Deep extractive desulfurization of oil over 12-Molibdophosphoric acid encapsulated in metal-organic frameworks

Ezzat Rafiee[*,**,†] **and Narges Nobakht**[**]

*Faculty of Chemistry, Razi University, Kermanshah 67149, Iran
**Institute of Nano Science and Nano Technology, Razi University, Kermanshah 67149, Iran

Abstract–A desulfurization process for model oil and real oil was investigated based on the chemical oxidation of mixed sulfur containing compounds in the presence of nitrogen compounds (indole and quinoline) using hydrogen peroxide as oxidizing agent and dodecamolibdophosphoric acid ($H_3PMo_{12}O_{40}$) encapsulated in a kind of metal-organic framework (HKUST-1) as PMo@HKUST-1. The effect of isopropanol, ethanol and acetonitrile as extractive solvent and 1-ring (toluene, xylene and mesitylene) and 2-ring (naphthalene) aromatic hydrocarbons in desulfurization of model oil was studied. The desulfurization of sulfur-containing compounds was accelerated in the presence of aromatic hydrocarbons. In fact, a higher desulfurization efficiency of the heterogeneous catalyst could be achieved with system containing a polar solvent in contact with an aromatic hydrocarbon. Quinoline had no effect on oxidative desulfurization (ODS) reaction, whereas indole had a slightly negative effect. Presence of aromatic compounds had slightly positive effect on ODS reaction.

Keywords: Oxidative Desulfurization, Real Oil, Polyoxometalates, Metal-organic Frameworks

INTRODUCTION

The production of transportation fuels free from polluting compounds is clearly required. It is well known that sulfur- and nitrogen-containing impurities are important sources of air pollution, besides being potential agents in the formation of acid rain [1]. This problem has placed pressure to limit the sulfur content in fuels to ultralow levels in order to improve air quality [2]. Conventionally, sulfur-containing compounds in fuels are removed via hydrodesulfurization (HDS) in a refinery. However, polyaromatic sulfur-containing compounds, such as dibenzothiophene (DBT) and its derivatives, show significantly low HDS activity [3]. It is necessary to operate the HDS process under elevated temperature and pressure to achieve deep desulfurization, leading to increased operation costs.

Oxidative desulfurization (ODS) operates at atmospheric pressure, under eco-sustainable conditions, and without requiring hydrogen. This process conciliates the oxidation of the refractory sulfur compounds into more polar molecules [4]. In ODS reactions, the divalent sulfur can be oxidized by the electrophilic addition reaction of oxygen atoms to form the hexavalent sulfur of sulfones. The chemical and physical properties of sulfones are significantly different from those of hydrocarbons in fuel oil. Therefore, they can easily be removed by separation operations such as distillation, solvent extraction, adsorption, and decomposition [5]. The presence of an efficient catalyst in the oxidation step of the ODS procedure is crucial for the success of this process [6]. ODS in the presence

of a solid catalyst and extraction solvent is defined in two consecutive steps [7]: oxidation to the corresponding sulfones, followed by removal of sulfur compounds by extraction from the treated fuel to the extractive solvent. Thus the solvent is very important in the process. Ishihara et al. [8], Prasad et al. [9], and García-Gutiérrez et al. [10] reported that molybdenum oxide catalysts have shown activity in ODS of the refractory sulfur compounds. However, molybdenum oxide catalysts have critical drawbacks of Mo-leaching in the course of ODS. Chica et al. [11] reported that Ti-MCM-41 catalyst was more active and stable in ODS than MoO_3/Al_2O_3 catalyst without Ti-leaching. Hulea et al. [12] and Corma et al. [13] found that Ti-MCM-41 was more active than TS-1, proving that the accessibility of the S compounds to the active centers is important in ODS of refractory sulfur compounds. Cedeno-Caero et al. [14] reported that titanium oxide nanotube catalyst was more active in ODS than TiO_2 catalysts. More recently, Ti-SBA-15 catalysts were reported to exhibit high activity in the ODS [15].

In ODS catalysis, only a few papers have investigated the influence of nitrogen-containing compounds [16-19]. Cedeño et al. found that quinoline, indole, and carbazole poisoned the catalytic sites and thus decreased the ODS activity in the V_2O_5/Al_2O_3-H_2O_2 system [20]. Jia et al. compared the effect of oxidation denitrogenation (ODN) reactivity of basic and non-basic nitrogen compounds on the ODS of thiophene (T) and benzothiophene (BT) [21]. The production of light oil, with low level of sulfur, therefore requires inevitably the application of severe operating conditions and the use of especially active catalysts.

Polyoxometalates (POMs) are a class of compounds constituted by bulky clusters of transition metal oxide anions that have been extensively investigated as homogeneous catalysts [22,23]. Although the homogeneous POMs are remarkably efficient, they have a com-

†To whom correspondence should be addressed.
E-mail: ezzat_rafiee@yahoo.com, e.rafiei@razi.ac.ir

mon drawback: separation and reuse of the catalyst is extremely difficult also, specific surface area of POMs is low. For these reasons, future practical applications of POMs will also require methods for catalyst engineering.

One of the strategies to overcome these drawbacks consists of their encapsulation within porous solid matrixes [24-29]. Metal-organic frameworks (MOFs) have been shown to be effective supports to incorporate POMs to form efficient heterogeneous catalysts [30-34]. MOFs generally exhibit high porosity, specific functionality, selective interaction and many other desirable properties and are currently applied in a large number of fields such as catalysis [35-39]. As a well-known MOF, a stable host HKUST-1, can encapsulate various Keggin-type POMs, and attractive catalytic performance can be endowed by these POMs @HKUST-1 [23,29,38].

In the present work, a hybrid material dodecamolibdophosphoric acid ($H_3PMo_{12}O_{40}$, PMo) encapsulated in HKUST-1 (PMo@HKUST-1) was evaluated in the oxidation of BT, T and DBT, and the effects of different solvents, quinoline, indole as nitrogen compounds and aromatic hydrocarbons on the ODS activity were also investigated.

