



Extractive oxidative desulfurization of model oil/crude oil using KSF montmorillonite-supported 12-tungstophosphoric acid

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Abstract 12-Tungstophosphoric acid (PW) supported on KSF montmorillonite, PW/KSF, was used as catalyst for deep oxidative desulfurization (ODS) of mixed thiophenic compounds in model oil and crude oil under mild conditions using hydrogen peroxide (H₂O₂) as an oxidizing agent. A one-factor-at-a-time method was applied for optimizing the parameters such as temperature, reaction time, amount of catalyst, type of extractant and oxidant-to-sulfur compounds (S-compounds) molar ratio. The corresponding products can be easily removed from the model oil by using ethanol as the best extractant. The results showed high catalytic activity of PW/KSF in the oxidative removal of dibenzothiophene (DBT) and mixed thiophenic model oil under atmospheric pressure at 75 °C in a biphasic system. To investigate the oxidation and adsorption effects of crude oil composition on ODS, the effects of cyclohexene, 1,7-octadiene and *o*-xylene with different concentrations were studied.

Keywords Tungstophosphoric acid · Montmorillonite · Catalyst · Oxidative desulfurization · Clean fuel

1 Introduction

A major cause of air pollution is the burning of fossil fuels and producing compounds such as NO_x and SO_x, which is released from factories and vehicle exhausts. Sulfur content in crude oil is highly significant due to the high toxicity, corrosivity and air pollution that results from the burning of sulfur-containing fuel products (Collins et al. 1997). In accordance with the increasingly stringent environmental regulations on sulfur concentration in transportation fuels and the demand for diesel fuel with low sulfur content, removal of sulfur-containing compounds is an important issue for the petroleum refining industry (Mei et al. 2003).

To achieve this goal, most sulfur-containing compounds are easily desulfurized by hydrodesulfurization (HDS), in which H₂ gas is used to remove the S-compounds through the formation of hydrocarbons and H₂S. It is difficult to decrease the sulfur content from several hundred ppm to a few ppm by the HDS method which is extremely efficient in removing thiols, sulfides and disulfides, but less effective for thiophenic compounds (García-Gutiérrez et al. 2008). Due to the high capital and operating costs of the HDS process due to factors such as reduced catalyst lifetime, higher hydrogen consumption, high temperature and pressure, oxidative desulfurization (ODS) is proposed as an appropriate substitute for the traditional HDS process and complementary method with ambient pressure, relatively low temperature, high selectivity and no consumption of hydrogen (Khenkin and Neumann 2011; Caero et al. 2005). The integration of an ODS unit with a conventional hydro-treating unit can improve the economics of diesel desulfurization process in comparison with the current HDS technology (Stanislaus et al. 2010).

Generally, an ODS process consists of two steps: The first step is the oxidation of sulfur; various oxidants such as

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hydrogen peroxide (H_2O_2) (Rafiee and Eavani 2013; Gao et al. 2010a, b), formic acid (Shojaei et al. 2014), acetic acid (Abdalla et al. 2009a, b), O_2 (Dooley et al. 2013) and $t\text{-BuOOH}$ (Hui-Peng et al. 2007; Ishihara et al. 2005) are used in ODS process. Among these oxidants, H_2O_2 is mostly chosen as an oxidant due to its innocuous side product (H_2O). Thus, some studies of H_2O_2 have been conducted for investigation of its use in ODS reactions (Rafiee and Mirnezami 2014; Lei et al. 2013; Da Silva and Dos Santos 2013). The second step is the removal of products (sulfoxide or sulfone) by solvent extraction. These compounds are removed by polar solvents such as methanol (Abdalla and Li 2012), N,N -dimethylformamide (DMF) (Bakar et al. 2012), acetonitrile (MeCN) (Li et al. 2013) and DMSO (Hassan et al. 2013). In recent years, there has been an increasing interest in polyoxometalates (POMs) as catalysts due to their composition, size, shape, photochemical response, ionic charge, acidic properties and tunable redox properties (Zhang et al. 2013). Heteropoly acids (HPAs) and supported HPAs are widely used as catalysts in various acid-catalyzed reactions and partial oxidation reactions because of their strong acidity and oxidation activity (Chamack et al. 2014; Zhang et al. 2011a, b; Te et al. 2001). Among the different types of HPAs, Keggin-type HPAs and their salts have been widely used for acid–base and oxidation reactions (Zhang et al. 2011a, b). In general, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo), $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW), $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ (SiMo) and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (SiW) are employed in the first instance for many applications (Katsoulis 1998). The results show that Keggin-type HPA catalysts with H_2O_2 may be promising for ODS of model oils (Kozhevnikov 1998). Previous reports have demonstrated the effective catalytic performances of supported HPAs for the oxidation of thiophene (T) and its derivatives with different oxidants (Hui-Peng et al. 2007; Kukovec et al. 2002; Yan et al. 2009b). However, most of the research up to now has investigated homogenous or amphiphilic catalysts and oxidants (Gao et al. 2006; Zhang et al. 2012a, b; Maity et al. 2009; Qiu et al. 2009; Xue et al. 2012; Bhutto et al. 2016). In these systems, the catalysts are usually dissolved in the continuous phase or inside the emulsion droplets; thus, it is difficult to separate the catalysts and recycle them from the emulsion systems.

