



A polymer-supported Fe-salen complex as a heterogeneous catalyst for deep-desulfurization of the petroleum diesel

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In present study, a heterogeneous polymer-supported Fe-salen complex i.e. PS-Fe-salen catalyst for oxidative deep-desulfurization of model oil (i.e. dibenzothiophene in isooctane) by 30 wt% H₂O₂ as a green oxidant, for a first time. First, consequence of various parameters like catalyst loading, reaction temperature, reaction time, and H₂O₂ concentration on the desulfurization of model oil are studied. The reduction of dibenzothiophene from the model oil is found to be 96% at a molar amount of the H₂O₂ to S-content (sulfur) of 4:1 at 65°C in 4 h with 20 mg of the catalyst. The optimized reaction parameters are successfully used to investigate the oxidative desulfurization of a real petro-diesel sample.

Keywords: Heterogeneous catalysis, PS-Fe-salen, dibenzothiophene, oxidative desulfurization.

Introduction

Oxidative desulfurization can be achieved using only the oxidant i.e. without the addition of the catalyst. However, it results in the less removal of sulfur-containing compounds and also requires extreme reaction conditions. Extractive and catalytic oxidative desulfurization (ECODS) route permits the convenient deep-desulfurization of fuel under mild reaction environments by green oxidant such as H₂O₂. H₂O₂ is a green oxidant because it releases only water as a by-product. ECODS involves the oxidation of S-content to the corresponding sulfoxide or sulfone, can be simply removed from the fuel medium by solvent extraction^{1,2}. Consequently, discovery of an effective catalyst for oxidative desulfurization is required for the cost-effective treatment³.

Recently, Kareem *et al.*⁴ studied the microwave-assisted catalytic desulfurization of gas oil fraction using (Ni@SiO₂/PWA) as a heterogeneous nanocatalyst with H₂O₂

as a green oxidant. The microwave-assisted Ni@SiO₂/PWA-H₂O₂ system displayed high desulfurization efficiently of up to 94.5%. Li and coworkers⁵ used ionic liquid based PMoO catalyst and achieved 99% oxidative desulfurization of DBT, which depicted the ultrafast and sustainable protocol for oxidative desulfurization reaction.

The salen ligands have been reported to form metal complexes that are analogous to the catalytic activity of metal-porphyrins⁶. Based on the potential of the Fe-salen complexes, we have successfully synthesized, characterized and used PS-Fe-salen as a heterogeneous catalyst in an earlier study for benzimidazoles synthesis⁷. To our knowledge, a polymer-supported Fe-salen complex i.e. PS-Fe-salen has not been used for the desulfurization of dibenzothiophene (DBT) till date. To explore this potential application, in this study, a heterogeneous polymer-supported Fe-salen complex catalyst was effectively prepared and used for oxidative

desulfurization of DBT using H_2O_2 as a green oxidant. In this study, DBT compound was oxidized in to the resultant sulfone with PS-Fe-salen and hydrogen peroxide under mild reaction conditions. Proposed method can be a good substitute for the production sulfur free fuel.

Experimental

Materials:

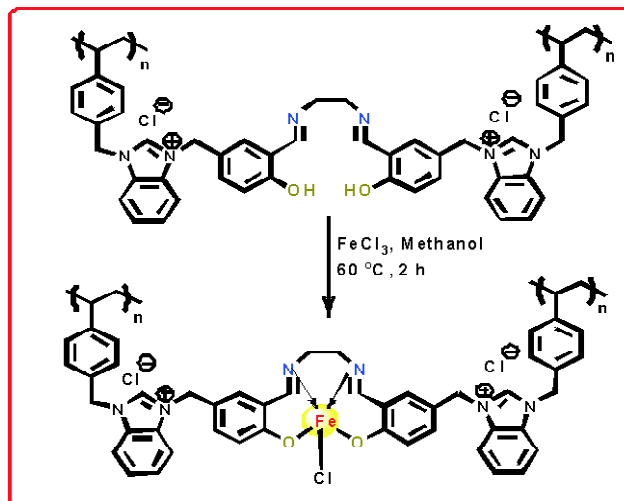
Entirely chemicals used were of analytical mark with the utmost available purity. 4-Vinylbenzyl chloride (90%), CDCl_3 (99.96%), and $\text{DMSO}-d_6$ (99.90%) were received from Sigma Aldrich. FeCl_3 (96%), benzaldehydes (98%), *o*-phenyldiamine (98%), ethylenediamine (98%), azobisisobutyronitrile, sodium sulfide (98%), H_2O_2 (37%), dibenzothiophene (98%) and tributyl phosphate (99.9%) were purchased since SDFCL and Avra Synthesis Pvt. Ltd. Ethanol (99.9%) was obtained from Changshu-Yangyuan Chemicals China. Acetonitrile (99.8%), tetrahydrofuran (99%), benzimidazole (99%) and chloroform (99%) were obtained from Spectrochem Pvt. Ltd.

