

Deep Extractive Oxidative Desulfurization of Model Oil by Magnetically Recoverable Polyoxometalate-Based Nano Catalyst

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Dibenzothiophene (DBT), benzothiophene (BT) and thiophene (T) were catalytically oxidized to their corresponding sulfone products by H₂O₂ in the presence of magnetically recoverable polyoxometalate-based nano catalyst. Different extracting solvents including ethanol, acetonitrile, and dimethylformamide were tested. The best results were obtained by ethanol extraction. The oxidative desulfurization (ODS) of model oils was investigated using different sulfur levels (100-1000 ppm). The removal of DBT could reach >99% and the sulfur content would be reduced from initial 100 to lower than 1 ppm, which can meet the standards of deep desulfurization. Two main aspects including the effects of nitrogen containing compounds and aromatic compounds on ODS of model oil were studied. Effect of indole, quinoline, toluene, xylene, mesitylene and naphthalene in ODS conversion were investigated. The catalyst could be easily separated from the reaction mixture using an external magnetic field, demonstrated an effective and simple separation method, and reused several times without significant change on ODS results.

Keywords: Oxidative desulfurization, Dibenzothiophene, Benzothiophene, Thiophene, Polyoxometalate

INTRODUCTION

Clean fuels research has become an important subject of environmental catalysis studies worldwide. Organosulfur compounds in fuel oils are known to have a negative impact onto the environment because of sulfur dioxide emitting which is one of the key precursors of acid rain. Dibenzothiophene (DBT), benzothiophene (BT) and thiophene (T) are predominantly present in the highest proportion in the diesel fuels. Therefore, in the past decade, much attention has been given to remove of these thiophenic compounds from petroleum and industrial effluents [1-3].

Oxidative desulfurization (ODS) is an important organic process for ultra-deep desulfurization of oil. Compared with conventional catalytic hydrodesulfurization (HDS), ODS can be carried out under very mild conditions [2-11]. It

leads to a significant reduction of contaminating sulfides down to ultra-low levels. As a novel alternative deep desulfurization process, ODS without hydrogen consumption under mild conditions has been aroused great interest in many research groups [12-20].

Usually, ODS process involves the following two steps: first, the refractory organosulfur compounds in oil are oxidized to their corresponding sulfones; second, the sulfones obtained are removed by extraction. Now, various catalytic oxidation systems for deep desulfurization have been investigated [12-16]. Among them, H₂O₂-based ODS system is attractive owing to high effective-oxygen content, cleanliness and acceptable safety in operation [17-20].

Polyoxometalate (POM) catalysts have received increasing attention for H₂O₂-based ODS process because of their less corrosion and high structural stability [21-24]. The homogeneous POMs are remarkably efficient, but they have some drawbacks including low surface area, low porosity and difficult catalyst recovery. For this reason, future

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practical applications of POMs will also require heterogenization of such catalysts for ease of catalyst recovery and recycling.

For heterogeneous POM systems, it is possible to increase the accessibility to the active sites and control catalytic activity by supporting POM on different carriers. Furthermore, wastes are not produced, helping to incorporate in clean technologies. The use of magnetic nanoparticle as support has an additional advantages. The strategy of magnetic separation is typically more effective than filtration or centrifugation as it prevents loss of the catalyst.

Along this line, a magnetically recoverable POM nano catalyst (designed as Fe@Si/PW) was evaluated in the oxidative desulfurization of model oil using DBT, BT and T as organosulfur compounds (Scheme 1). Different extracting solvents were tested. Effects of catalyst loading and oxidant to sulfur (O/S) molar ratios were studied to optimize reaction conditions. The effects of quinoline, indole, and aromatic compounds on the ODS performance of the catalyst were investigated.

MATERIAL AND METHODS

General

Ethanol (EtOH), acetonitrile (MeCN) and dimethylformamide (DMF) were obtained from Merck. The $H_3PW_{12}O_{40}$ (PW) from Aldrich was used. Other reagents and solvents used in this work were obtained from Fluka, Aldrich or Merck and were used without further purification. Sulfur content of model oils was measured using Analytik Jena AG-multi EA 3100 elemental analyzer. The products were analyzed by gas chromatography mass spectroscopy (GC-MS) Agilent Technologies 6890N Instrument, equipped with a capillary column 19019J-413 HP-5, and a flame ionization detector.