EXPERIMENTAL

1. Materials and Methods

Model compounds and chemicals, including BT (Aldrich, 98%), DBT (Aldrich, 98%), T (Aldrich, 96%), indole (Aldrich, 99%), quinoline (Aldrich, 98%), toluene (Aldrich, 97%), xylene (Aldrich, 98%), mesitylene (Aldrich, 96%) naphthalene (Aldrich, 98%) were used. The light cycle oil (LCO) feed was supplied from a refinery in Iran with API 41.67. Copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot$

$3H_2O$) (99-104%), 1,3,5-benzen-tricarboxylic acid (BTC) (98%), cetyltrimethylammonium bromide (CTAB) (99+%), PMo (99+%), H_2O_2 (30%) and other reagents and solvents used in this work were obtained from Merck, Aldrich or Fluka and used without further purification. Both feed and products were analyzed by gas chromatographic-mass spectroscopy (GC-MS) Agilent Technologies 6890N Instrument, equipped with a capillary column 19019J-413 HP-5, and a flame ionization detector. Total sulfur contents were determined by using an Analytic Jena AG- multi EA® 3100 Element Analyzer. In all tests control experiments were performed.

2. Catalyst Preparation

PMo@HKUST-1 was synthesized according to the procedure reported previously [41]. For the synthesis of PMo@HKUST-1 catalyst, a mixture of BTC (0.21 g, 1 mmol) and 0.07 g of CTAB in absolute ethanol (12 mL) was prepared and then 0.1 g of PMo and 1.45 g of copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) were dissolved in distilled water (10 mL). Both solutions were combined and mixed under vigorous stirring for approximately 30 min and were aged without stirring for a further two days at room temperature. Light green precipitate was then collected, washed with distilled water three times, and dried at 60 °C for 24 h. CTAB was removed by Soxhlet extraction with ethanol (laboratory use, Chem-Lab) performed for 24 h. The product was dried in air at 60 °C.

3. Activity Test

3-1. Oxidative Desulfurization of Model Oil (Table 1, Entry 1)

Model oil was prepared by dissolving DBT, BT and T in 10 mL of n-heptane (see, Scheme 1), with corresponding S-content of 500, 250 and 250 ppmw, respectively. Model oil was combined by 0.08 g of the catalyst. The ODS experiments were under air (atmospheric

Table 1. Composition of model feed oils

Entry	Model feeds		Extracting solvents	Notation
1	Dibenzothiphene (DBT)	500 ppmw S	-----	F
	Benzotiophene (BT)	250 ppmw S		
	Thiophene (T)	250 ppmw S		
	n-Heptane	Balance		
2	Feed+MeCN	1000 ppmw S	MeCN	F_1
3	Feed+^{i}PrOH	1000 ppmw S	DMF	F_2
4	Feed+EtOH	1000 ppmw S	EtOH	F_3
5	Feed+MeCN+indole	1000 ppmw S+100 ppmw indole	MeCN	F_1I
6	Feed+^{i}PrOH+indole	1000 ppmw S+100 ppmw indole	DMF	F_2I
7	Feed+EtOH+indole	1000 ppmw S+100 ppmw indole	EtOH	F_3I
8	Feed+MeCN+quinoline	1000 ppmw S+100 ppmw quinoline	MeCN	F_1Q
9	Feed+^{i}PrOH+quinoline	1000 ppmw S+100 ppmw quinoline	DMF	F_2Q
10	Feed+EtOH+quinoline	1000 ppmw S+100 ppmw quinoline	EtOH	F_3Q
11	DBT+EtOH+naphthalene	1000 ppmw DBT+100, 200 and 300 ppmw naphthalene	DMF	F_4
12	Feed+EtOH+(toluene +xylene+mesitylene)	1000 ppmw S+10-50 vol% toluene+xylene+mesitylene (in similar vol% of each one)	DMF	F_5
13	Feed+EtOH+indole+(toluene+xylene +mesitylene)+naphthalene	1000 ppmw S+100 ppmw indole+30 vol% toluene+xylene+ mesitylene (in similar vol% of each one)+100 ppmw naphthalene	DMF	F_6

(DBT)   (T)   (BT)
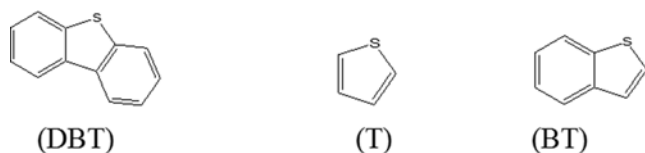
Scheme 1. Chemical structures of refractory sulfur compounds.

pressure) in a closed borosilicate reaction vessel, equipped with a magnetic stirrer and immersed in a thermostatically controlled
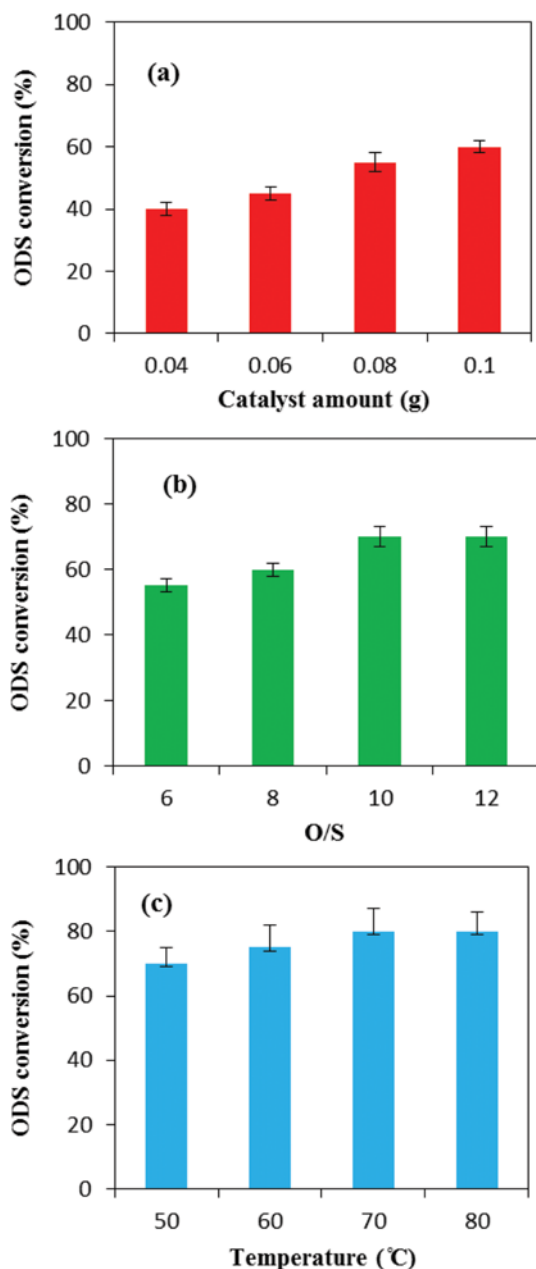

