Deep Extractive Oxidative Desulfurization of Model Oil/Crude Oil using Different Keggin Heteropoly Acids Supported on K10 Montmorillonite

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ARTICLE INFO	ABSTRACT
	This study investigated the catalytic performance of three polyoxometalates ($H_3PMo_{12}O_{40}$ (PMo), $H_3PW_{12}O_{40}$ (PW), and $H_4SiW_{12}O_{40}$ (SiW)) supported on montmorillonite K10 for oxidative desulfurization (ODS) of thiophenic model oil, crude oil, and gasoline. Experimental results revealed that PW exhibited higher activity than PMo and SiW. The best solvent for mixed model oil was found to be EtOH, while MeCN was optimal for crude oil to remove oxidized sulfur compounds in a biphasic system under atmospheric pressure at 75°C in the presence of H_2O_2 as an oxidating agent. Using PW/K10 as the catalyst, the conversion of mixed model/EtOH and crude oil/MeCN reached 98.76% and 51.36%, respectively, under optimal conditions for 80 minutes. To investigate the impact of real oil composition on the desulfurization process, various unsaturated and N-compounds (pyrrole and pyridine) were added to mixed model oil. Finally, PW/K10 was recycled five times, and the results indicated no significant decrease in catalytic activity.

Introduction

In recent decades, the presence of S-compounds (sulfur compounds) in petroleum fractions has been a major source of acid rain and air pollution, causing problems for both the environment and catalytic processes [1]. Since 2006, the United States has enforced regulations requiring refineries to lower the threshold level of sulfur in diesel fuel to less than 15 ppm, while Europe has implemented similar regulations since 2015 to reduce sulfur content to less than 10 ppm [2].

Based on previous findings, hydrodesulfurization (HDS) process is effective in eliminating aliphatic and acyclic S-compounds, but less efficient in removing thiophenic compounds like benzothiophene (BT) and dibenzothiophene (DBT) [3-5]. However, the HDS process requires harsher operating conditions, such as high temperatures, pressure (3-7 MPa cobalt-nickel based catalysts), larger reactor volumes, and high hydrogen consumption, all of which can escalate capital and operational costs [6-7].

However, the HDS process requires more severe operating conditions, including high temperatures, pressure (593-653 K, 3-7 MPa over sulfided CoMo or NiMo catalysts), larger

reactor volumes, and high hydrogen consumption, which can increase both capital and operational costs [6-7]. To overcome these limitations, researchers have focused on unconventional approaches such as adsorption [8], extraction [9], biodesulfurization [10], and oxidation [11] as possible technologies to produce ultralow sulfur diesel. Among these approaches, oxidative desulfurization (ODS) has received more attention due to its mild reactor conditions, low operational costs, and no hydrogen requirement, making it a potential cost-effective technology for desulfurization process [12-14].

In general, the ODS process combined with extraction transforms refractory thiophenic compounds such as DBT to its corresponding sulfone and sulfoxide species by using different oxidants such as H_2O_2 [15-17], molecular oxygen [18], formic acid [19] and ozone [20]. Among these oxidants, H_2O_2 has been widely used due to its effective oxygen content, low cost, and producing water as a byproduct [21]. In order to eliminate oxidized sulfur compounds, different extractant solvents such as DMF [22], MeCN [23], DMSO [24], and methanol [25] have been reported.

Several research studies have demonstrated the effectiveness of various heteropolyacids (HPAs) as acid catalysts, with particular attention given to HPAs possessing versatile properties such as low toxicity, non-corrosiveness, and high stability in humid environments, for the removal of thiophenic compounds [26-28]. Among Keggin-type HPAs, $H_3PW_{12}O_{40}$ (PW), $H_4SiW_{12}O_{40}$ (SiW), and $H_3PMo_{12}O_{40}$ (PMo) are widely utilized as catalysts in ODS of thiophenic compounds, owing to their redox properties, stability, and availability with H_2O_2 [29-30].

The catalytic ability of heteropolyacid (HPAs) can be difficult to fully utilize due to high solubility in extraction phases and their low specific surface area (1-10 m^2/g) [31]. In order to increase surface area, the facility of recovery and reusing of solid insoluble catalysts, different HPAs such as SiMo, PMo, PW supported on mesoporous silica [32], carbon supported [33], alumina [34], zeolite [35], have been studied. It is important to use a support with large surface area, high recyclability, and reactivity. Montmorillonite K10 clay is one of the most catalysis support due to its low cost, high surface area, and Brönsted and Lewis acid sites [36].