Catalyst Preparation

The catalyst was synthesized according to our previously published papers [25,26]. Briefly, $\gamma\text{-Fe}_2\text{O}_3$ was prepared through chemical co-precipitation method, and subsequently was coated with silica shell by the Stöber process that is the hydrolysis of tetraethyl orthosilicate (TEOS) in an ethanolic solution containing water and

ammonia. After the surface coating by silica, the magnetic solid (designed as Fe@Si) was used as support for immobilization of PW. The obtained catalyst (designed as Fe@Si/PW) was collected by a permanent magnet and dried.

Optimization of the Reaction Conditions

5 ml of model oil containing DBT in *n*-heptane with the initial DBT content of 1000 ppm was used for optimization of the reaction conditions. Different extracting solvents, O/S molar ratio, and catalyst loading were tested. At the end of the reaction, the catalyst was separated from the reaction mixture using an external magnet. The sulfur content in model oil was analyzed using Elemental analyzer multi EA® 3100. The product was extracted with Et_2O and analyzed using GC-MS.

ODS of Model Oils

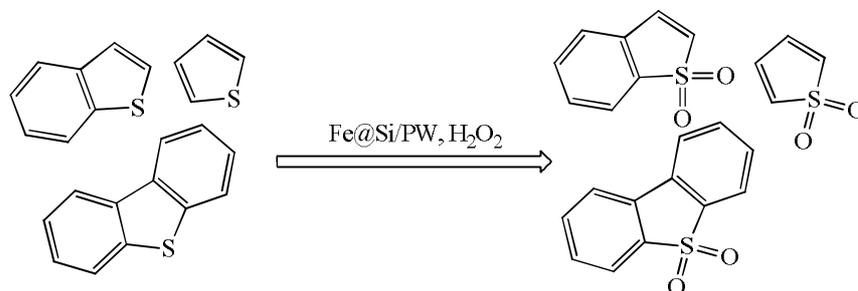
The detailed composition of model oils is summarized in Table 1. The effects of nitrogen containing compounds and aromatic compounds on ODS reaction were studied using different model oils that prepared by dissolving various amounts of sulfur compounds, nitrogen compounds and aromatics in *n*-heptane. The oxidation reaction was investigated using 5 mL of each model oil and catalyst (0.6 mg mL^{-1} model oil) in EtOH (5 mL) as the best extracting solvent. A certain amount of H_2O_2 (O/S: 8) was added to the mixture and stirred at 60 °C. At the end of the reaction, the catalyst was separated from the reaction mixture using an external magnet. The sulfur content in model oil was analyzed using Elemental analyzer multi EA® 3100.

RESULTS AND DISCUSSIONS

Optimization of the Reaction Conditions

The optimized experiments were performed using DBT, which is one of the most difficult sulfur compounds to remove from diesel by conventional HDS processes. 5 ml of model oil containing DBT in *n*-heptane with the initial DBT content of 1000 ppm was used for optimization of the reaction conditions. In all studies H_2O_2 was used as oxidant and the reactions were performed at 60 °C (Scheme 2).

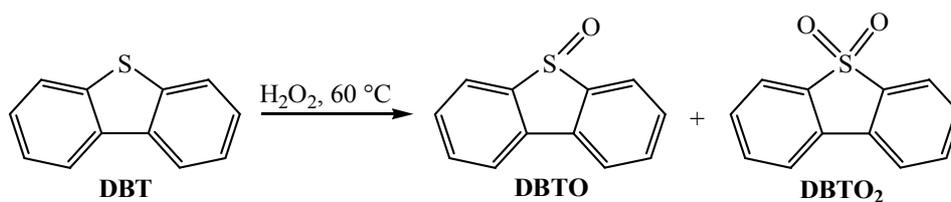
The ODS process consists of two main steps: catalytic



Scheme 1. Desulfurization process

Table 1. Composition of Model Oils Used in this Study

Feed name	Content
Feed 1	DBT (500 ppm) + BT (250 ppm) + T (250 ppm)
Feed II	Feed 1 + indole (60 ppm)
Feed 1Q	Feed 1 + quinolone (60 ppm)
Feed 1T40	Feed 1 + toluene (40% v/v)
Feed 1T60	Feed 1 + toluene (60% v/v)
Feed 1X	Feed 1 + xylene (60% v/v)
Feed 1M	Feed 1 + mesitylene (60% v/v)
Feed 1N40	Feed 1 + naphthalene (40 ppm)
Feed 1N60	Feed 1 + naphthalene (60 ppm)
Feed 1T60I	Feed 1T60 + indole (60 ppm)



