five groups; polyoxometalates, transition metal oxide, carbon materials, ionic liquids and metal-organic frameworks (MOF). Also, different nanocatalysts and oxidants and optimal conditions to achieve the highest conversion percentage for the removal of sulfur compounds were investigated.

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## 1. Introduction

The presence of sulfur in petroleum feeds has adverse environmental effects. Sulfur compounds in crude oil include thiophenes (T), benzothiophenes (BT), and dibenzothiophenes (DBT) and mercaptans which produces sulfur oxide (SO<sub>x</sub>), these are the main causes of environmental pollution (Figure 1) (Hossain, 2019). In recent years, desulfurization of crude oil has received much attention and refineries are required by world law to reduce sulfur to less than 10ppm (Kalantari, 2016). Also, the amount of sulfur allowed for fuel cells should be less than 0.1ppm (Stanislaus, 2010). Many different methods, such as hydrodesulfurization (HDS), biodesulfurization (BDS), adsorption desulfurization (ADS) and oxidative desulfurization (ODS), have been used to desulfurize fuel oil (Hossain, 2019). The hydrodesulfurization reaction takes place in the presence of metallic catalysts (Ni, Mo and Co) and hydrogen gas at high temperatures (up to 400 °C) and pressures (up to 100 atm) (Ahmed, 2020; Meman, 2014). Hydrodesulfurization (HDS) is very efficient in removing T, BT, DBT, but some sulfur compounds in heavy oil cuts require higher operating conditions (High temperature and pressure) and that means more operating costs (Campos-Martin, 2010; Rezvani, 2020). It is very difficult and expensive to achieve ultra-clean fuel using hydrodesulfurization method for environmental reasons (Meman, 2014).

Oxidative desulfurization (ODS) method has attracted a lot of attention compared to HDS method due to the mild reaction conditions (low temperature and pressure) and no need to use hydrogen (Dai, 2008). Oxidation desulfurization has two main steps. At first, sulfur compounds are oxidized to other compounds such as sulfone. This conversion occurs in the presence of oxidants. In the second stage, oxidized compounds will be removed from the reaction mixture by the extraction methods (Hossain, 2019). In recent years, different catalysts have

been used for oxidative desulfurization. One of the cases that has been widely used in the production of catalysts is the use of nanotechnology. This paper reviewed the works about the applications of nanotechnology in the oxidative desulfurization method.

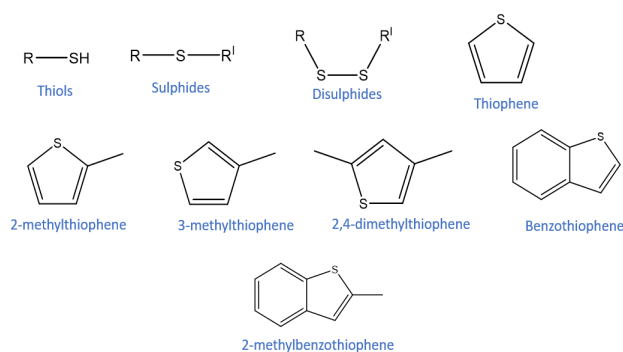


Figure 1. Sulfur compounds in crude oil (Hossain, 2019)

## 2. Nanotechnology in Catalytic Oxidation Desulfurization Process

### 2.1. Polyoxymetalate Catalytic Oxidation System

Polyoxymetalates are one of the subdivisions of transitional metal ions and polyoxoanions. They are robust catalysts due to the presence of multifunctional active sites in their structure. like protons, oxygen atoms, and metals. Polyoxymetalates have been considered in the desulfurization process as efficient catalysts in the presence H<sub>2</sub>O<sub>2</sub> oxidant (Wang, 2015).

Rezvani et al. applied polyoxometalate@ceramic@polyaniline nanocatalyst for oxidative desulfurization of simulated fuels and gasoline containing sulfur refractory compounds (such as Th, BT, and DBT) in a mixture of hydrogen peroxide/acetic acid as an oxidizing agent and acetonitrile was used as an extraction solvent. The sulfur content was finally reduced to 97% at optimal condition; reaction temperature of 35 °C and reaction time 1 h (Rezvani, 2019).