Fig. 1. Effect of (a) catalyst amount (temperature 50 °C; O/S: 6), (b) O/S molar ratio (temperature 50 °C, catalyst amount: 0.08 g) (c) temperature (catalyst amount: 0.08 g, O/S: 10) in the ODS reaction of model oil containing n-heptane/ethanol (50/50 vol%) as solvents.

liquid paraffin bath at 70 °C. The mixture was performed using the model oil:solvent (EtOH or ^{i}PrOH or MeCN) (1:1 volume ratio) (Table 1, entries 2-13). The catalytic reaction was initiated by addition of H_2O_2 as oxidant (molar ratio of H_2O_2 to S-compounds (O/S) was 10). After completion of the reaction, the catalyst was separated by centrifugation for 15 min at 1,500 rpm. In this study, the sulfur compounds were oxidized to their corresponding sulfones, and the products were removed by extraction.

3-2. Oxidative Desulfurization of Real Oil

In the ODS of real oil, 10 mL of oil (sulfur content: 530 ppmw) was used. Catalyst (0.04 g) and aqueous solution of H_2O_2 (O/S mole ratio, 10) were added. Vigorous stirring was maintained for 60 min at 70 °C. After completion of the reaction, solid catalyst was separated by centrifugation for 15 min at 1,500 rpm and products could be separated from the polar phase by simple decantation. The sulfur content of the real oil was measured on a total sulfur analyzer.

RESULTS AND DISCUSSION

The influence of the catalyst amount, temperature and O/S on the ODS conversion in model feed containing n-heptane/ethanol (50/50 vol%) as solvents was studied using PMo@HKUST-1 (Fig. 1). These experimental results indicated that 0.08 g of the catalyst and O/S=10 at 70 °C were the most appropriate for ODS conversion. According to the optimized reaction conditions, oxidation of other model feeds was investigated (Table 1, entries 2-13).

1. Effect of Various Solvents on the ODS

Solvent has an important effect on the ODS process, although this effect is strongly dependent on the type of the catalyst and nature of the substrate. To examine the effect of various solvents on the ODS, different solvents such as MeCN, ^{i}PrOH and EtOH were used in the model feed oil (F), and their feed mixtures were denoted as F_1, F_2 and F_3, respectively (Table 1). These solvents are more attractive because of rather low price and no environmental problems. ODS conversion is shown in Fig. 2, with only n-heptane as solvent. In this case sulfur-containing compounds were removed on average 46.6% after 60 min. According to Fig. 2 the use of second solvent led to an increase in the ODS activity, and the ODS conversion
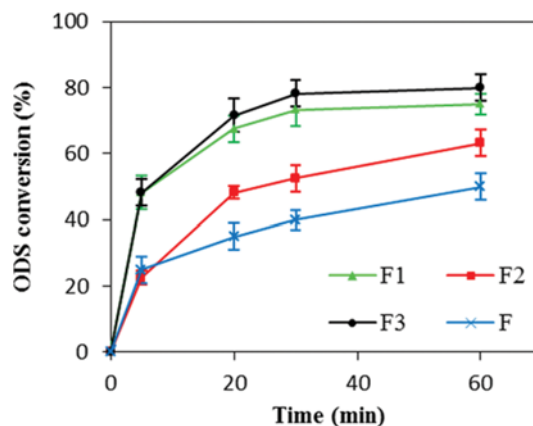

Fig. 2. Effect of different solvents on the ODS in a batch reactor: (F, F_1, F_2 and F_3). Reaction conditions: O/S, 10; PMo@HKUST-1, 0.08 g; at 70 °C for 60 min.

was found to be depend strongly on the type of second solvent. The results show that higher amounts of sulfur can be removed with EtOH and MeCN as second solvent (F_1 and F_3), whereas with ^iPrOH, only 63% was attained. It seems that polarity of the second solvent has a positive effect on ODS because the products have higher polarity than the corresponding sulfides. Therefore, solvents with higher polarity extracted the products effectively. Also, the affinity of the solvent with the catalyst is also a parameter that must be taken into account to optimize the ODS process [6]. The reason for this enhancement in ODS reaction rate with MeCN and especially EtOH may be that the formation of micro-droplets of the products was prevented and the reaction rate was improved due to removal of reaction products from the nonpolar phase [42].

Fig. 3 shows oxidation of different S-compounds in the feed separately when using different solvents. All three solvents had the same trend in removal of S-compound, which was in decreasing order, DBT>T>BT.