Scheme 2. Oxidation of DBT to the corresponding sulfoxide (DBTO) and sulfone (DBTO₂); Substrates used in this work (similar reaction for T and BT)

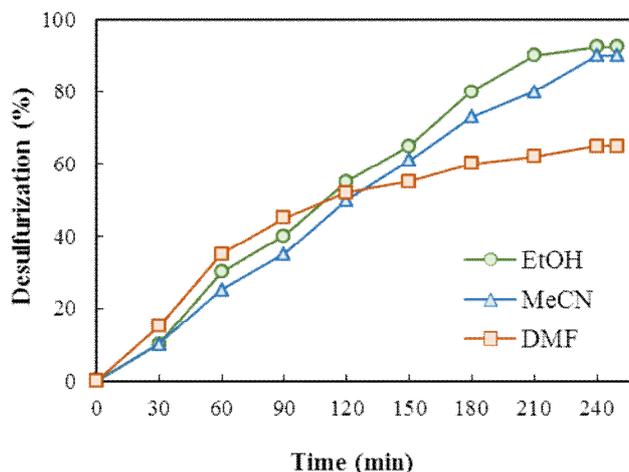


Fig. 1. Effects of extracting solvents on the catalytic oxidation of DBT using Fe@Si/PW catalyst (catalyst loading: 0.5 mg mL⁻¹ model oil, O/S: 2, *n*-heptane: extraction solvent (1:1 v/v), 60 °C).

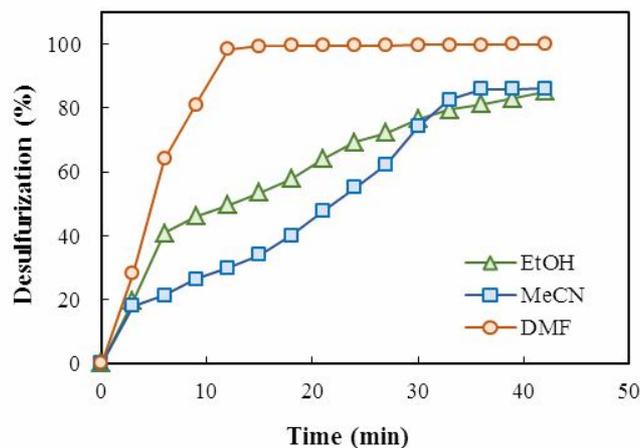


Fig. 2. Transfer of DBTO and DBTO₂ from the model oil into the extracting solvents (*n*-heptane: extraction solvent (1:1 v/v), 60 °C).

oxidation of sulfur contents using H₂O₂ as oxidant followed by extraction of the oxidized products from the oil phase. The nature of the solvent plays an important role in the performance of the catalyst to oxidize the DBT. Figure 1 displays the reaction profiles of catalytic oxidation of DBT using different polar organic solvents. The results obtained from oil/EtOH and oil/MeCN systems were very similar. Oil/DMF system showed lower yield in comparison with the others.

Figure 2 displays the transfer of oxidized products (DBTO and DBTO₂) from the model oil into the extracting solvent. For this purpose, the catalytic oxidation of the model oil was carried out without extracting solvent. Then, the reaction was stopped, the catalyst was separated, the filtrate was added to 5 mL of extracting solvent and stirred. The sulfur content in model oil was analyzed at regular time intervals. Among the solvents used, DMF showed the best extraction. For EtOH, complete desulfurization was

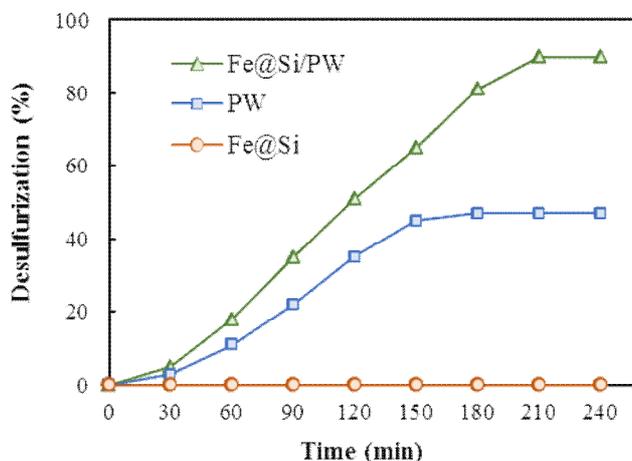


Fig. 3. Comparison of the oxidation activity of the catalysts in the oxidation of DBT (catalyst loading: 0.5 mg mL^{-1} model oil, O/S: 2, *n*-heptane: EtOH (1:1 v/v), 60°C).