Nogueira et al. examined silica nano-sized sphere catalysts [PW<sub>11</sub>Zn (H<sub>2</sub>O) O<sub>39</sub>]<sup>5-</sup>, for oxidative desulfurization of olefins. The nanocomposite proved to be a very powerful

and versatile heterogeneous catalyst for the oxidation of various olefins and also for the oxidative desulfurization of a model oil, in the presence of  $H_2O_2$  as the oxidant and MeCN as the solvent. After 1 h, in temperature of 50 °C and three consecutive ODS cycles desulfurization of DBT reached 100%. Also, desulfurization of 4, 6-DMDBT after three consecutive ODS cycles, 2h and temperature of 50 °C reached 100% efficiency (Xiong, 2015).

Ahmed et al. studied oxidative desulfurization (ODS) of light naphtha feedstock in a batch reactor using new homemade nano-catalyst, zinc oxide supported on zeolite nanoparticles, and used air as oxidant. The experimental results showed that at 54.4 °C for 163.6 minutes and an initial concentration of 335.3 ppm and in the presence of nanocatalysts (ZnO/zeolite nanoparticles) the conversion was more than 99% (Ahmed, 2020).

Liu et al. studied the removal of sulfur compounds from crude oil using the oxidative desulfurization method, with magnetically recoverable catalysts  $Cs_{2.5}H_{0.5}PW_{12}O_{40}/nano-Fe_3O_4/SiO_2$  and  $H_3PW_{12}O_{40}/nano-Fe_3O_4/SiO_2$ . The results of catalyst characterization showed that the produced catalyst had a magnetic property, which makes it easily extracted under a magnetic field. Under the experiment conditions (temperature 60 °C and 180min), the sulfur removal rates by using  $H_3PW_{12}O_{40}/nano-Fe_3O_4/SiO_2$  and  $Cs_{2.5}H_{0.5}PW_{12}O_{40}/nano-Fe_3O_4/SiO_2$  reached 99.4% and 91.4% respectively in the model oil. This catalyst had a good catalytic effect for model oil and was also recyclable, but its effect on real oil was not yet acceptable (Liu, 2017).

Mohammadi Meman et al. investigated the deep oxidative desulfurization of sour petroleum fractions with  $H_2O_2$  as oxidant and MnOx/FMWNT heterogeneous nano-catalyst. The sulfur removal efficiency reached 99.85% at temperature of 25 °C and time 30 min and atmospheric pressure (Meman, 2014).

Chen et al. used the HPW-NH<sub>2</sub>-HHSS catalyst

as an effective catalyst for Oxidative-adsorptive desulfurization of fuels. They investigated the effect of reaction parameters such as reaction temperature, reaction time, initial DBT concentration, catalyst dose and O/S molar ratio on sulfur removal of the OADS reaction efficiency. Under optimal conditions; temperature of 60 °C, sulfur concentration 300 mg/l, O/S molar ratio 2.5 and time of 30 minutes, DBT removal reached 99.36%. At the end they, considered the polarity and size of the catalyst pores to be the main factors influencing the reaction efficiency (Chen, 2020).

Ghahramaninezhad et al. used a polyoxometalate ( $Mo_{132}$ ) nanoballs supported over the Zeolitic imidazolate framework-8) and tert-butyl hydroperoxide (TBHP) as oxidant to desulfurize the model fuel. The reaction was performed in a batch reactor system. Under the optimal conditions, temperature of 80 °C, time of 8 h, catalyst dosage 150 mg, O/S molar ratio 1 and initial sulfur concentration 500 ppm reached 95% conversion (Ghahramaninezhad, 2019). Saha et al. Used nano silver supported on titanium dioxide ( $Ag/TiO_2$ ) as catalyst and Tertiary-butyl hydroperoxide as oxidant to remove thiophene from the model oil. They examined the effect of various parameters such as catalyst weight, O/S molar ratio, silver charge on the catalyst and reaction temperature. Finally, the conversion rate of 63 was the highest reported in 90 minutes and 10 wt%  $Ag/TiO_2$  catalyst (Saha, 2019).

Jarullah et al. used the new nano-catalyst CuO+NiO supported on HY zeolite and air as an oxidizer to oxidative desulfurize the light gas oil. Under optimal conditions; the temperature of 413 K and the time of 90min using the (20%CuO+10%NiO) catalyst reached a conversion rate of 92.15 to remove sulfur (Jarullah, 2020).