The current study aims to investigate a kind of catalyst which is not soluble in the oil phase or extractant solvent. PW supported on KSF (PW/KSF) was prepared by impregnation and used as catalyst for the ODS of model oil. Thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) in n -hexane were the simulated model oils. Different extractants were EtOH, MeCN and DMF. H_2O_2 was chosen as an oxidant. The effect of various parameters such as temperature, oxidant-to-S-compounds molar ratio

(O/S), type of extractant, reaction time and amount of the catalyst was investigated and optimal conditions of the process were evaluated for real oil. The catalytic activity of PW/KSF was investigated for crude oil before and after the HDS process. Additionally, for assessing the influence of crude oil composition, 5 vol%, 15 vol% and 25 vol% of o -xylene, cyclohexene and 1,7-octadiene were, respectively, added to 1000 ppm mixed model oil. For testing real catalytic activity of PW/KSF, ODS of a crude oil and HDS-treated crude oil was conducted under optimal conditions.

2 Experimental

2.1 Materials and methods

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW) hydrate was purchased from Aldrich, and KSF montmorillonite was obtained from the Fluka Company. n -Hexane (98 %), ethanol (99 %), acetonitrile (98 %), N,N -dimethylformamide (DMF, 99.5 %), T (98 %), BT (98 %), DBT (98 %), H_2O_2 (30 %), cyclohexene (99 %), o -xylene (99 %) and 1,7-octadiene (97 %) were purchased from the Merck Company and used without further purification.

The ODS experiments were carried out at atmospheric pressure in a 50-mL glass batch reactor, equipped with a temperature controller, a condenser and a mechanical stirrer. Fourier transform infrared spectroscopy (FTIR) spectra were recorded with KBr pellets using a Rayleigh WQF-510 FTIR. The total sulfur content was analyzed with a Multi EA 3100 Element Analyzer (Analytik Jena AG Company). The Multi EA 3100 model can achieve detection limits of 10 ppb for sulfur determination by UV fluorescence and 50 ppb for nitrogen determination by chemiluminescence. All experiments were conducted and repeated twice more to ensure reproducibility of the results.

2.2 Catalyst preparation

The PW/KSF was prepared by the impregnation method, which was developed by our research group (Rafiee et al. 2009). For preparation of the PW/KSF, KSF montmorillonite was oven-dried at 120 °C for 2 h prior to its use as support. An appropriate amount of PW (to produce 40 wt% of PW to support) was dissolved in 5 mL of dry methanol and added dropwise to pre-dried KSF while stirring with a glass rod. Initially with addition of PW solution, the PW/KSF clay was in a powdery form, but with further addition of PW solution, the clay turned to a paste form. The paste changed to free flowing powder with further stirring as the methanol evaporated. Characterization of the catalyst was reported previously (Rafiee et al. 2009, 2011).

2.3 Activity test

2.3.1 Oxidation of DBT

In a typical experiment, the water bath was first heated to reach and maintain the reaction temperature (55, 65 and 75 °C), and then model oil was prepared by dissolving DBT in *n*-hexane/EtOH (50/50 vol. ratio) to get 1000 ppm, 500 ppm and 100 ppm solution of DBT. In addition, required amounts of 30 vol% aq. H₂O₂ solution (O/S molar ratio 8:1, 10:1, 12:1 and 14:1) and certain amounts of the catalyst (0.02 g (0.0028 mmol), 0.03 g (0.004 mmol) and 0.04 g (0.0056 mmol)) were added to the mixture and stirred vigorously while still in the water bath to start the reaction.

With the aid of thin-layer chromatography (TLC) analysis (with *n*-hexane/ethyl acetate, 2:1 volume ratio as eluent), the oxidized DBT (sulfones and sulfoxides) spots could be seen by illuminating the TLC plate with ultraviolet (UV) light. After completion of the reaction (80 min), the mixture was left to settle for 30 min at room temperature and the products were extracted by extractant solvent. The heterogeneous catalyst was separated by centrifuging at 1500 rpm. For quantification of ODS products, upper liquid layer (*n*-hexane) was withdrawn and analyzed for S by the Analytik Jena AG—Multi EA 3100 Element Analyzer.

2.3.2 Oxidation of mixed thiophenic model oil

A typical reaction procedure for ODS of mixed model oil was as follows: Mixed model oil was prepared by dissolving required amounts of DBT, BT and T (DBT/BT/T, 500:250:250 ppm) in 5 mL *n*-hexane to get mixed model oil with sulfur concentration of 1000 ppm. PW/KSF (0.03 g, 0.004 mmol), 5 mL extraction phase and required amount of 30 % aq. H₂O₂ solution (O/S molar ratio 10:1) were added to the model oil, and the resulting mixture was stirred at atmospheric pressure at 75 °C for 80 min. After completion of the reaction, the mixture was left to settle for 30 min at room temperature and the corresponding products were extracted by extractant solvent. TLC was performed with *n*-hexane/ethyl acetate, in 3:1 volume ratio, as eluent. The ODS of 500 ppm and 100 ppm (sulfur concentration) mixed model oil was performed in the same way for ODS of 1000 ppm (sulfur concentration) mixed model oil, with O/S molar ratio fixed at 10:1 in the presence of PW/KSF (0.03 g) at 75 °C.