The purpose of this work was to prepare a series of different HPAs-Keggin types on the commercial montmorillonite K10 by using impregnating method (PW/K10, SiW/K10, and PMo/K10), then heterogeneous catalysts were used for ODS of the mixed model oil (thiophene (T), BT, and DBT in *n*-hexane) and real oil (crude oil and gasoline). For extracting of oxidized products, different extractants such as DMF, EtOH, and MeCN were tested. Furthermore, to investigate the impact of crude oil compositions, the effects of xylene, cyclohexene, and 1,7-octadiene, as well as the effects of nitrogen heterocycles such as pyridine and pyrrole were studied.

Experimental

Materials and Methods

The HPAs used in the study were purchased from Aldrich, while K10 montmorillonite was obtained from Fluka. n-hexane (98%), N, N-dimethylformamide (DMF, 99.5%), hydrogen peroxide (30%), ethanol (99%), thiophene (98%), dibenzothiophene (98%), benzothiophene (98%), acetonitrile (98%), cyclohexene (99%), 1,7-octadiene (97%), o-xylene (99%), pyridine (99%), and pyrrole (97%) obtained from Merck were used without further purification. To conduct desulfurization experiments, a 50 mL batch reactor was utilized, which was equipped with a mechanical stirrer, a temperature controller, and a condenser. The reactor was operated under atmospheric pressure. The total sulfur content was determined using an Analytik Jena AG-multi EA 3100 Element Analyzer.

Catalyst Preparation

The PW/K10 catalyst was synthesized using the impregnation method described in a previous publication by our research group [38]. To prepare the PW/K10 catalyst, the montmorillonite was dried in an oven at 120 °C for 120 minutes before being used as a support. An appropriate amount of PW was dissolved in 5 mL of methanol and added dropwise to the pre-dried K10 support with constant stirring using a glass rod. As more PW solution was added, the clay turned into a paste form, and the resulting paste was stirred for 10 minutes to produce a free-flowing powder. The SiW/K10 and PMo/K10 catalysts were synthesized using a similar procedure. The catalysts' characterizations, including acidity and pore size distribution, were previously reported [39-40].

Catalytic tests
ODS of Mixed Model Mil

The reaction was conducted at a temperature of 75 °C, which was maintained using a water bath. To prepare the mixed model oil, DBT, BT, and T were dissolved in n-hexane to achieve a sulfur concentration of 1000 ppm. PW/K10 was added to the model oil, along with an extraction phase (EtOH, DMF, or MeCN) and an oxidant (30% aq. H_2O_2) in a specific ratio to sulfur (O/S; 10/1). The mixture was stirred under air pressure at 75 °C for 80 minutes until extraction equilibrium was reached. The reaction progress is monitored by TLC using n-hexane/ethyl acetate as the eluent. Following the completion of ODS, the solution was allowed to settle for 30 minutes at room temperature, and the products were extracted using a solvent. The n-hexane layer was withdrawn and analyzed using a total sulfur analyzer to measure the catalytic activity of PW/K10, as well as other catalysts like PMo/K10 and SiW/K10. The catalytic recyclability of PW/K10 is also tested by separating the catalyst by centrifugation, washing it with ether, and reusing it in the next run with fresh reactants. Overall, the experiment aims to study the catalytic activity and recyclability of PW/K10 in the ODS 1000 ppm mixed model oil. The use of a water bath, extraction phase, oxidant, and TLC allows for the monitoring and extraction of the reaction products, while the use of different catalysts (PW/K10, PMo/K10, and SiW/K10) allows for the comparison of their catalytic activity.

Oxidation of Crude Oil and Gasoline

To perform the ODS reaction, 5 mL of crude oil (1000 ppm, API 41.67) was added to 0.03 g of PW/K10, 50 μL of oxidating agent (H_2O_2), and 5 mL of MeCN as solvent. The mixture was stirred under air pressure at 75 °C. After the reaction was complete, the polar phase was analyzed using a total sulfur analyzer. For the HDS-treated crude oil, 5 mL of HDS-treated crude oil with a 300 ppm total sulfur concentration in the presence of 0.03 g of PW/K10 and 15 μL of H_2O_2 (under the same conditions as mentioned above) was added, and the mixture was stirred at 75 °C for 80 minutes. The upper phase was withdrawn and analyzed using a total sulfur analyzer. For the ODS of 1000 ppm gasoline and 300 ppm HDS treated process, a similar procedure was applied in the presence of PW/K10, H_2O_2, and MeCN at 75 °C for 80 minutes.