Xiao et al. Used a flower-like  $WO_3 \cdot H_2O$  catalyst and  $H_2O_2$  as an oxidant to remove dibenzothiophene in the sample oil. Under

optimal conditions, the temperature of 70 °C, Sulfur compounds was reduced from 4000 to 220 µg/g in 60 minutes (Xiao, 2016).

He et al. used PtCu/BNNS as a catalyst and O<sub>2</sub> as an oxidizer to oxidative desulfurization of fuel oil. They examined the effect of the

reaction parameters and in the optimal reaction conditions; the temperature of 110 °C and the time of 7h, the amount of sulfur reached 7.9ppm, and the conversion was 92.1% (He, 2020). (Table 1) compares some of the Polyoxymetalate nanocatalysts in ODS process.

**Table 1. Polyoxymetalate Nanocatalysts in ODS Process**

Catalyst	Source of sulfur	Oxidizing agent	Reaction condition	Sulfur removal efficiency%	Ref.
Polyoxometalate@ Ceramic@ Polyaniline	Real gasoline	Hydrogen peroxide/acetic acid	T = 35 °C, t = 60 min	97	(Rezvani, 2020)
[PW <sub>11</sub> Zn (H <sub>2</sub> O) O <sub>39</sub> ] <sup>5-</sup>	DBT	H <sub>2</sub> O <sub>2</sub>	T = 50 °C, t = 60 min	100	(Xiong, 2015)
ZnO /Zeolite nanoparticle	light naphtha feedstock	air	T = 54.4 °C, t = 163.6 min	99	(Ahmed, 2020)
Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> / NanoFe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub>	Model oil	H <sub>2</sub> O <sub>2</sub>	T = 60 °C, t = 180 min	99.4	(Liu, 2017)
MnOx/FMWNT	sour petroleum	H <sub>2</sub> O <sub>2</sub>	T = 25 °C, t = 30 min	99.85	(Meman, 2014)
HPW-NH <sub>2</sub> -HHSS	DBT	H <sub>2</sub> O <sub>2</sub>	T = 60 °C, t = 30 min	99.36	(Chen, 2020)
ZIF-8@{Mo <sub>132</sub> }	DBT	TBHP	T = 80 °C, t = 8 h	95	(Ghahramanin-ezhad, 2019)
Ag/TiO <sub>2</sub>	Th	Tertiary-butyl hydroperoxide	T = Not specified, t = 90 min	63	(Saha, 2019)
CuO+NiO supported on HY zeolite	light gas oil	air	T = 140 °C, t = 90 min	92.15	(Jarullah, 2020)
WO <sub>3</sub> ·H <sub>2</sub> O	DBT	H <sub>2</sub> O <sub>2</sub>	T = 70 °C, t = 60 min		(Xiao, 2016)
PtCu/BNNS	real diesel fuel	O <sub>2</sub>	T = 110 °C, t = 7 h	92.1	(He, 2020)

## 2.2. Carbon Nano Materials

Recently, the use of carbon nanotubes in desulfurization has been considered due to its special structural properties. Wang et al. examined the performance of carbon nanotubes supported Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> as an effective catalyst for the oxidative desulfurization of diesel. According to laboratory studies, it was concluded that the catalyst has a high efficiency for oxidizing DBT. The efficiency obtained is equal to 100% under optimal conditions; temperature of 60 °C, catalyst dosage 1.0 wt. % and 30min (Wang, 2010). Zhang et al. Studied the effect of carbon nanotubes as a new catalyst and molecular oxygen as oxidant in the oxidation desulfurization of model oil.

Experimental results showed that when CNT-SZ was used as catalysts, the sulfur removal efficiency reached 100% at 150 °C within 40min (Zhang, 2020).

There are also studies showing that carbon nanotubes have been used as a support. Wang et al. used tungsten trioxide catalyst immobilized on CNT to remove dibenzothiophene by oxidative desulfurization method. H<sub>2</sub>O<sub>2</sub> was used as an oxidant. CNT was dispersed and the catalyst was charged on it in the presence of ionic liquid [C<sub>16</sub> mim] Cl. They also examined the effect of different forms of WO<sub>3</sub> catalysts based on the same CNT. Finally, it was concluded that the use of tungsten trioxide catalyst in the form

of tetrahedral was most effective and in the optimal reaction conditions, the conversion percentage of DBT reached 90.73 % (Wang, 2019).