In order to test the catalytic recyclability of PW/KSF in the ODS of 1000 ppm (sulfur concentration) mixed model oil, the heterogeneous catalyst was separated by centrifuge with 1500 rpm, washed three times with 2 mL MeCN and then dried at room temperature for 24 h. The recovered catalyst was charged into the next run with fresh reactants.

2.3.3 Oxidation of crude oil

In the same manner as the oxidation of the mixed thiophenic model oil, PW/KSF (0.03 g) catalyst, 50 μL 30 % aq. H₂O₂ and 5 mL extractant (EtOH, DMF or MeCN) were added to 5 mL crude oil (with sulfur concentration of 1000 ppm, API 41.67). The mixture was stirred vigorously at atmospheric pressure at 75 °C. After completion of the reaction, the polar phase was analyzed for S. For crude oil after HDS, 5 mL of HDS-treated crude oil (with sulfur concentration of 300 ppm), PW/KSF (0.03 g) catalyst and 15 μL 30 % aq. H₂O₂ (under the same conditions as above mentioned) were added and the mixture stirred at 75 °C for 80 min. The upper phase was withdrawn and analyzed by the total sulfur analyzer.

3 Results and discussion

3.1 DBT oxidative desulfurization (ODS)

In order to investigate the activity of PW/KSF and optimize the reaction conditions, deep desulfurization of 1000 ppm DBT in *n*-hexane was carried out, with EtOH as extractant, at different temperatures, O/S molar ratios and amounts of the catalyst (Table 1). As the temperature increased from 55 °C to 75 °C, the conversion of DBT increased greatly from 31 % to 99 % at an O/S molar ratio of 10:1. The corresponding TON = $N_{\text{product}}/N_{\text{PW}}$ was calculated (where TON is the mole number of converted DBT per mole of PW supported on KSF). The TON value increased with an increase in reaction time at each reaction temperature (Table 1, Nos. 5, 6 and 8). With an increase in temperature, the TON value for ODS increased at each reaction time. Above an O/S molar ratio 10:1, TON value increased very little.

Table 1 shows that at 75 °C, the conversion of DBT and corresponding reaction time changed very little when the amount of the catalyst increased from 0.03 g to 0.04 g. In addition, the ODS activity of PW/KSF increased only slightly when the O/S molar ratio was higher than 10:1. Based on the above experimental results, it was found that optimum conditions for ODS were O/S (10:1), temperature (75 °C) and amount of the catalyst (0.03 g). These optimum conditions were used in the next experiments. Prior to investigating the effect of the catalyst (PW/KSF) loading on ODS, two more experiments were conducted for comparison: one with O/S molar ratio 10:1 in the presence of 0.03 g of KSF and another without using any catalyst at optimum reaction conditions. The results showed that the conversion of DBT was 46 % and 28 %, respectively, which did not meet the requirement of deep desulfurization. It was due to the lack of a suitable reaction medium,

Table 1 Optimization of reaction conditions for oxidation of DBT (1000 ppm) in *n*-hexane, using EtOH as extractant and H₂O₂ as oxidant

No.	Catalyst, g:mmol	O/S molar ratio	Temperature, °C	Time, min	Conversion of DBT, %	TON value
1	0.03:0.004	10	55	80	31	2.1
2	0.03:0.004	10	65	80	68	4.62
3	0.03:0.004	10	75	80	99	6.73
4	0.03:0.004	8	75	80	92	6.26
5	0.03:0.004	12	75	60 (80)	94 (99)	6.39 (6.73)
6	0.03:0.004	14	75	60 (80)	95 (99)	6.46 (6.73)
7	0.02:0.0028	10	75	80	87	8.45
8	0.04:0.0056	10	75	60 (80)	96 (99)	4.66 (4.81)
9	–	10	75	80	28	–
10	0.03 g KSF	10	75	80	46	–

and DBT could not effectively contact the H₂O₂ (Zhang et al. 2013). In both cases, noticeable transformation of DBT into sulfone was not observed on the TLC plate.

During the reaction, it was found that the mixture (EtOH, *n*-hexane and DBT) tended to form two phases. The active polyoxoperoxo (peroxo-metallate complexes) species converted DBT to DBTO₂ and the oxidized DBT moved into the EtOH phase. The catalyst was a separate phase during the entire reaction process (Scheme 1).