Results and Discussion
Mixed Model Oil Desulfurization

The experiments were conducted using a fixed O/S molar ratio of 10:1, with 0.03 g of PW/K10, PMo/K10, and SiW/K10 at 75 °C for 80 minutes, as shown in Table 1. These results provide insight into the effects of loading, catalyst reactivity, and solvent on the extraction of oxidized products (sulfone or/and sulfoxide). Table 1 demonstrates that EtOH is the most effective extractant solvent for removing oxidized thiophenic compounds in the model oil after

oxidation and extraction. During the reaction, the active polyoxoperoxo species alter thiophenic compounds to oxidized compounds, which move into the EtOH phase, causing the homogeneous phase to form two phases. The catalyst remains heterogeneous throughout the reaction (as shown in Scheme 1).

Table 1. ODS of mixed model oil, different catalysts loading and extractants

Entry	Type of Catalyst	Loading Catalyst	Conversion (%)		
			EtOH	DMF	MeCN
1	PW/K10	60	99.99	94.95	98.68
2	PW/K10	40	98.76	93.45	96.47
3	PW/K10	20	85.48	75.67	81.45
4	SiW/K10	40	94.56	87.69	92.73
5	PMo/K10	40	89.95	82.49	86.34
6	K10	---	31.24	27.05	29.47
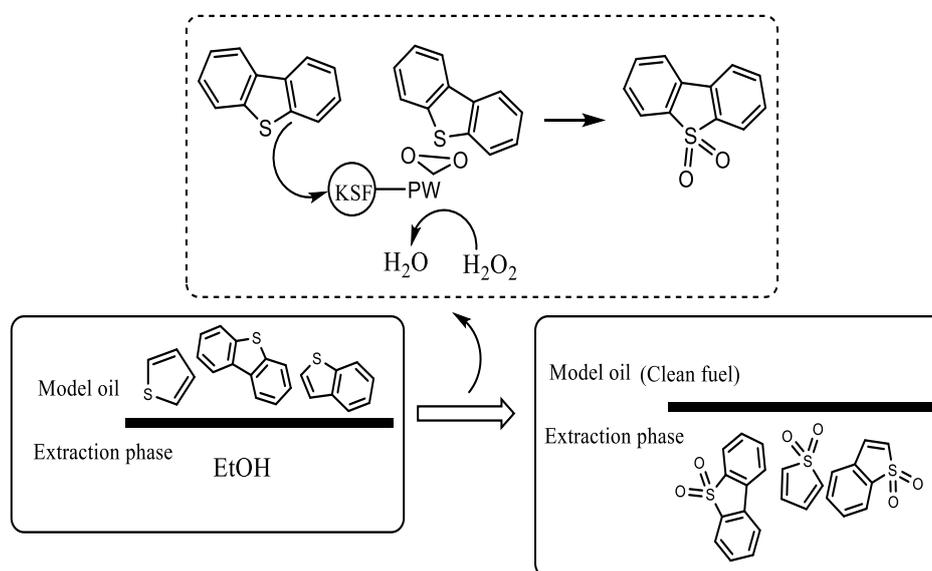
Scheme 1. Desulfurization process

As seen in Table 1, desulfurization capacity followed the order: PW/K10 (40 wt. % loading) > SiW/K10 > PMo/K10. The results show that the PW catalyst is more effective than the SiW catalyst. The conversion of S-compounds to corresponding sulfone or solfoxides was increased with increase in loading of HPAs on K10. In the presence of K10 but without HPAs, a small reduction (31.24 %) of sulfur content was observed with EtOH as an extractant. The removal rate increased with reaction time, and it was almost stable after 80 minutes.