2. Effect of Nitrogen Compounds on the ODS

The effect of different amounts of indole on DBT conversion in a batch reactor (EtOH as second solvent) is shown in Fig. 4. The
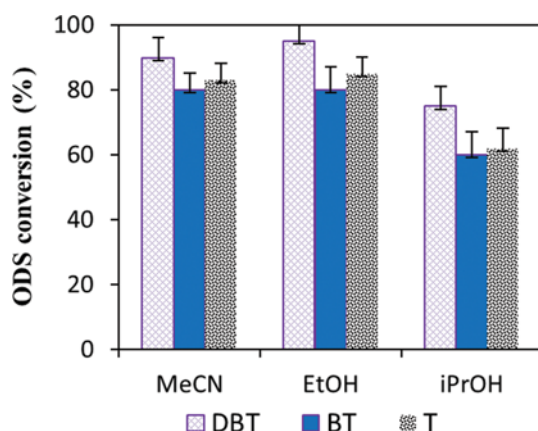

Fig. 3. Oxidation of different S compounds obtained over several solvents. Reaction conditions: O/S, 10; PMo@HKUST-1, 0.08 g; at 70 °C for 60 min.
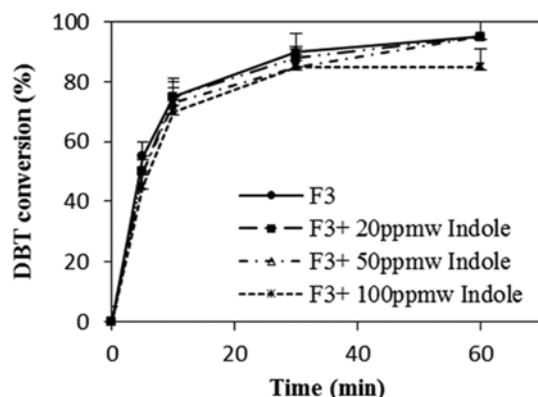

Fig. 4. Effect of different amounts of indole on DBT desulfurization in a batch reactor. Reaction conditions: O/S, 10; PMo@ HKUST-1, 0.08 g; ethanol and n-heptane as solvents with 1 : 1 volume ratio at 70 °C for 60 min.

content varied from 20 to 100 ppmw. DBT gave over 85% conversion at 100 ppmw indole content. When indole was added, greater inhibition behavior was observed. Also, indole was converted prior to the ODS of sulfur compounds. But, for up to 100 ppmw of indole the catalytic activity was fairly stable and DBT oxidation was high. It is apparent that the oxidation of DBT takes place in parallel to that of indole in low and high amounts in the presence of PMo@HKUST-$1/H_2O_2$. These results suggest that N-compounds are competitive with the sulfur compounds in oxidation, as indole has a higher reactivity than sulfur compounds in the oxidation reaction. Moreover, indole or product of indole oxidation might not strongly adsorb on the catalytic sites to poison the catalyst even in high concentration. The slight decrease in DBT oxidation is due to the competitive
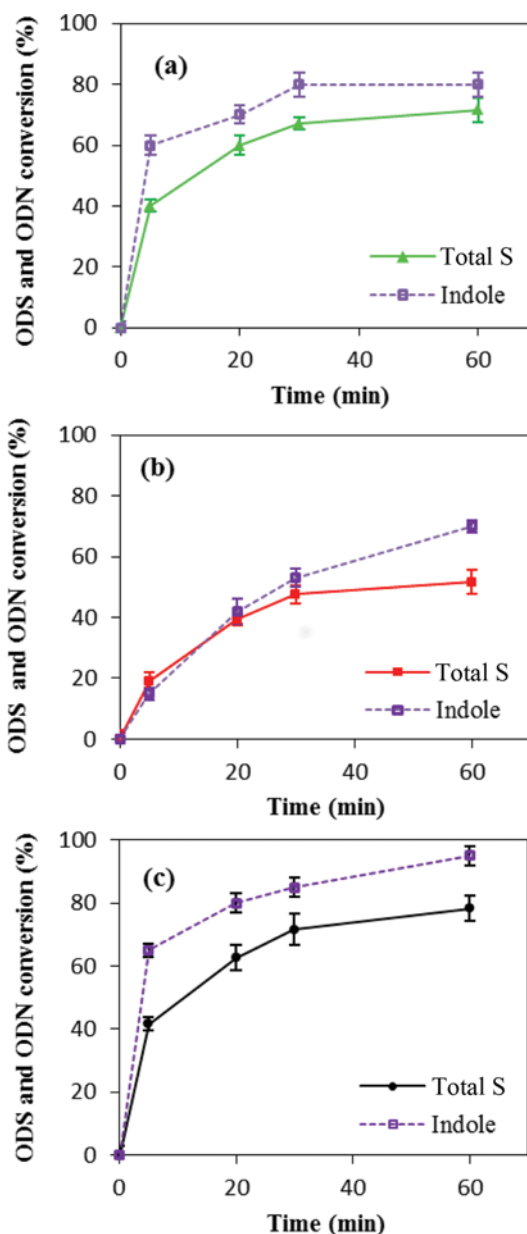

Fig. 5. Effect of indole on the ODS in a batch reactor with different solvents: (a) F_1I, (b) F_2I, (c) F_3I. Reaction conditions: O/S, 10; PMo@HKUST-1, 0.08 g; at 70 °C for 60 min.
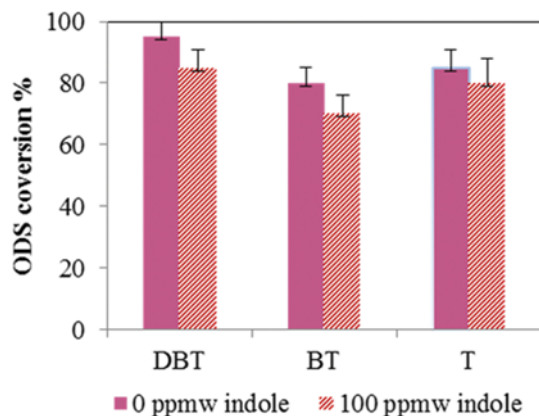
Fig. 6. Effect of indole on oxidation of different S compounds. Reaction conditions: O/S, 10; PMo@HKUST-1, 0.08 g; ethanol and *n*-heptane as solvents with 1 : 1 volume ratio at 70 °C for 60 min.

utilization of H_2O_2 by DBT and indole. Polar solvent could effectively dissolve the oxidized compounds to be readily desorbed from catalyst surface.