The experiment was also conducted with 500 ppm and 100 ppm DBT in *n*-hexane with EtOH as extractant. Figure 1 shows the catalytic performance of PW/KSF for 1000, 500 and 100 ppm of DBT in *n*-hexane at optimum reaction conditions. The results showed that the catalyst was active for all the concentrations of DBT in *n*-hexane with EtOH as extractant. It can be seen that DBT was almost fully converted by PW/KSF. Table 2 shows the comparison of catalytic activity of PW/KSF with that of other reported catalysts. The results indicated that PW/KSF was quite reliable for ODS in comparison with other

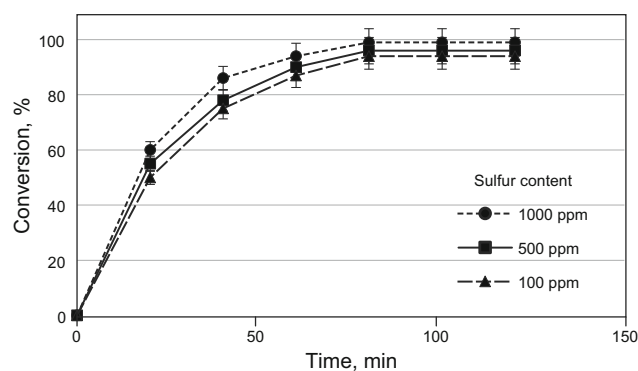
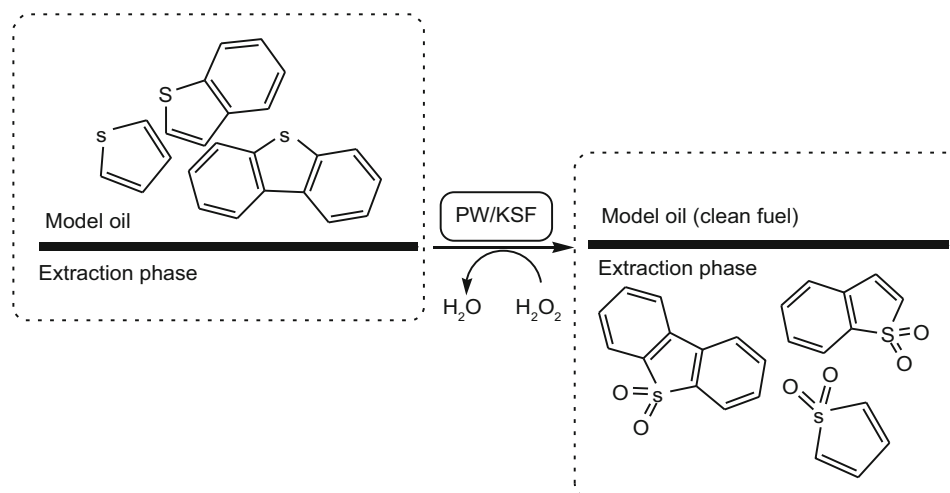


Fig. 1 Deep desulfurization of DBT in *n*-hexane and ethanol (O/S = 10, *T* = 75 °C, 0.03 g of PW/KSF)

catalysts. There are some disadvantages of these reported systems (compared with our system) such as long reaction time, high reaction temperature or large amount of catalyst and using ionic liquids as additives.



Scheme 1 Desulfurization process

Table 2 Comparison of the reaction data in this work with that using other catalyst

No.	Catalyst	S-compounds	Concentration, ppm	Reaction conditions (O/S; Temp, °C; time, min; additives)	Conversion, %	Reference
1	PW/KSF	DBT	1000	(10, 75, 80)	99	–
2	V ₂ O ₅ /TiO ₂	DBT	445	(4, 70, 20)	>80	Caero et al. (2005)
3	[PyPs]PW [PhPyPs]PW	Mixed thiophenic model	1000	(1.6, 60, 120)	95 98	Rafiee and Eavani (2013)
4	PW/SiO ₂ –Al ₂ O ₃	DBT	200	(3, 70, 120)	79.9	Hui-Peng et al. (2007)
5	MoO ₃ /SiO ₂	DBT	2000	(4, 50, 120)	90	Ishihara et al. (2005)
6	[PhPyBs]PW	Sulfide	1000	(1, 70, 50)	98	Rafiee and Mirnezami (2014)
7	PW/SiO ₂	BT, DBT, 4,6-DMDBT	500	(12, 60, 120)	94.8, 99.6, 97.6	Lei et al. (2013)
8	PW/CeO ₂	DBT	1000	(6, 30, 30, [C ₈ mim]BF ₄)	99.4	Zhang et al. (2013)
9	Ag-modified PW/SiO ₂	DBT	800	(12, 70, 240)	89.8	Yan et al. (2009b)
10	PW/TiO ₂ –SiO ₂	DBT	1000	(12, 70, 120)	96	Yan et al. (2013)
11	PW/AC	T	489	(4 mL/20 mL model oil, 90, 120)	90	Xiao et al. (2014)
12	PW/TiO ₂	BT, DBT, 4,6-DMDBT	500	(12, 80, 120)	94.6, 100, 97.8	Yan et al. (2009a)
13	PW/SPC	DBT	500	(3, 60, 120)	98.6	Li et al. (2011)
14	Mn–Co/Al ₂ O ₃	4,6-DMDBT	450	(Air, 150, 25)	65	Sampanthar et al. (2006)
15	WO ₃ /Al ₂ O ₃	Diesel fuel	320	(11, 60, 60)	70	García-Gutiérrez et al. (2014)
16	[(C ₄ H ₉) ₄ N]{PO ₄ {MoO ₂ } ₂] ₄ }	DBT	758	(2, 70, 180, [C ₈ mim]PF ₆)	94	Lo et al. (2003)
17	[C ₄ mim]HSO ₄	DBT	1000	(5, Room Temp., 120)	85	Gao et al. (2010a, b)
18	[Bmim]HSO ₄	Sulfide	10 mmol/4 mL solvent	(2, 25, 240)	83	Zhang et al. (2012a, b)