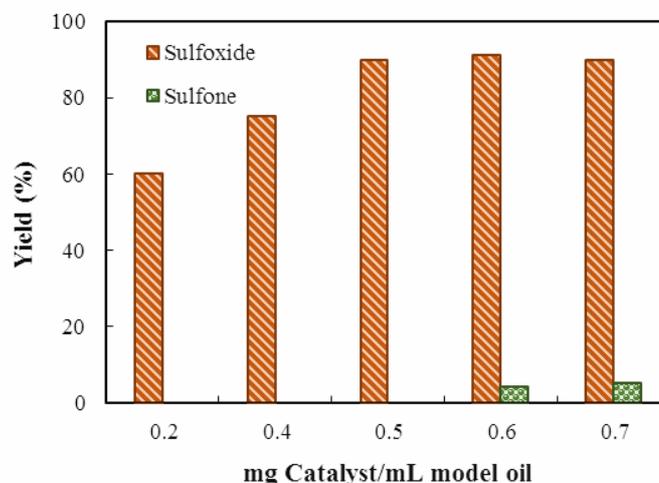


Fig. 4. Effect of catalyst loading in the selective oxidation of DBT (O/S: 2, *n*-heptane: EtOH (1:1 v/v), 60°C , 210 min).

achieved in longer time compared with DMF. In the case of MeCN desulfurization was remained incomplete after 1 h.

The DMF solvent presents the highest boiling point, which makes it less suitable for the future experiments since the separation of the sulfur compounds during solvent recovery by distillation will be more difficult. Indeed, the effect of the solvent on the catalyst performance is also a parameter that must be taken into account to optimize the ODS process. So, EtOH was selected as the best

extraction solvent for this process and used in further studies.

The catalytic performances of Fe@Si, PW and Fe@Si/PW were investigated in model reaction (Fig. 3). In the absence of the catalyst no oxidation of DBT occurred. The Fe@Si showed no activity while pure PW gave a relatively good conversion but it suffer from tedious work up. The best result was obtained in the presence of Fe@Si/PW as a heterogeneous nano catalyst with very

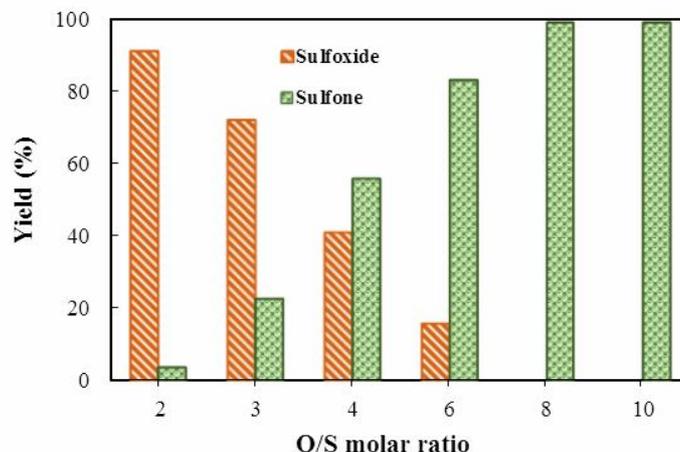


Fig. 5. Effect of O/S molar ratio in the selective oxidation of DBT (catalyst loading: 0.6 mg mL^{-1} model, *n*-heptane: EtOH (1:1 v/v), $60 \text{ }^\circ\text{C}$, 210 min).

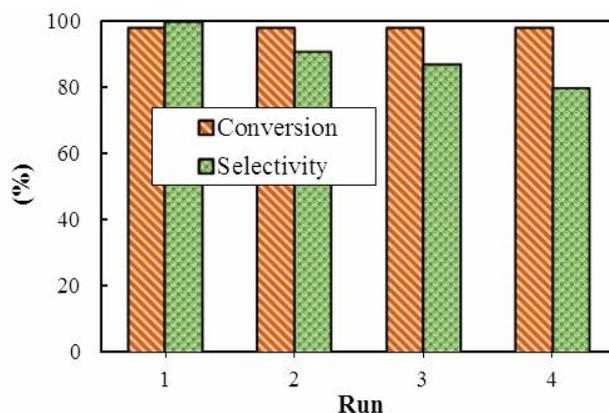


Fig. 6. Reusability of Fe@Si/PW catalyst in the oxidation of DBT (catalyst loading: 0.6 mg mL^{-1} model oil, O/S: 8, *n*-heptane: EtOH (1:1 v/v), $60 \text{ }^\circ\text{C}$, 210 min).

easy recoverability.