In next step, to examine the effect of nitrogen compounds (indole and quinoline) on the ODS, activity tests were carried out for different model feed mixtures containing various solvents and two types of nitrogen compounds. Fig. 5 shows the ODS and ODN conversion for the model feeds with indole (F_1I), (F_2I) and (F_3I) as a function of reaction time. The effect of different solvents such as MeCN, EtOH and ^iPrOH in ODS was investigated in the presence of 100 ppmw of indole. It is apparent that the oxidation of sulfide compounds takes place in parallel to oxidation of N-containing compounds in the presence of EtOH as solvent. Fig. 5 (b) indicates that with ^iPrOH as solvent, ODN decrease the ODS conversion. Note that indole is in competition with sulfides, and the decrease in sulfides oxidation is due to this competitive utilization of H_2O_2. The higher conversion of sulfides to corresponding products may be due to good solubility of ODS products in EtOH compared with other solvents.

Fig. 6 shows the comparison between the conversion of DBT, BT and T in the presence of indole obtained over EtOH as solvent. Fig. 7 shows the ODS and ODN conversion for the model feeds with quinoline (F_1Q), (F_2Q) and (F_3Q) as a function of reaction time. From the results, ODS was significantly more than ODN and quinoline oxidation had lower effect on ODS than indole. The higher activity of indole than quinoline was ascribed to the higher electron density on the nitrogen atom in indole [17]. Indole was reported to be oxidized under mild reaction conditions [43]. But for the oxidation of quinoline, many studies were focused at higher reaction temperature (>200 °C) [44].

3. Effect of Aromatic Hydrocarbons on the DBT Conversion

Actual oils contain large quantities of aromatic hydrocarbons; hence, it is necessary to identify the effect of these compounds during the ODS process. The DBT removal rate with addition of 1-ring aromatics (toluene, xylene and mesitylene) is shown in Fig. 8. Addition of these aromatic hydrocarbons from 10 to 50 vol% indicates that aromatic compounds had slightly positive effect on the oxidation of
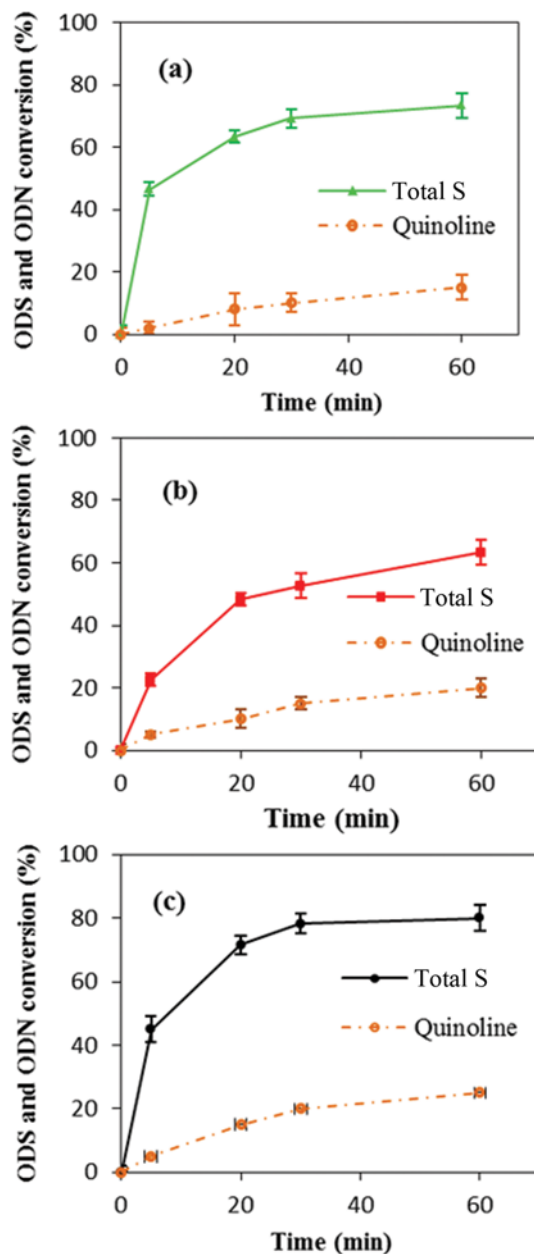

Fig. 7. Effect of quinoline on the ODS in a batch reactor in different solvents: (a) F_1Q, (b) F_2Q, (c) F_3Q. Reaction conditions: O/S, 10; PMo@HKUST-1, 0.08 g; at 70 °C for 60 min.

DBT. This suggests that the desulfurization of DBT was accelerated by the presence of 1-ring aromatic compounds. In the presence of 1-ring aromatics in this experiment the aggregation of PMo@HKUST-1 was decreased and the catalyst dispersed; thus, surface area was increased.

Naphthalene was used as the model component to represent the 2-ring aromatic in light oils in our research. The effect of naphthalene on the desulfurization of DBT was studied with respect to desulfurization yield of DBT; as shown in Fig. 9, DBT removal was slightly increased in the presence of naphthalene even at a high concentration of 300 ppmw. It is reported that acceleration of the desulfurization of DBT in the presence of aromatics is caused by R-oxy-
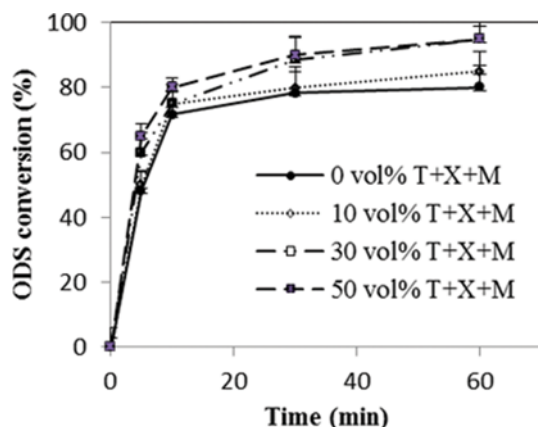
Fig. 8. Effect of 1-ring aromatic compounds (toluene (T), xylene (X), mesitylene (M)) (in similar vol% of each one) on DBT desulfurization at various volume percentages (vol%) on DBT desulfurization (F_5). Reaction conditions: O/S, 10; PMo@HKUST-1, 0.08 g; ethanol and *n*-heptane as solvents with 1 : 1 volume ratio at 70 °C for 60 min.