The optimum conditions were determined to be PW/K10 with 40 wt. % loading and EtOH as the extractant. Under these conditions, the total sulfur concentration of the 1000 ppm mixed model oil was reduced to 12.4 ppm without any loss of n-hexane. To check the recyclability of the catalyst, 1000 ppm mixed model oil was evaluated for five successive runs, which was shown no obvious decrease in the catalytic activity (Fig. 1). However, the recycled catalyst showed almost the same performance as the original one and ODS removal decreased to 89.78% after 5th run. PW/K10 has the advantage of being easily separable from the reaction and the average recovery rate of PW/K10 was 93.15%.
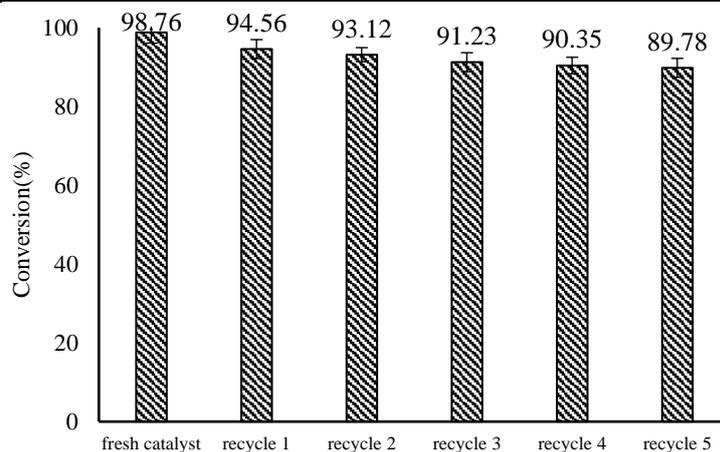
Fig. 1. Influence of the recycle times on ODS of mixed model oil

Table 2 summarizes the catalytic activity of PW/K10 in comparison to other supported PW catalysts reported in the literature. The results demonstrate that PW/K10 is a highly effective catalyst for ODS, providing the highest yield among the catalysts compared. Notably, our system offers several advantages over the reported systems, including shorter reaction times, lower reaction temperatures, lower catalyst loadings, and the absence of surfactants or ionic liquids as additives or solvents.

Table 2. Comparison of the PW/K10 with supported PW catalysts

Entry	Catalyst	S-compound	Conditions (O/S, Temp. (°C), time (min.), additives)	Conv. (%)	Ref.
1	PW/K10	DBT	(10, 75, 80)	99.64	−
2	PW/ TiO$_2$- SiO$_2$	DBT	(12, 70, 120)	96	[3]
3	PW/SPC	DBT	(3, 60, 120)	98.6	[5]
5	PW/SiO$_2$-Al$_2$O$_3$	DBT	(3, 70, 120)	79.94	[28]
6	PW/ Al$_2$O$_3$	DBT	(14, 70, 120)	98.1	[31]
7	Ag-modified PW/SiO$_2$	DBT	(12, 70, 240)	89.8	[32]
8	PW/HMS	BT	(8, 60, 60)	97.81	[41]
9	PMo/ SiO$_2$	DBT	(12, 60, 120)	97.1	[42]
10	PMoV$_2$/SBA-15	DBT	(16, 60, 120)	98.1	[43]
11	WO$_3$/Al$_2$O$_3$	Diesel fuel	(11, 60, 60)	70	[49]
12	[(C$_4$H$_9$)$_4$N]{PO$_4$ [MoO$_2$)$_2$]$_4$}	DBT	(2, 70, 180, [C$_8$mim]PF$_6$)	94	[50]
13	[C$_4$mim] HSO$_4$	DBT	(5, Room Temp., 120)	85	[51]
14	[Bmim] HSO$_4$	Sulfide	(2, 25, 240)	83	[52]

Crude Oil and Gasoline Desulfurization

The sulfur content of crude oil and its fractions typically varies from about 1000 to over 30000 ppm [37]. To evaluate the activity of PW/K10, the ODS process was conducted on two types of real oil, namely 1000 ppm crude oil and gasoline, using different extractants under optimal conditions. The findings indicate that the extractability of S-compounds in crude oil follows this order of decreasing effectiveness: MeCN > DMF > EtOH (as illustrated in Fig. 2).
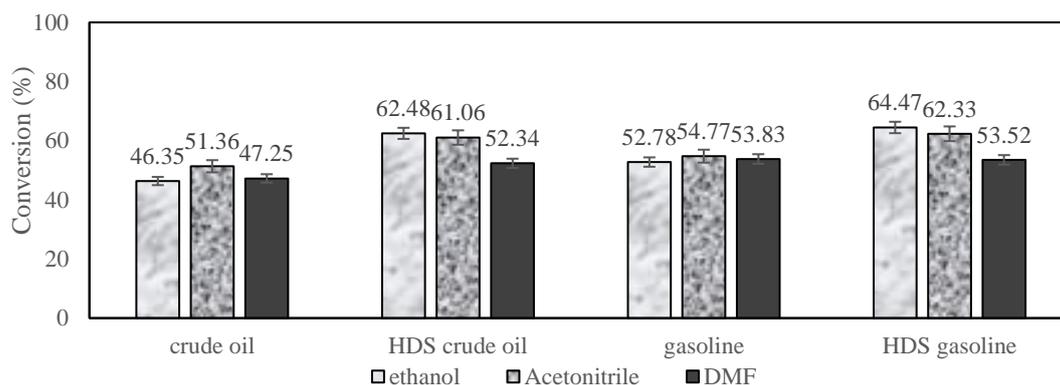
Fig. 2. Desulfurizationof crude oil, HDS crude oil, gasoline and HDS gasoilne