Gao et al. synthesized and compared two types of carbon nanotube-based polyoxometalate catalysts (POM@CNTs, CNTs@

PDDA@Mo<sub>16</sub>V<sub>2</sub>) for oxidative desulfurization of model fuels. Finally, they concluded that the CNTs@PDDA@Mo<sub>16</sub>V<sub>2</sub> catalyst was more efficient in the presence of H<sub>2</sub>O<sub>2</sub> oxidant and the conversion rate of dibenzothiophene reached 99.4% at 70 °C (GAO, 2018). (Table 2 )shows the applications of carbon materials in ODS process.

**Table 2. Carbon Materials in ODS Process**

Catalyst	Source of sulfur	Oxidizing agent	Reaction condition	Sulfur removal efficiency%	Ref.
Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> / MWNT	DBT	H <sub>2</sub> O <sub>2</sub>	T = 60 °C, t = 30 min	100	(Wang, 2010 )
CNT-SZ	DBT	H <sub>2</sub> O <sub>2</sub>	T = 150 °C, t = 40 min	100	(Zhang, 2020 )
WO <sub>3</sub> /CNT	DBT	H <sub>2</sub> O <sub>2</sub>	T = 60 °C, t = 60 min	90.73	(Wang, 2019 )
CNTs@PDDA@Mo <sub>16</sub> V <sub>2</sub>	DBT	H <sub>2</sub> O <sub>2</sub>	T = 70 °C, t = min	99.4	(Gao, 2018 )

### 2.3. Ionic Liquids

Today, the use of ionic liquids as catalysts in the desulfurization process has been studied and considered. Ionic liquids, also known as green solvents, have unique physical and chemical properties such as electrical conductivity and high partial vapor pressure, fluidity over a wide temperature range, and good solubility. However, some weaknesses, such as high prices, difficult separation of these compounds, and the retention of some ionic liquid in the fuel, have limited the use of ionic liquids. Of course, there are solutions to these problems. One of these solutions is the stabilization of ionic liquids on the basis of solid catalysts such as silica and gamma alumina. Also, Saber et al. used the magnetic separation method using iron oxide nanoparticles to solve the separation problem (Azimzadeh, 2017; Cruz, 2019; Poursaberi, 2013).

Poursaberi et al. investigated the efficiency of iron oxide magnetic nanoparticles as catalysts for oxidative desulfurization of model and real oil. Ionic liquid was used to synthesize the catalyst and modify the surface of iron oxide nanoparticles. The conversion of sulfur aromatic compounds using this catalyst (Fe<sub>3</sub>O<sub>4</sub>/APTES/IL) in 15 minutes and 25 °C reached 51.3% and after

5 repetitions reached 90.3%. Also, using this catalyst, oxidized compounds were removed magnetically (Poursaberi, 2013 ).

Cruz et al. synthesized two types of titanium catalysts for the oxidative desulfurization of model oil and the removal of dibenzothiophene. One catalyst was synthesized using ionic liquid (Titanium hybrid mesoporous silica nanoparticles (ILBF4-x%TiCp<sub>2</sub>-MSN)) and the other without ionic liquid (TiCp<sub>2</sub>-MSN). The results showed that the catalyst synthesized with ionic liquid has a better efficiency for removing sulfur compounds and under optimal conditions: Temperature 60 °C and time 6h and in the presence of H<sub>2</sub>O<sub>2</sub> as an oxidizer the conversion rate of DBT reached 99.1% (Cruz, 2019).

Wang et al. Used ionic liquid to synthesize photocatalytic nano-titanium oxide (nano-TiO<sub>2</sub>) catalysts. The results showed that this catalyst had a good ability to remove sulfur compounds in gasoline using the ODS method and using UV radiation for 10 hours reduced amount of sulfur in gasoline to 8 ppm (Wang, 2012). Li et al. also used this catalyst without UV irradiation to remove DBT and 4,6-dimethyldibenzothiophene, and reached a conversion rate of 100% (Li, 2016).



Xun et al. synthesized a Phosphomolybdate-based ionic liquid  $[(C_8H_{17})_3NCH_3]_3PMo_{12}O_{40}$  catalyst based on magnetic mesoporous silica ( $\gamma-Fe_2O_3@SiO_2@mSiO_2$ ) to produce a magnetic catalyst for oxidative desulfurization of DBT in model oil. Using this magnetic catalyst in the

presence of air as an oxidant, debenzothiophene was completely removed in 5 hours at a temperature of 120 °C and reached a conversion rate of 100% (Xun, 2019). (Table 3) indicates the applications of Ionic liquids nanocatalysts in ODS process.