Fig. 10. Effect of 2-ring aromatic compound (naphtalene) on oxidation of different S compounds. Reaction conditions: O/S, 10; PMo@HKUST-1, 0.08 g; ethanol and n-heptane as solvents with 1 : 1 volume ratio at 70 °C for 60 min.
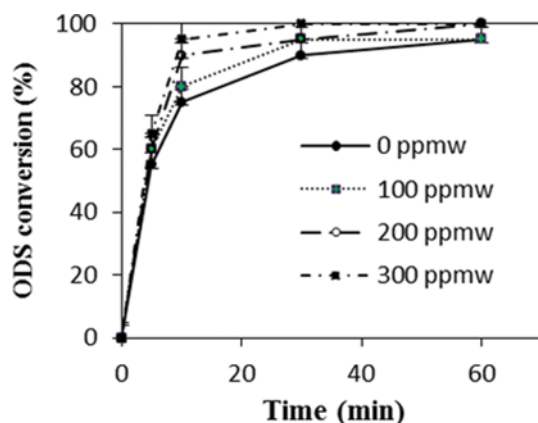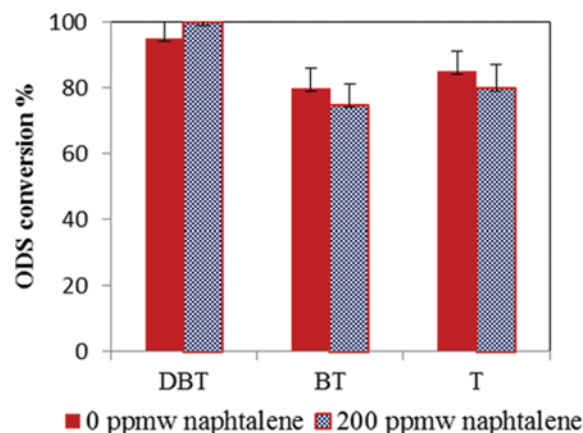

Fig. 9. Effect of 2-ring aromatic compound (naphtalene) at various amounts on DBT desulfurization (F_4). Reaction conditions: O/S, 10; PMo@HKUST-1, 0.08 g; ethanol and *n*-heptane as solvents with 1 : 1 volume ratio at 70 °C for 60 min.
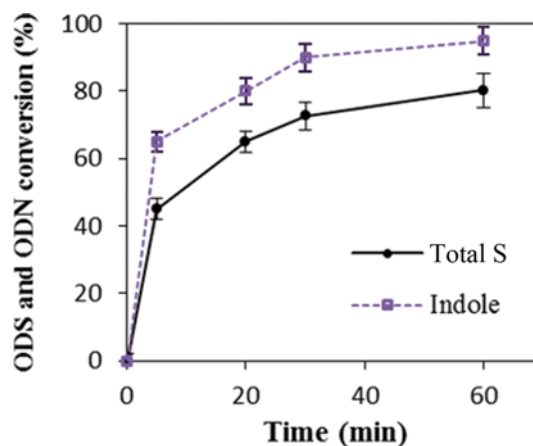

Fig. 11. Effect of ethanol+30 vol% (toluene+xylene+mesitylene, in similar vol% of each one)+200 ppmw naphtalene on the ODS and ODN in a batch reactor (F_6). Reaction conditions: O/S, 10; PMo@HKUST-1, 0.08 g; ethanol and *n*-heptane as solvents with 1 : 1 volume ratio at 70 °C for 60 min.

hydroperoxide, which is formed via the reaction of the oxidation products of aromatics with H_2O_2 [16]. The oxidation reactivity of sulfur compounds to R-oxyhydroperoxide is reported to depend on the net electron density on the S atom [45]. This suggests that the desulfurization of sulfur compounds, of high electron density, was accelerated by the presence of aromatics owing to the oxidation by R-oxyhydroperoxide, whereas the desulfurization of compounds, of low electron density was decelerated by the presence of aromatics owing to competitive oxidation of the aromatics to that of the sulfur compounds by the oxidizing agent. However, no naphthalene conversion was observed in our experiment. As shown in Fig. 10, this study showed that the desulfurization yield for BT and T silently decreased in the presence of 200 ppmw naphthalene, but desulfurization yield for DBT was enhanced. Although the presence of naphthalene decreases the desulfurization of BT and T (Fig. 10) but increases DBT desulfurization, leading higher total sulfur

removal from actual light oils containing high aromatic compounds.

4. Effect of Aromatic Hydrocarbons and Indole on the ODS

To simulate the ODS activity in real oil, the ODS activity in the presence of 1-ring and 2-ring aromatic compounds and indole in feed oil (F_6) (Fig. 11) was carried out. The ODS conversion of model oil in the presence of aromatic compounds was not remarkably affected by indole. The oxidized compounds were nearly insoluble in n-heptane, while they could well dissolve in aromatics. The results indicated that aromatics do not play a beneficial role in increasing of oxidation of S or N-compounds (compare Fig. 11 with Fig. 5(b)). When both aromatic compounds and N-compound were added, decreasing in ODS conversion related to presence of indole remained. It means that decreasing effect of indole is more important in the ODS conversion than effect of aromatic compounds. Table 2 shows catalytic activity of PMo@HKUST-1 catalyst in comparison with some reported ODS reactions in the presence of other

Table 2. Catalytic activity of PMo@ HKUST-1 in comparison with other reported catalysts