Characterization methodologies:

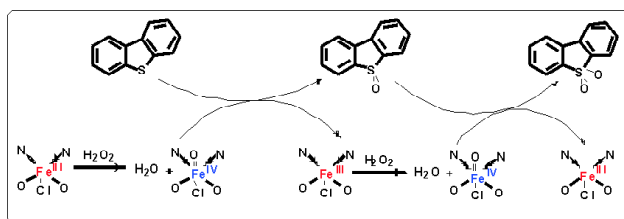
Bruker 400 MHz device was used for recording Nuclear magnetic resonance (NMR) spectra. Tetramethylsilane was used as an inner standard in CDCl_3 and $\text{DMSO}-d_6$. Thermogravimetric examination (TGA) was conducted by a TGA instrument (TG/DTA thermoanalyser SII, Seiko) under the N_2 blanketing through heating rate of $10^\circ\text{C min}^{-1}$ and temperature of $30\text{--}800^\circ\text{C}$. FT-IR spectra were noted using a Shimadzu spectrometer using KBR pellet method and operated at room temperature. Brunauer-Emmett-Teller (BET) surface region was determined using a Quantachrome Nova 1000 analyzer at a temperature of 77 K in liquid N_2 . N_2 adsorption-desorption isotherms was used for the estimation of surface area (specific), pore capacity and pore diameter. Scanning electron microscopy (Carl Zeiss EVO/18SH, UK) furnished with EDX facility was used to estimate the superficial morphology and elemental analysis of the complex. GC spectrum was obtained from Shimadzu GC-2010 plus (Rtx-1 $30\text{ m}\times 0.32\text{ mm}\times 0.5\text{ }\mu\text{m}$, Max Prog. Temp. 350°C).

Preparation and characterization of PS-Fe-salen:

PS-Fe-salen was synthesized using procedure reported in our previous articles⁷.



Scheme 1. Production of polymer supported Fe-salen complex (PS-Fe-salen).



Scheme 2. Mechanism for oxidative desulfurization of DBT⁸.

Influence of reaction conditions on the percentage of sulfur reduction

Influence of oxidant amount:

The oxidant to sulfur molar ratio plays an significant role in the sulfur removal using oxidative desulfurization. $\text{H}_2\text{O}_2/\text{S}$ (oxidant to sulfur) molar ratios were varied to verify the effect of the quantity of H_2O_2 on catalytic oxidative S-removal of DBT (Fig. 1). Initially, the removal of the DBT was found to be the lowest 65% at 2:1 (O/S) ratio in 4 h, which may be due to the decomposition of H_2O_2 ⁹. Later, increasing O/S ratio from 2:1 to 4:1 improved the elimination of DBT up to 96%. Furthermore, increasing the ratio up to 6:1 showed no improvement on DBT removal. It could be due to the plausible increased decomposition of H_2O_2 and production of H_2O as a result of the oxidation of DBT, which inhibit the oxidative desulfurization of DBT. Similar findings were reported by Ding *et al.*¹⁰ Fig. 1 clearly showed that the O/S proportion of 4:1 is

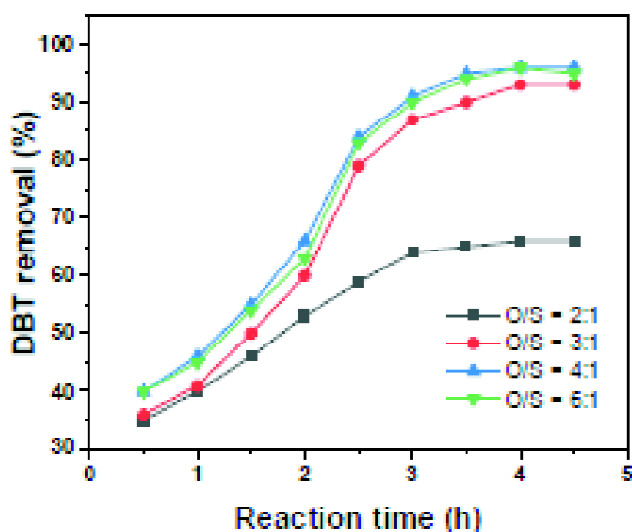


Fig. 1. Influence of molar proportion of O:S on DBT-removal (Reaction parameters: S-content ($500 \mu\text{g mL}^{-1}$); model oil - 5 mL; Ps-Fe-salen - 20 mg; reaction temperature - 65°C).

optimum for maximum removal DBT in 4 h. Accordingly, O/S ratio of 4:1 confirmed for further studies.