The conversion only reached 51.36, 47.25 and 46.35 % by employing MeCN, DMF, and EtOH respectively as extractants. For 1000 ppm gasoline, the results show the same as crude oil and the S-compounds removal followed the order of MeCN>DMF> EtOH.

Desulfurization of petroleum fractions has been a long-standing challenge in the refining process, and ODS has shown promise as a complementary method to hydrotreating. To test the catalyst's performance, 300 ppm crude oil after HDS processing was selected. Optimum conditions were determined using EtOH, MeCN, and DMF as extractants, resulting in sulfur removal of 62.48%, 61.06%, and 52.34%, respectively. After the HDS process, crude oil has reduced levels of the -SH functional group, while aromatic S-compounds, specifically thiophenic compounds, remained in the crude oil. It is noteworthy that while EtOH is an efficient extractant for oxidized aromatic S-compounds extracted from crude oil after HDS, it is less effective for crude oil itself (as seen in Fig. 2). The results suggest that EtOH is most effective as an extractant for the HDS product due to the less stringent material in crude oil and its fractions.

Effects of Composition

To assess the impact of crude oil composition on ODS, the effects of adding benzene, toluene, and xylene isomers as aromatics, ethylene and propylene as olefins, and pyridine and pyrrole as N-containing compounds were investigated on ODS [44-45]. However, 5%, 15%, and 25% vol. % of o-xylene, cyclohexene, and 1,7-octadiene were added to mixed model oil to examine their effects on ODS. The results indicated a significant difference in conversion between crude oil and simulated model oil. The PW/K10 (40 wt. % loading) catalyst was utilized with H_2O_2 under optimal conditions, and conversion was measured after 80 minutes of reaction time. As demonstrated in Fig. 3, the addition of o-xylene at various concentrations to the mixed model oil resulted in a decline in conversion from 98.76% to 87.52%, 71.69%, and 64.15% for 5%, 15%, and 25% vol. % of o-xylene, respectively.
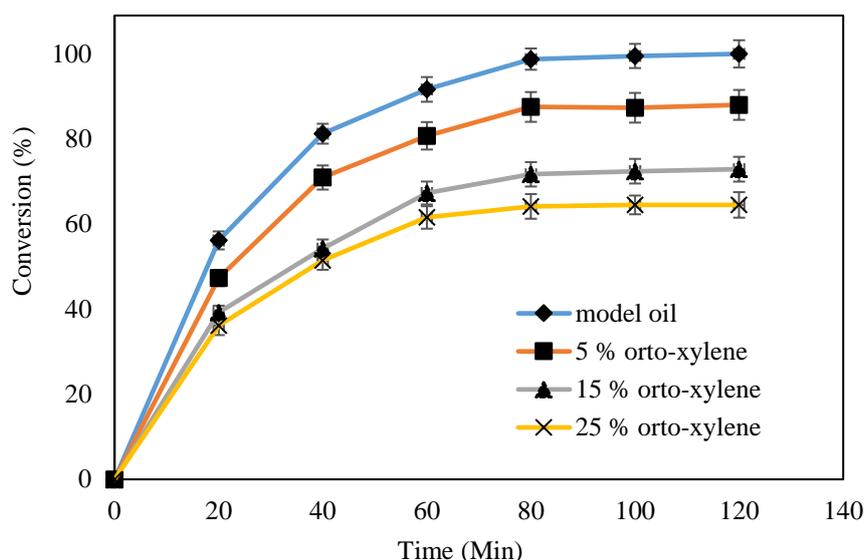
Fig. 3. The impact of *o*-xylene on ODS mixed model oil