Another factor that should be concerned is the catalyst loading. It was found that increasing the catalyst quantity up to 0.6 mg mL^{-1} model oil enhances the conversion. Further increasing in catalyst loading has negligible effect (Fig. 4).

The oxidation reaction of DBT was also carried out under various O/S molar ratios (Fig. 5). The DBTO₂ was obtained as sole product with increasing the O/S molar ratio up to 8. Further increasing the O/S molar ratio did not change the reaction time. The sulfone function is preferred in the ODS. Sulfone-containing molecules are more polar

than the sulfoxides. Hence, it is easier to separate them from fuels up to ultra-low levels. Therefore, the O/S = 8 was chosen as the optimized ratio.

Reusability of Fe@Si/PW catalyst was investigated in the oxidation of DBT under optimized reaction conditions. After the reaction, the catalyst was separated from the reaction mixture using an external magnet onto the reaction vessel. Consequently, the catalyst was washed with EtOH, dried and used in next run. The results showed that Fe@Si/PW catalyst could be recovered and subsequently reused several times (Fig. 6). Over four times of the recycle

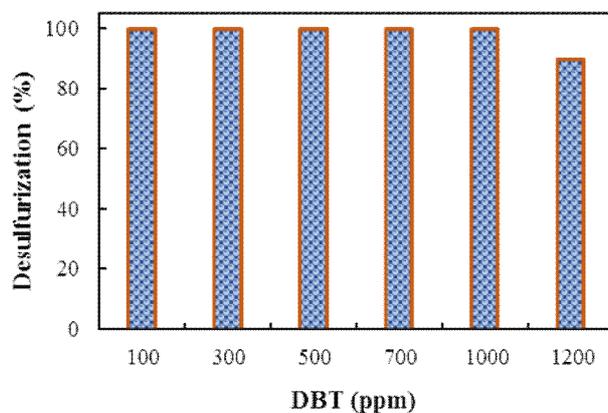


Fig. 7. ODS of model oils with various sulfur levels (catalyst loading: 0.6 mg mL^{-1} model oil, O/S: 8, *n*-heptane: EtOH (1:1 v/v), 60°C , 210 min).

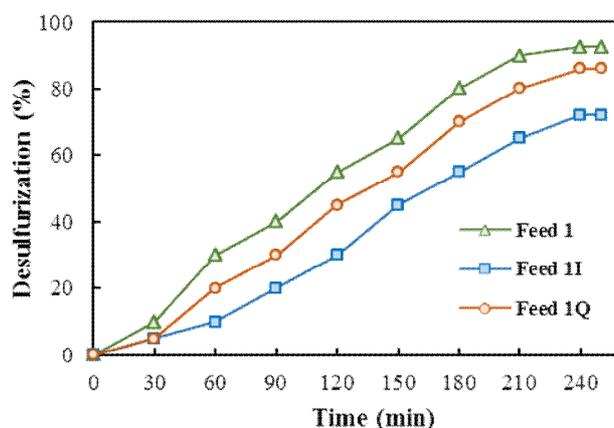


Fig. 8. Effect of nitrogen compounds on ODS of model oils (catalyst loading: 0.6 mg mL^{-1} model oil, O/S: 8, *n*-heptane: EtOH (1:1 v/v), 60°C).

experiments, the conversion of DBT kept constant, while the selectivity to DBTO_2 decreased to about 80%.

ODS of Model Oils

In order to investigate the ODS efficiency of the catalyst, the catalytic system was used for oxidation of DBT models with various concentrations under optimized conditions (Fig. 7). It can be seen that, within the initial sulfur content range from 100-1000 ppm, the complete desulfurization were achieved (Fig. 7). As the initial sulfur content increase to 1200 ppm, the final desulfurization was

found to be 90%. It was demonstrated that agreeable effect of deep desulfurization has been achieved within the initial sulfur content below 1200 ppm.