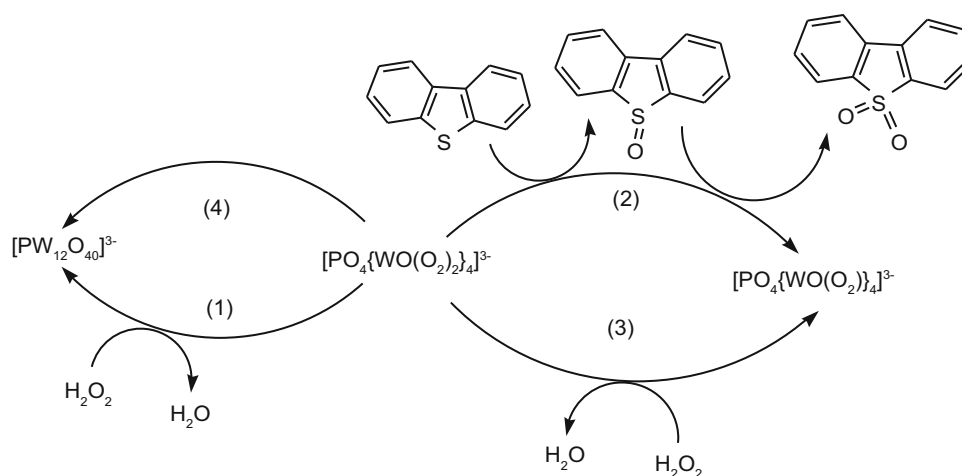
The mechanism of the catalytic desulfurization process (Scheme 2) is assumed to include the following steps: (1) transformation of [PW₁₂O₄₀]³⁻ (denoted as PW) into its peroxide form [PO₄{WO(O₂)₂]₄]³⁻ (denoted as PW₄) in the presence of H₂O₂; (2) oxidation of the extracted DBT to DBTO (corresponding sulfoxide) and DBTO₂ (corresponding sulfone) by PW₄, and reduction of PW₄ to [PO₄{WO(O₂)₂]₄]³⁻; (3) regeneration of PW₄ via oxidizing its reduced form [PO₄{WO(O₂)₂]₄]³⁻ by H₂O₂; (4) transformation of PW₄ into PW₁₂ species with free tungsten species, after the desulfurization (Zhang et al. 2012a, b).

3.2 Desulfurization of mixed thiophenic model oil

Another model oil was prepared by dissolving required amounts of DBT, BT and T in *n*-hexane to get mixed model oil with sulfur concentration of 1000, 500 and 100 ppm, respectively. The experiments were performed under the conditions of O/S molar ratio 10:1, 0.03 g of PW/KSF, 75 °C and reaction time of 80 min (Figure 2). The result showed that the catalyst was effective for mixed

thiophenic compounds models. It was clear that the conversion rate of 1000, 500 and 100 ppm mixed model could reach 97 %, 95 % and 93 %, respectively. As shown in Figs. 1 and 2, the initial S-compounds concentration did not have much more effect on ODS after 80 min.

It is instructive to compare the catalytic activity of PW/KSF with different extractants (EtOH, DMF and MeCN) in the oxidation process (Fig. 3). In general, the performance of the extractant solvent depends considerably on the solubility of the sulfur oxidation products in the reaction mixture. During ODS process, the oxidized S-compounds are transferred to the extractant solvent, and the solvent can influence the mass transport and subsequently have diffusional problems, especially with porous catalysts (Caero et al. 2005). As shown in Fig. 3, EtOH was the best extractant for removing oxidized thiophenic compounds in the model oil. It can be found that the catalytic activity of PW/KSF depended on the kind of the extractant (Fig. 3). To study the recyclability of the catalyst, 1000 ppm mixed model oil was used successively seven times and the catalytic activity decreased a little (Fig. 4). The recycled



Scheme 2 Probable mechanism for catalytic desulfurization process using KSF/PW and H₂O₂