As shown in Fig. 4, the addition of cyclohexene at 5%, 15%, and 25% vol. % resulted in a decline in catalyst activity and a decrease in ODS conversion of the model oil to 65.25%, 53.64%, and 47.77%, respectively. This suggests that cyclohexene has an unfavorable impact on the ODS process. Similarly, the addition of 1,7-octadiene at 5%, 15%, and 25% vol. % to the model oil (Fig. 5) led to a decrease in ODS conversion to 82.64%, 68.54%, and 64.27%, respectively. These findings indicate that the presence of olefins and aromatics in crude oil can have an adverse effect on ODS conversion. This is because these compounds compete with S-compounds for oxidation, and conjugation occurs between the lone pair on the S-atom of thiophenic compounds and the π-electrons on the aromatic ring. The electron-donating ability of the olefin and aromatic double bond makes them susceptible to ODS. The inhibiting effect increased in the order of o-xylene < 1,7-octadiene < cyclohexene, which can be explained by electronic and steric effects. The partial electron charge on the alkenes and aromatics affects the oxidation reactivity of the catalyst [1, 44].
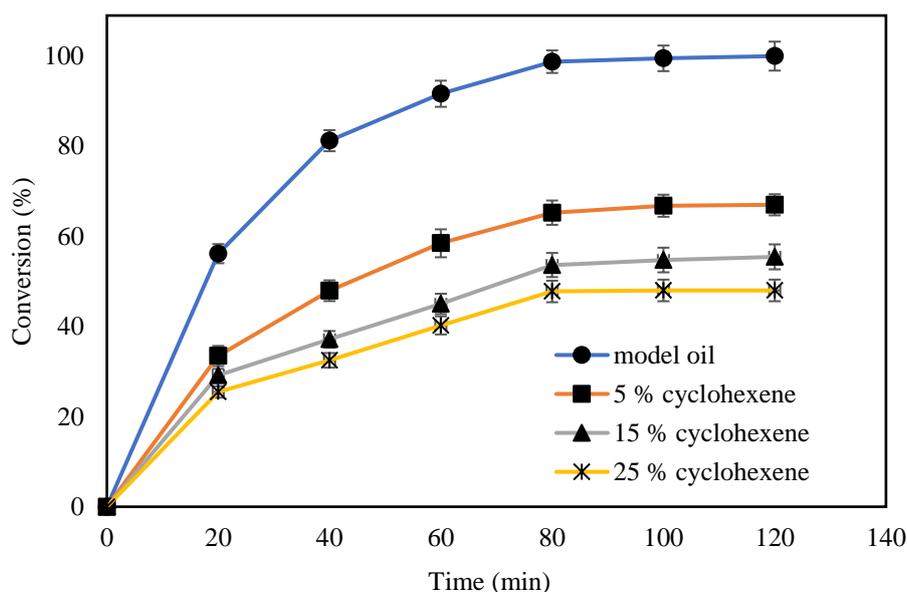

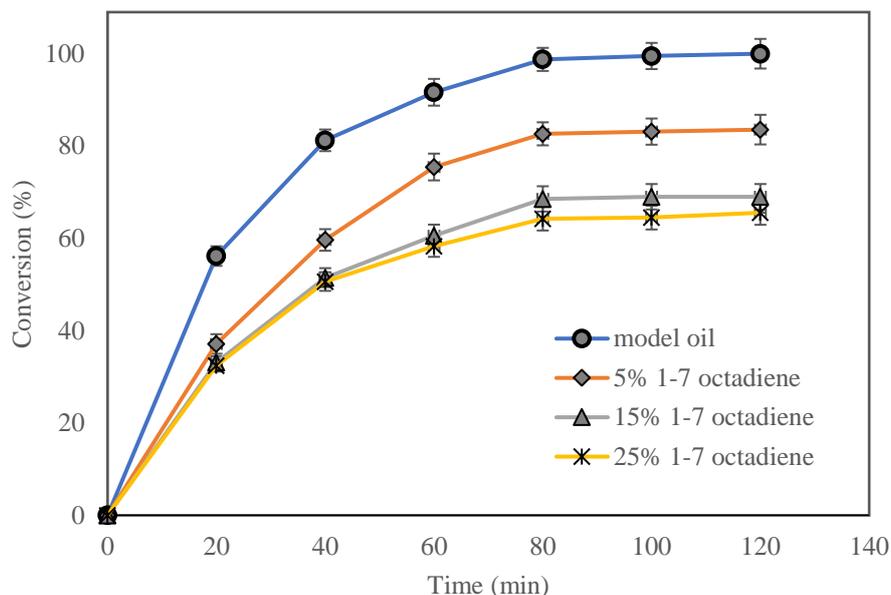**Fig. 4**. The impact of cyclohexene on ODS mixed model oil