**Table 3. Ionic Liquids Nanocatalysts in ODS Process**

Catalyst	Source of sulfur	Oxidizing agent	Reaction condition	Sulfur removal efficiency%	Ref.
$Fe_3O_4/APTES/IL$	DBT		T = 25 °C, t = min	90.3	(Poursaberi, 2013)
$ILBF_4-x\%TiCp_2-MSN$	DBT	$H_2O_2$	T = 60 °C, t = 6h	99.1	(Cruz, 2019)
nano-TiO <sub>2</sub>	Gasoline	O <sub>2</sub>	T = 25 °C, t = 10h	94.3	(Wang, 2019)
nano-TiO <sub>2</sub>	DBT	$H_2O_2$	T = 70 °C, t = 50s	100	(Li, 2016)
$[(C_8H_{17})_3NCH_3]_3PMo_{12}O_{40}/\gamma-MMS$	DBT	air	T = 120 °C, t = 5h	100	(Xun, 2019)

## 2.4. Transition Metal Oxide

The choice of heterogeneous catalyst for oxidative desulfurization has been considered due to its easy separation and good catalytic properties. One of the types of heterogeneous catalysts used in the oxidative desulfurization process is transition metal oxides (MTO<sub>2</sub>). Catalysts such as molybdenum, vanadium, tungsten, zinc, cobalt, etc. These catalysts are based on materials such as alumina, silica, titanium oxide, etc. for stabilization and usability. One of the best cases in which the supports can be used is to use them in the nanostructure mode, because in this structure the support has the best performance and the catalyst is spread on it better (Haghighi, 2020).

Yao et al. used molybdenum oxide nanoparticles based on graphene-analogous boron nitride to remove DBT from oil by oxidative desulfurization. Due to the effect of particle size control and the interaction of catalyst particles with the support on improving aerobic oxidative desulfurization, the catalyst and the support are used as nanostructures. Using this catalyst and molecular oxygen as an oxidant under optimal conditions, DBT was

completely removed within 3 hours and the conversion reached 100% (Yao, 2018).

Chen et al. also used molybdenum oxide nanocatalysts for oxidative desulfurization of model oil. To stabilize the nanocatalysts, they fixed them on a mesoporous titanium phosphonates support. High specific surface area and high and uniform dispersion of molybdenum oxide on the support as well as more active sites and the coupling property between the support and the active component are the reasons for using the support in the nanostructured state. Using this catalyst at a temperature of 40 °C and a time of 30 minutes, the removal of sulfur compounds reaches 100% (Chen, 2021).

Zou et al. used vanadium pentoxide nanoparticles ( $V_2O_5$  NP<sub>s</sub>) for aerobic oxidation desulfurization. Using oxygen in the air as an oxidant and under optimal conditions: the temperature of 120 °C and the time of 4 hours conversion reached 99.7% (Zou, 2021).

Li et al. used pure nano-TiO<sub>2</sub> as catalyst for the oxidative desulfurization of simulated fuels

directly without UV irradiation and with  $H_2O_2$  as an oxidant. The results showed that the nanocatalyst had very good properties and high catalytic activity, because the conversion rate was near to 100% after 50 seconds under optimal operating conditions; the molar ratios of  $H_2O_2$  to sulfide as well as DBT to 4,6DMDBT were 10:1 and 15:1, respectively (Li, 2016).

Bazyari et al. studied ultra-deep desulfurization of model fuel oil with titania-silica nanocomposite catalysts. The effects of various parameters such as metal loading, reaction temperature and calcination temperature were investigated. The experimental results showed that loading the metal at 50% at high acidity caused the conversion rate of 98% in 20 minutes (Bazyari, 2016).

Lu et al. applied  $CeO_2/TiO_2$  nanotubes for photocatalytic oxidative desulfurization of model oil. It was found that nearly 90% of the sulfur compounds in the model oil were photocatalytically oxidized and removed by the catalyst  $CeO_2/TiO_2$  nanotube arrays in 5 hours (Lu, 2016).