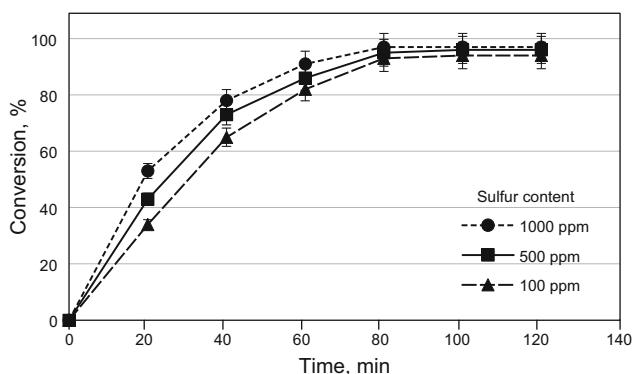


Fig. 2 ODS deep desulfurization of mixed model oil (DBT/BT/T, 2:1:1 in mass ratio) in *n*-hexane and EtOH (O/S = 10, *T* = 75 °C, 0.03 g of PW/KSF)

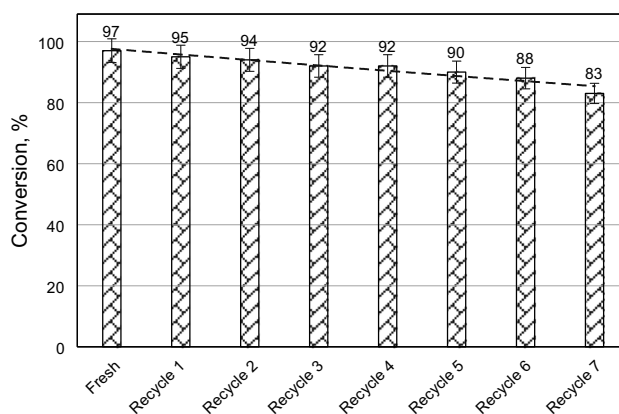


Fig. 4 Influence of the recycle times on ODS deep desulfurization mixed model oil (DBT/BT/T, 500:250:250 ppm) containing 1000 ppm of sulfur in *n*-hexane and EtOH (O/S = 10, *T* = 75 °C, 0.03 g of PW/KSF, reaction time = 80 min.)

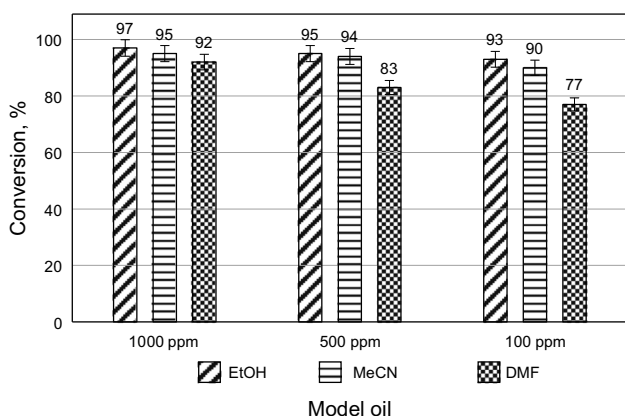


Fig. 3 ODS desulfurization of mixed model oil (DBT/BT/T, 2:1:1 in mass ratio) containing 1000, 500 or 100 ppm of elemental sulfur in *n*-hexane with different extractants (EtOH, DMF and MeCN), reaction time = 80 min, model oil/solvent ratio = 1:1 (O/S = 10, *T* = 75 °C, 0.03 g of PW/KSF)

catalyst showed 83 % ODS removal after seventh recycling. The average recovery weight was ~93 % and ~92 % for PW/KSF and model oil, respectively. The FTIR spectrum of

the recovered PW/KSF after fourth run confirmed no significant change in the Keggin structure of the catalyst (Fig. 5). The $\text{PW}_{12}\text{O}_{40}^{3-}$ Keggin ion structure consists of a PO_4 tetrahedron surround by four W_3O_{13} groups formed by edge-sharing octahedral. These groups are connected with each other by corner-sharing oxygens. This structure consists of four types of oxygens, being responsible for the fingerprint bands of the Keggin ion between 700 cm^{-1} and 1200 cm^{-1} . Bulk PW shows the typical bands for absorptions of P–O (1080 cm^{-1}), $\text{W} = \text{O}_t$ (985 cm^{-1}), $\text{W}-\text{O}_c-\text{W}$ (890 cm^{-1}) and $\text{W}-\text{O}_e-\text{W}$ (814 cm^{-1}). For PW supported on KSF, the bands at 1078, 986, 899 and 802 cm^{-1} are attributed to stretching vibrations of P–O, $\text{W}=\text{O}_t$, $\text{W}-\text{O}_c-\text{W}$ corner-shared bonds and $\text{W}-\text{O}_e-\text{W}$ edge-shared bonds, respectively, which indicates the encapsulation of PW in the KSF frameworks, respectively (Rafiee et al. 2009; Zhang et al. 2011a, b). After catalytic experiments on 1000 ppm mixed model oil using ethanol as extractant solvent, the PW/KSF exhibits a TON = 8.69 at optimum conditions.