Fig. 5. The impact of 1-7 octadiene on ODS mixed model oil

Effects of Nitrogen Compounds

To examine the effect of N-containing compounds in crude oil, pyrrole, and pyridine were selected and investigated for mixed model oil under optimized conditions, using ethanol as the extractant. However, the system did not reach a two-phase state in the presence of pyridine and pyrrole, and MeCN was thus tested as the extractant solvent. As shown in Fig. 6, the number of N-containing compounds had a negative impact on the ODS of the model oil in the presence of MeCN as the solvent. The poisoning effect of pyridine was observed to be greater than that of pyrrole. As reported in a previous study [45], the presence of N-compounds does not affect the ODS mechanism reaction, and the inhibition effect could be attributed to the adsorption and poisoning of active sites where reactive polyoxoperoxo complexes are formed. According to Jia et al., negative effects were observed due to the strong adsorption of N-compounds and oxidized products on the active sites of solid catalysts [46]. The lower reactivity of mixed model oil in the presence of pyridine compared to pyrrole may be explained by the fact that the nitrogen lone electron pair of pyridines is in an sp^2 orbital and does not participate in aromatic bonding, while the nitrogen in pyridine possesses a formal double bond. In contrast, the nitrogen in pyrrole donates its lone pair into the π ring, leading to the delocalization of its lone pair [47, 48]. Finally, to investigate the effect of N-compounds and unsaturated compounds simultaneously, a catalytic test was carried out for 1000 ppm mixed model oil containing 100 ppm of pyrrole and 15 Vol. % of o-xylene. The result showed 65.81% desulfurization of mixed model oil in the presence of MeCN under optimal conditions.
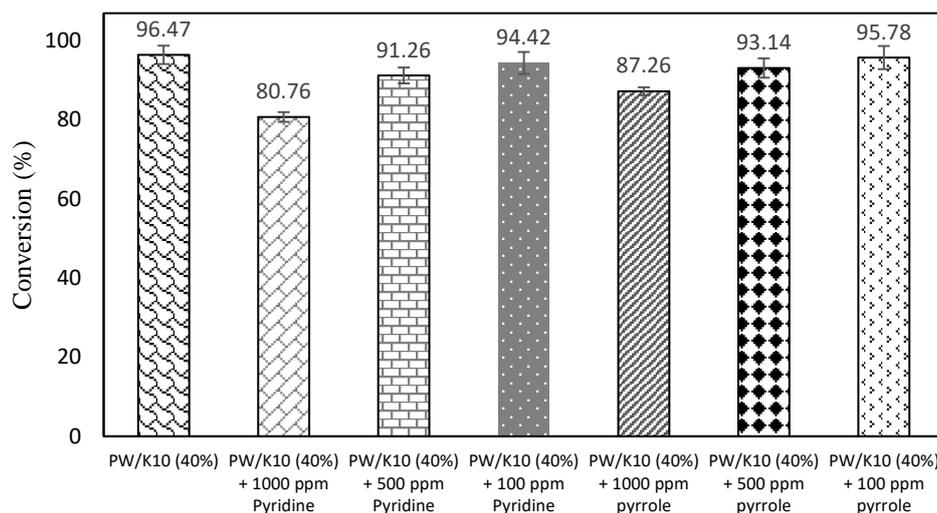
Fig. 6. The effects of pyridine and pyrrole on ODS 1000 ppm mixed model oil and MeCN

Conclusions

Various heterogeneous catalysts were successfully tested for ODS of mixed model and real oil. Among these catalysts, 40 wt.% PW supported on K10 was found to be the optimal catalyst, displaying a high degree of purification. The effect of oil composition revealed that unsaturated compounds have negative impacts on the conversion of S-compounds. The ODS activity of model oil decreased in the presence of N-compounds. The results for real models demonstrated a high potential of PW/K10 as an effective catalyst for the ODS of HDS treated real model. The recovered catalyst after the 5th run retained excellent catalytic activity for mixed model oil.

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