Rezvani et al. also used a titanium oxide supported catalyst ((TBA)4PW<sub>11</sub>Fe@TiO<sub>2</sub>@PVA) for oxidative desulfurization of the fuel. Using this catalyst and  $H_2O_2/HOAc$  as oxidant and

benzothiophene (BT) 96%, dibenzothiophene (DBT) 99%, 4-MDBT 97% and 4,6-DMDBT 98% were removed. Under optimal reaction conditions: at 60 °C and 2 hours, 97% of the sulfur compounds were removed (Rezvani, 2019).

Zhao et al. used copper phthalocyanine molecular sieve catalyst supported on HZSM-5 zeolite ( $Cu_2$  (PcTN) 2/W-HZSM-5) to desulfurize fuel oil. They examined the effect of reaction temperature, reaction time, and catalyst load. Under optimal reaction conditions: temperature 60 °C, time of 3 hours and catalyst loading of 0.1 g, conversion percentages reached 93.82%, 91.23%, 87.32% for TH, BT and DBT, respectively (Zhao, 2015).

Yang et al. used molybdenum supported on 4A molecular sieve catalyst ( $MoO_3/4A$ ) to oxidative desulfurization of BT and DBT from n-octane. They used cyclohexanone peroxide (CYHPO) as an oxidant and examined the effect of the reaction parameters; molybdenum loading, reaction temperature, reaction time, the molar ratio of CYHPO/DBT and the weight of catalyst  $MoO_3/4A$  and achieved 99% conversion rate under optimal conditions (Yang, 2016). (Table 4) summarized the conditions and removal efficiency of Transition metal oxide nanocatalysts in ODS process.

**Table 4. Transition Metal Oxide Nanocatalysts in ODS Process**

Catalyst	Source of sulfur	Oxidizing agent	Reaction condition	Sulfur removal efficiency%	Ref.
MoOxNPs/g-BN	DBT	O <sub>2</sub>	T = Not specified, t = 3 h	100	(Yao, 2018 )
5%Mo/TiO <sub>2</sub> -350	DBT	TBHP	T = 40 °C, t = 30 min	100	(Chen, 2021 )
V <sub>2</sub> O <sub>5</sub> NPs	Fuel oil	O <sub>2</sub>	T = 120 °C, t = 4 h	99.7	(Zou, 2021 )
TiO <sub>2</sub> -SiO <sub>2</sub>	DBT	TBHP	T = 80 °C, t = 20 min	98	(Bazyari, 2016 )
CeO <sub>2</sub> /TiO <sub>2</sub>	Model oil	H <sub>2</sub> O <sub>2</sub>	T = Not specified, t = 5 h	90	(Lu, 2016 )
(TBA)4PW <sub>11</sub> Fe@TiO <sub>2</sub> @PVA	Model oil	H <sub>2</sub> O <sub>2</sub> /HOAc	T = 60 °C, t = 2 h	97	(Rezvani, 2019 )
Cu <sub>2</sub> (PcTN) 2/W-HZSM-5	DBT	H <sub>2</sub> O <sub>2</sub>	T = 60 °C, t = 3 h	87.32	(Zhao, 2015 )
MoO <sub>3</sub> /4A	DBT	CYHPO	T = 100 °C, t = 30 min	99	(Yang, 2016 )

## 2.5. Metal Organic Frameworks

Metal organic frameworks (MOFs) are a type of crystalline material that have been considered for their unique properties such as large internal surface area and high porosity. This material consists of the bonding of small metal ions, including metal, to several organic ligands, such as sulfoxalate, and carboxylate, via a coordination bond. One of the most important properties of MOFs is that the size and shape of the pores can be precisely controlled by selecting its components such as metals and organic binders and how they are connected to each other. Using this property, nanostructured catalysts can be produced from these materials (Soleimani, 2017).

Li et al. used POM@MOF-199@MCM-41 catalysts and molecular oxygen (O<sub>2</sub>) as oxidants for oxidative desulfurization of the model fuel. POM and MOF-199 were used in the nanostructured state, which improved the catalyst synthesis. By examining different

reaction parameters: temperature, time and amount of catalyst, it was concluded that at a temperature of 85 °C and time of 180 minutes and the amount of catalyst 2 g / l, benzothiophene was removed up to 98.5% (Li, 2016).

GhahramaniNejad et al. used ZIF-8@{Mo<sub>132</sub>} nano catalyst to remove DBT from model oil by oxidative desulfurization method. Using TBHP as an oxidant under optimal conditions: temperature of 80 °C and time 12 hours conversion of DBT reached 92% (Ghahramaninezhad, 2019).