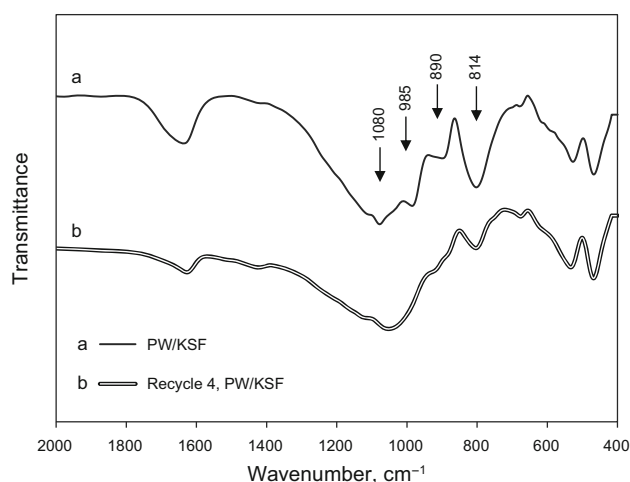


Fig. 5 FTIR spectrum of PW/KSF and fourth recovered PW/KSF, mixed model oil (DBT/BT/T, 500:250:250 ppm) containing 1000 ppm of sulfur in *n*-hexane and EtOH (O/S = 10, $T = 75\text{ }^{\circ}\text{C}$, 0.03 g of PW/KSF, reaction time = 80 min.)

3.3 ODS desulfurization of crude oil

For investigating the industrial performance of PW/KSF, the ODS was tested using 1000 ppm crude oil as a real model oil with different extractants (MeCN, DMF and EtOH). The results showed that the extractability of S-compounds decreased in the order of MeCN > DMF > EtOH (Fig. 6). The conversion of S-compounds of 1000 ppm crude oil only reached 60 %, 53 % and 47 % by employing MeCN, DMF and EtOH, respectively, as extractant.

Desulfurization of crude oil has been a challenge for a long time, and ODS can be a promising complementary method for hydro-treated crude oil. So, the HDS-treated crude oil was selected for testing performance of the catalyst. By using EtOH, MeCN and DMF as extractants at optimum conditions, the conversion of S-compounds of 300 ppm HDS crude oil only reached 41 %, 38 % and 39 %, respectively (Fig. 6). Indeed, when crude oil was first desulfurized with HDS process, thiols, sulfides and disulfides were removed but aromatic S-compounds (thiophenic compounds) were remained in crude oil. It should be noted that EtOH is the most effective extractant for crude oil after HDS process but it is not as efficient for crude oil without HDS.

3.4 Effect of composition of mixed model oil on the ODS conversion

With respect to the considerable decrease in ODS conversion of crude oil in comparison with simulated model oil (see Fig. 6), the effect of crude oil composition on ODS conversion was investigated. Crude oil is the most

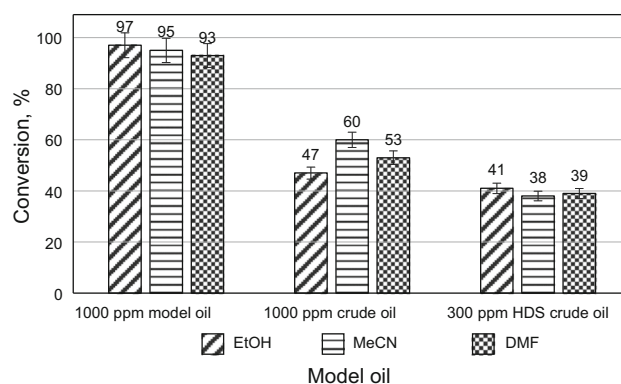


Fig. 6 ODS deep desulfurization of crude oil, HDS-treated crude oil and mixed model oil (DBT/BT/T, 500:250:250 ppm) in *n*-hexane and different extractants, reaction time = 80 min, model oil/solvent ratio = 1:1 (O/S = 10, $T = 75\text{ }^{\circ}\text{C}$, 0.03 g of PW/KSF)

important source of aromatics and olefins, and they may have a significant effect on ODS (Abdalla et al. 2009a, b; Yan et al. 2013; Xiao et al. 2014). In these systems (PW catalysts), the active sites of the catalyst with H_2O_2 exhibited considerable activity in epoxidation of alkenes (Wenjia et al. 2013; Aoto et al. 2014). For investigation of the effects of composition of crude oil and epoxidation of alkenes, 5 vol%, 15 vol% and 25 vol% (according to crude oil properties of west Iranian oil wells) of *o*-xylene, cyclohexene and 1,7-octadiene were, respectively, added to the 1000 ppm model oil (DBT/BT/T, 500:250:250 ppm) to examine their effects on ODS using the PW/KSF catalyst with H_2O_2 at optimum reaction conditions. Figure 7 shows the ODS conversion of the model oil with addition of *o*-xylene at various concentrations. The ODS conversion (97 %) of model oil decreased by 10 %, 24 % and 28 %, respectively, after 80 min of reaction time when 5 vol%, 15 vol% and 25 vol% of *o*-xylene were added to the model oil.