The catalytic system was used to ODS of multicomponent oil (Feed 1). At the end of the reaction, sulfur content in model fuel was reduced from 1000 ppm to 75 ppm. (Fig. 8). Nitrogen compounds coexist with sulfur compounds in fuels. It has been reported that nitrogen compounds have a negative effect in ODS process [15,27]. Two different model oils containing indole (Feed 1I) and quinoline (Feed 1Q) were tested to investigate the effect of

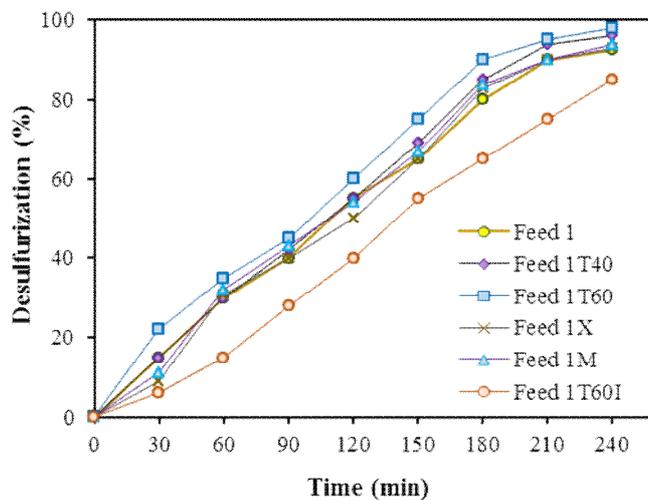


Fig. 9. Effect of aromatic compounds on ODS of model oils (catalyst loading: 0.6 mg mL^{-1} model oil, O/S: 8, *n*-heptane: EtOH (1:1 v/v), 60°C).

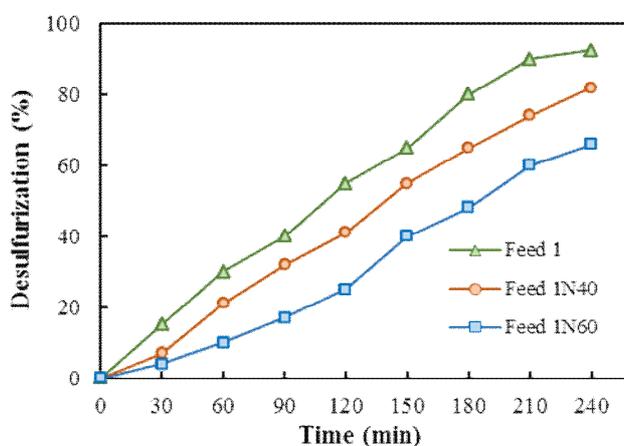


Fig. 10. Effect of naphthalene on ODS of model oils (catalyst loading: 0.6 mg mL^{-1} model oil, O/S: 8, *n*-heptane: EtOH (1:1 v/v), 60°C).

nitrogen compounds. Figure 8 shows that desulfurization decreased in the presence of indole and quinoline to 72% and 86%, respectively. Probably, the negative effect of indole and quinoline on ODS of model fuel is related to their adsorption on the active sites of the solid catalyst, and oxidation of these compounds in the ODS system.

Crude oil is the important source of aromatic compounds and they may have significant effect on ODS.

Therefore, the effect of aromatic compounds was studied on ODS of model oil using toluene in different volume percent (Fig. 9, Feeds 1T40 and 1T60). Feed 1T60 showed higher desulfurization efficiency and therefore, 40% v/v ratio was selected for more experiments. ODS of Feed 1 with 40% v/v of xylene and mesitylene were also investigated (Fig. 9, Feeds 1X and 1M). It seems that xylene and mesitylene show lower positive effect on desulfurization compared

with toluene. Effect of indole and toluene simultaneously in ODS was investigated (Fig. 9, Feed 1T60I). With the addition of indole, desulfurization was significantly decreased.

ODS of Feed 1 was carried out at optimized reaction conditions in the presence of naphthalene as two ring aromatic compound (Fig. 10). The presence of naphthalene showed a negative effect and decreased the ODS conversion.

CONCLUSIONS

In conclusion, Fe@Si/PW combined with H₂O₂ and EtOH provides a very effective ODS system for the removal of DBT, BT and T from model oils. Additionally, ODS was investigated in the presence of nitrogen and aromatic compounds. The nitrogen compounds and naphthalene were found to inhibit the ODS activity. In contrast, 1-ring aromatic compounds facilitate the ODS activity. The catalyst can be easily separated from the reaction system using a magnet and reused at least four times without obvious loss of ODS activity.

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