Xu et al. synthesized a POM Co-MOF catalyst in Nano sheet structure using the top-down method. By comparing the performance of the nano sheets catalyst and the bulk state, it was found that the nanostructured state has a better performance for oxidative desulfurization. Using this nanostructured sheet catalyst, DBT in the model oil was completely removed in 60 minutes. (Table 5) shows the applications of Metal organic framework nanocatalysts in ODS process.

**Table 5. Metal organic framework nanocatalysts in ODS process**

Catalyst	Source of sulfur	Oxidizing agent	Reaction condition	Sulfur removal efficiency%	Ref.
POM@MOF-199@MCM-41	DBT	O <sub>2</sub>	T = 85 °C, t = 180 min	98.5	(Li, 2016)
ZIF-8@{Mo <sub>132</sub> }	DBT	TBHP	T = 80 °C, t = 12 h	92	(Ghahramaninezhad, 2019)
[Co <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> (BTX) <sub>3</sub> ][PMo <sub>12</sub> O <sub>40</sub> ]	DBT	H <sub>2</sub> O <sub>2</sub>	T = Not specified, t = 60 min	100	(Xu, 2018)

## 3. Conclusion

Hydrogen desulfurization is used as a well-known method in oil refineries. However, this method alone is not effective due to high operating conditions as well as high cost and inability to remove some sulfur compounds. One of the effective methods along with HDS method is oxidation desulfurization method (ODS). The oxidation method has received much attention due to its moderate operating

conditions as well as its selectivity in the removal of sulfur compounds. Various studies have been conducted on the factors affecting this method. One of the investigated factors is the effect of different nanostructured catalysts on this method. According to studies, titanium nanocatalysts have a significant effect on the removal of sulfur and have achieved a high conversion rate in a relatively short period of



time. Also, carbon nanotubes have achieved a 100% conversion rate in the removal of sulfur compounds due to their suitable structure and high surface area.

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## مروری جامع بر مزایا و مسائل نانوتکنولوژی در روش گوگردزدایی اکسایشی برای تولید سوخت‌های فوق تمیز

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### چکیده

امروزه تولید سوخت پاک یکی از چالش‌های بزرگ در جهان است. یکی از عواملی که باعث آلودگی محیط‌زیست می‌شود، ترکیبات گوگردی موجود در نفت خام است. در دنیای امروز قوانین سخت‌گیرانه‌ای برای کاهش میزان گوگرد در سوخت وجود دارد. روش‌های مختلفی برای حذف ترکیبات گوگرد از سوخت‌ها وجود دارد، مانند گوگردزدایی هیدروژنی (HDS)، تقطیر استخراجی، گوگردزدایی زیستی، گوگردزدایی جذبی و گوگردزدایی اکسایشی (ODS). برخی از ترکیبات گوگردی که توسط روش گوگردزدایی هیدروژنی از سوخت حذف نمی‌شوند را می‌توان به راحتی با روش اکسیداسیون حذف کرد. امروزه روش گوگردزدایی اکسایشی به عنوان مکمل روش گوگردزدایی هیدروژنی شناخته می‌شود. در روش گوگردزدایی اکسایشی، ترکیبات گوگردی توسط کاتالیزورها و اکسیدکننده‌ها به سولفونات‌های مربوطه تبدیل می‌شوند و سپس توسط محلول‌ها یا جاذب‌های قطبی از خوراک جدا می‌شوند. تحقیقات مختلفی بر روی کاتالیزورها و اکسیدکننده‌های روش گوگردزدایی اکسایشی انجام شده است. در این مطالعه مروری جامع بر روی کاربرد نانوتکنولوژی در روش گوگردزدایی اکسایشی انجام شده است. بر اساس تحقیقات قبلی و مقالات موجود، نانوکاتالیست‌های مورد استفاده در فرآیند اکسیداسیون را می‌توان به پنج گروه طبقه‌بندی کرد: پلی اکسومتالات‌ها، اکسید فلزات واسطه، مواد کربنی، مایعات یونی و چارچوب‌های فلزی-آلی (MOF). همچنین نانوکاتالیست‌ها و اکسیدکننده‌های مختلف و شرایط بهینه برای دستیابی به بالاترین درصد تبدیل برای حذف ترکیبات گوگردی مورد بررسی قرار گرفت.

واژگان کلیدی: نانوکاتالیست، گوگردزدایی اکسایشی، نفت کوره