Figure 8 shows that when 5 vol%, 15 vol% and 25 vol% of cyclohexene were added to the model oil, the ODS conversion decreased to 63 %, 52 % and 47 %, respectively, compared to that of model oil. Under the same reaction conditions, the ODS conversion of model oil decreased to 84 %, 72 % and 66 % by the addition of 5 vol%, 15 vol% and 25 vol% of 1,7-octadiene (Fig. 9). The results of olefins and aromatics addition showed strong negative effects on ODS. Therefore, the presence of aromatics and olefins in crude oil will decrease ODS conversion.

The high electron-donating ability of the olefins and aromatics double bonds is considered to be the problem factor in ODS of crude oil (Te et al. 2001; Xiao et al. 2014). Figures 7, 8 and 9 show that the inhibiting effect on ODS conversion increased in the order of *o*-xylene < 1,7-

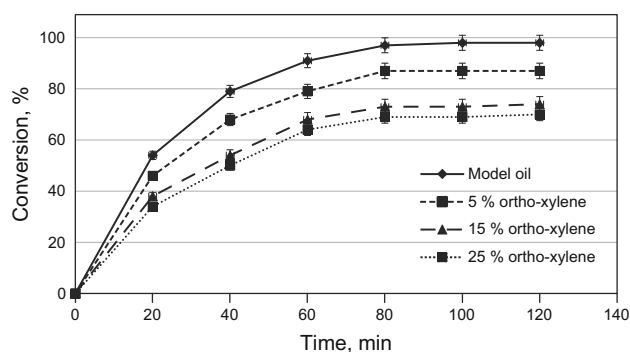


Fig. 7 Effect of *o*-xylene on ODS conversion of mixed model oil (DBT/BT/T, 500:250:250 ppm) in *n*-hexane and EtOH (*O/S* = 10, *T* = 75 °C, 0.03 g of PW/KSF)

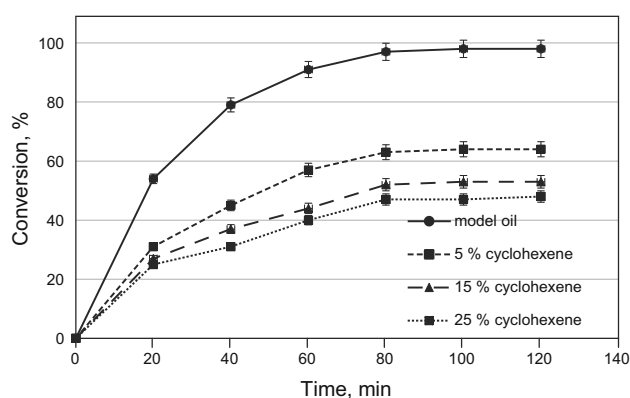


Fig. 8 Effect of cyclohexene on ODS conversion of mixed model oil (DBT/BT/T, 500:250:250 ppm) in *n*-hexane and EtOH (*O/S* = 10, *T* = 75 °C, 0.03 g of PW/KSF)

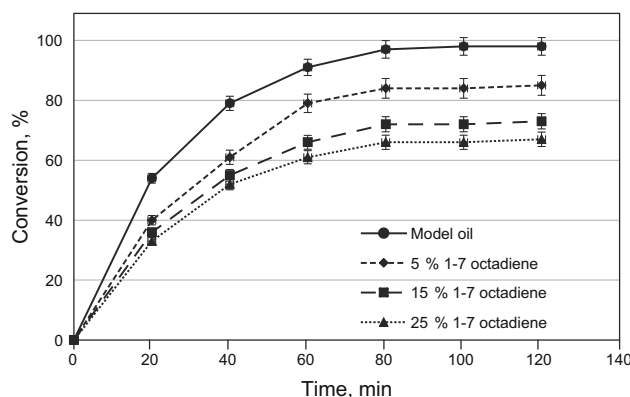


Fig. 9 Effect of 1,7-octadiene on ODS conversion of mixed model oil (DBT/BT/T, 500:250:250 ppm) in *n*-hexane and EtOH (*O/S* = 10, *T* = 75 °C, 0.03 g of PW/KSF)

octadiene < cyclohexene. To explain this trend, the electronic and steric effects should be taken into consideration. The partial electron charge on the alkenes and aromatics

plays a detrimental role for oxidation reactivity of the catalyst (Xiao et al. 2014; Yan et al. 2009a).

4 Conclusions

Catalytic activity of PW/KSF was investigated for ODS of DBT and mixed thiophenic model oils and crude oil. First, effects of temperature, *O/S* molar ratio, amount of the catalyst and type of the extractant solvent on ODS of DBT were investigated. The results of the experiments show that DBT conversion in model oil was excellent for 100 ppm, 500 ppm and even 1000 ppm and conversion for 1000, 500 and 100 ppm mixed thiophenic compounds was 97 %, 95 % and 93 %, respectively. For 1000 ppm crude oil and 300 ppm HDS-treated crude oil, catalytic activities were 47 % and 41 % by using EtOH as extractant. It was discovered that EtOH is the best extractant solvent for removing oxidized S-compounds of mixed model oil. In the second part of the study, effects of cyclohexene, 1,7-octadiene and *o*-xylene were investigated for mixed model oil and the ODS decreases in order of: *o*-xylene < 1,7-octadiene < cyclohexene.

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