Entry	Catalyst (g)	S compounds	Reaction conditions	ODS conv. in the absence/ presence of indole (%)	Ref.
1	[Bmim]$_3$PMo$_{12}$O$_{40}$/SiO$_2$	DBT	60 $^\circ$C, O/S=3, 180 min	70%/100%	17
2	Ti-SBA-15	BT, DBT, 4,MDBT, 4,6-DMDBT	80 $^\circ$C, TBHP/S=2.5, 180 min	100%/20%	18
3	V19/Al	DB, DBT, 4-DMBT	60 $^\circ$C, 30 min, O/S=4	37%/57.7%	19
4	PMo@HKUST-1	BT, DBT, T	70 $^\circ$C, O/S=4, 60 min	95%/80.3%	This work
5	MgAl-PMo$_{12}$	DBT, 4,6-DMDBT, BT, T	O/S=20, 70 $^\circ$C, 120 min	100%	5
6	V$_2$O$_5$/Al$_2$O$_3$	BT, DBT, 4-MDBT, 4,6-DMDBT	70 $^\circ$C, 60 min, O/S=8	70-85%	46
7	W/D1$_{52}$	DBT	CYHPO/DBT of 2.5, 100 $^\circ$C, 40 min	99.1%	47
8	[C$_{18}$H$_{37}$N(CH$_3$)$_3$]$_7$[PW$_{10}$Ti$_2$O$_{38}$(O$_2$)$_2$]	DBT	90 $^\circ$C, O$_2$	100%	48
9	Mo/γ-Al$_2$O$_3$	Diesel fuel	O/S=11, 50 $^\circ$C, 60 min	97%	49
10	HPW/SiO$_2$	DBT, BT, 4,6-DMDBT	80 $^\circ$C, CH$_3$CN, O/S=12, 2 h	97%	50

catalysts.

5. Oxidative Desulfurization of LCO

The PMo@HKUST-1/H$_2$O$_2$ oxidation system was evaluated in the ODS of light cycle oil with a sulfur content of 530 ppmw. 71.7% of the sulfur in the real oil was removed in this oxidation system at O/S of 10 and 70 $^\circ$C after 60 min. The sulfur content of the real oil after oxidation and extraction decreased to 150.5 ppmw. The results confirm that the PMo@HKUST-1/H$_2$O$_2$ oxidation system is effective in removing bulky sulfur compounds from light oil.

CONCLUSIONS

The PMo@HKUST-1 revealed to be a efficient catalyst for oxidative desulfurization of oils containing refractory sulfur compounds in the presence of an appropriate solvent: DBT, BT and T. This solvent must be capable of efficiently extracting the sulfur compounds from the oil phase. The best catalytic performance using PMo@HKUST-1 and H$_2$O$_2$ as oxidant was achieved with EtOH. For all model feeds, the results indicated that the oxidation reactivity of sulfur compounds decreased in the order of DBT>T>BT. The effects of quinoline, indole as nitrogen compounds in the presence of different solvents on ODS activity were also investigated. Indole as nitrogen-containing compound shows no negative effect in the oxidation of sulfur-containing compounds except when ^{i}PrOH is used as solvent. The desulfurization of the sulfur-containing compounds was accelerated in the presence of aromatic hydrocarbons. In fact, a higher desulfurization efficiency of the heterogeneous catalyst was achieved with system containing a polar solvent in contact with an aromatic hydrocarbon, such as n-heptane/(toluene+xylen+mesitylene)/naphthalene/EtOH. The yield of S-removal of actual oil was 71.7%.

ACKNOWLEDGEMENTS

REFERENCES

1. F. W. de Souzaa, I. R. Guimarães, M. C. Guerreiro and L. C. A. Oliveira, *Appl. Catal. A: Gen.*, **360**, 205 (2009).
2. A. Stanislaus, A. Marafi and M. S. Rana, *Catal. Today*, **153**, 1 (2010).
3. X. Jiang, H. M. Li, W. S. Zhu, L. N. He, H. M. Shu and J. D. Lu, *Fuel*, **88**, 431 (2009).
4. G. Zhang, F. Yu and R. Wang, *Petroleum & Coal*, **51**, 196 (2009).
5. F. Yu and R. Wang, *Molecules*, **18**, 13691 (2013).
6. S. Ribeiro, C. M. Granadeiro, P. Silva, F. A. Almeida Paz, F. F. de Biani, L. Cunha-Silva and S. S. Balula, *Catal. Sci. Technol.*, **3**, 2404 (2013).
7. D. Huang, Y. J. Wang, L. M. Yang, and G. S. Luo, *Ind. Eng. Chem. Res.*, **45**, 1880 (2006).
8. A. Ishihara, D. Wang, F. Dumeignil, H. Amano, E. W. Qian and T. Kabe, *Appl. Catal. A. Gen.*, **279**, 279 (2005).
9. V. V. D. N. Prasad, K. E. Jeong, H. J. Chae, C. U. Kim and S. Y. Jeong, *Catal. Commun.*, **9**, 1966 (2008).
10. J. L. García-Gutiérrez, G. A. Fuentes, M. E. Hernández-Terán, F. Murrieta, J. Navarrete and F. Jiménez-Cruz, *Appl. Catal. A: Gen.*, **305**, 15 (2006).
11. A. Chica, A. Corma and M. E. Dómine, *J. Catal.*, **242**, 299 (2006).
12. J. M. Campos-Martin, M. C. Capel-Sanchez and J. L. G. Fierro, *Green Chem.*, **6**, 557 (2004).
13. A. Corma, M. Iglesia and F. Sanchez, *Catal. Lett.*, **39**, 153 (1996).
14. L. Cedeño-Caero, M. Ramos-Luna, M. Méndez-Cruz and J. Ramírez-Solís, *Catal. Today*, **172**, 189 (2011).
15. T. W. Kim, M. J. Kim, F. Kleitz, M. M. Nair, R. G. Nicolas, K. E. Jeong, H. J. Chae, C. U. Kim and S. Y. Jeong, *ChemCatChem.*, **4**, 687 (2012).
16. Y. Shiraishi, K. Tachibana, T. Hirai and I. Komasawa, *Ind. Eng. Chem. Res.*, **41**, 4362 (2002).
17. J. Zhang, A. Wang, X. Li and X. Ma, *J. Catal.*, **279**, 269 (2011).
18. K. S. Cho and Y. K. Lee, *Appl. Catal. B: Environ.*, **147**, 35 (2014).
19. L. Cedeño-Caero, H. Gomez-Bernal, A. Fraustro-Cuevas, H. D.

Guerra-Gomez and R. Cuevas-Garcia, *Catal. Today*, **133**, 244 (2008).

20. J. F. Navarro-Amador, H. Gómez-Bernaly and L. Cedeño-Caero, *Revista Mexicana de Ingenieria Quimica*, **5**, 293 (2006).

21. Y. Jia, G. Li, G. Ning and C. Jin, *Catal. Today*, **140**, 192 (2009).

22. M. S. S. Balula, I. C. M. S. Santos, M. M. Q. Simoes, M. G. P. M. S. Neves, J. A. S. Cavaleiro and A. M. V. Cavaleiro, *J. Mol. Catal. A: Chem.*, **222**, 159 (2004).

23. R. Ishimoto, K. Kamata and N. Mizuno, *Angew. Chem. Int. Ed.*, **51**, 4662 (2012).

24. R. Yu, X. F. Kuang, X. Y. Wu, C. Z. Lu and J. P. Donahue, *Coord. Chem. Rev.*, **253**, 2872 (2009).

25. C. Y. Sun, S. X. Liu, D. D. Liang, K. Z. Shao, Y. H. Ren and Z. M. Su, *J. Am. Chem. Soc.*, **131**, 1883 (2009).

26. H. Yang, J. Li, L. Wang, Y. Dai, Y. Lv and S. Gao, *Catal. Commun.*, **35**, 101 (2013).

27. X. M. Yan, P. Mei, L. Xiong, L. Gao, Q. Yang and L. Gong, *Catal. Sci. Technol.*, **3**, 1985 (2013).

28. X. M. Yan, Z. M. Ping and M. Q. Yang, *J. Porous Mater.*, **21**, 729 (2014).

29. L. Tang, G. Luo, L. Kang, M. Zhu and B. Dai, *Korean J. Chem. Eng.*, **30**, 314 (2013).

30. D. Liu, Y. Lu, H. Q. Tan, W. L. Chen, Z. M. Zhang, Y. G. Li and E. B. Wang, *Chem. Commun.*, **49**, 3673 (2013).

31. N. Janssens, L. H. Wee, S. Bajpe, E. Breynaert, C. E. A. Kirschhock and J. A. Martens, *Chem. Sci.*, **3**, 1847 (2012).

32. F. Yu, P. Q. Zheng, Y. X. Long, Y. P. Ren, X. J. Kong, L. S. Long, Y. Z. Yuan, R. B. Huang and L. S. Zheng, *Eur. J. Inorg. Chem.*, 4526 (2010).

33. C. M. Granadeiroa, A. D. S. Barbosa, P. Silva, F. A. A. Paz, V. K. Saini, J. Pires, B. de Castro, S. S. Balula and L. Cunha-Silva, *Appl. Catal. A: Gen.*, **453**, 316 (2013).

34. N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A. N. Shmakov, Y. A. Chesalov, D. N. Dybtsev, V. P. Fedin and O. A. Kholde-

eva, *J. Catal.*, **257**, 315 (2008).

35. A. Corma, H. García and F. X. L. Xamena, *Chem. Rev.*, **110**, 4606 (2010).

36. J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, **38**, 1450 (2009).

37. H. Y. Liu, H. Wu, J. F. Ma, Y. Y. Liu, J. Yang and J. C. Ma, *Dalton Trans.*, **40**, 602 (2011).

38. L. M. Rodriguez-Albelo, A. R. Ruiz-Salvador, A. Sampieri, D. W. Lewis, A. Gomez, B. Nohra, P. Mialane, J. Marrot, F. Secheresse, C. Mellot-Draznieks, R. N. Biboum, B. Keita and L. Nadjo and A. Dolbecq, *J. Am. Chem. Soc.*, **131**, 16078 (2009).

39. M. Ranocchiari and J. A. van Bokhoven, *Phys. Chem. Chem. Phys.*, **13**, 6388 (2011).

40. J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle and C. L. Hill, *J. Am. Chem. Soc.*, **133**, 16839 (2011).

41. E. Rafiee and N. Nobakht, *J. Mol. Catal. A: Chem.*, **398**, 17 (2015).

42. V. Hulea, F. Fajula and J. Bousquets, *J. Catal.*, **198**, 179 (2001).

43. G. Chotani, T. Dodge, A. Hsu, M. Kumar, R. LaDuca, D. Trimbur, W. Weyler and K. Sanford, *Biochem. Biophys. Acta*, **1543**, 434 (2000).

44. A. B. Thomsen and F. Laturnus, *J. Hazard. Mater.*, **81**, 193 (2001).

45. M. Bonchio, S. Campestrini, V. Conte, F. Di Furia and S. Moro, *Tetrahedron*, **51**, 12372 (1995).

46. H. G. Bernal, L. C. Caero and A. Gutiérrez-Alejandre, *Catal. Today*, **142**, 227 (2009).

47. Z. Long, C. Yang, G. Zeng, L. Peng, C. Dai and H. He, *Fuel*, **130**, 19 (2014).

48. C. Jiang, J. Wang, S. Wang, H. Guan, X. Wang and M. Huo, *Appl. Catal. B: Environ.*, **106**, 343 (2011).

49. J. L. Garcıa-Gutierrez, G. A. Fuentes, M. E. Hernandez-Teran, P. Garcıa, F. Murrieta-Guevara and F. Jiménez-Cruz, *Appl. Catal. A: Gen.*, **334**, 366 (2008).

50. G. Luo, L. Kang, M. Zhu and B. Dai, *Fuel Process. Technol.*, **118**, 20 (2014).