Influence of catalyst dosage:

To understand the effect of the catalyst amount (PS-Fe-salen) on the elimination of DBT, the optimized molar ratio of the H_2O_2 (O/S, 4:1) was used and the amount of the catalyst was varied from 0 to 25 mg (Fig. 2). The elimination of the DBT increased with the increasing catalyst up to 20 mg, and it was found to be the maximum (i.e. 96%) at 20 mg of the catalyst. Further increase in the catalyst amount up to 25 mg resulted in no apparent increase in the removal of the DBT.

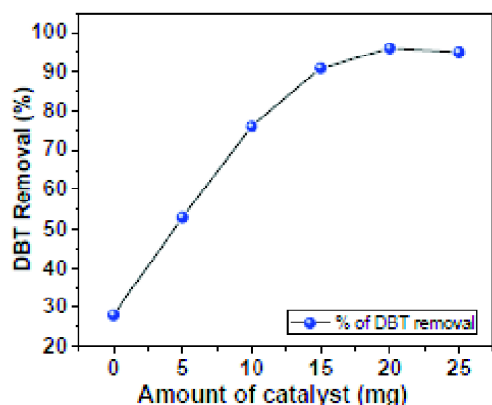


Fig. 2. Consequence of catalyst amount on DBT removal (Reaction parameters: S-content ($500 \mu\text{g mL}^{-1}$); model oil - 5 mL; H_2O_2 (4:1); temperature - 65°C).

To confirm the role of catalyst, a reaction was conducted without the addition of the catalyst (i.e. only in presence of oxidant); this resulted in very small removal of S-content (i.e. 28%) at 65°C in 4 h. The results clearly indicated that the catalyst amount has a direct and significant role in the oxidative sulfur of the DBT. For further study on the removal of DBT, an optimized amount of catalyst, i.e. 20 mg, was used.

Effect of temperature and reaction time on desulfurization:

Next, the effects of reaction temperature and time on the oxidative sulfur removal of DBT using PS-Fe-salen and H_2O_2 were studied (Fig. 3). Initially, to examine the effect of reaction temperature, the reaction was conducted by varying the temperature from room temperature to 75°C by altering the reaction time. The oxidative desulfurization of DBT at room temperature found to be less i.e. 36% in 4 h (Fig. 3). Moreover, on increase in the reaction temperature since 45 to 75°C , the removal DBT was found to increase from 38 to 96% in 4 h. From the Fig. 3, results displayed the maximum removal of DBT was observed at 65°C . Further increase of temperature up to 75°C yielded no significant improvement in the desulfurization. Although the higher reaction temperature improves the rate of desulfurization, the overall removal of sulfur is limited due to thermal decomposition of the H_2O_2 at high temperatures. Additionally, higher temperatures would also lead to high energy consumption and increased energy loss.

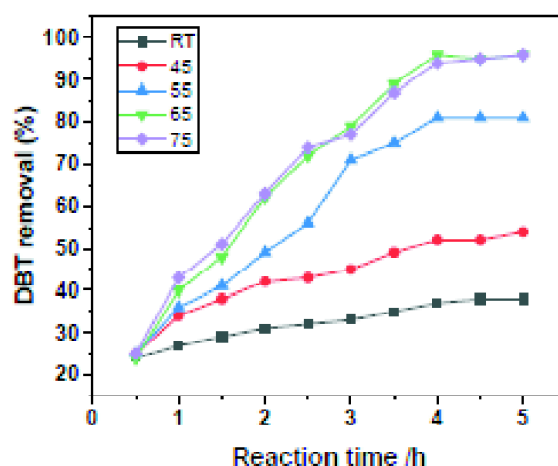


Fig. 3. Influence of the reaction temperature and time on DBT removal (Reaction parameters: S-content ($500 \mu\text{g mL}^{-1}$), model oil - 5 mL; H_2O_2 (4:1) Ps-Fe-salen - 20 mg).

The quantum of removal of DBT was also found to be dependent on the reaction time. The results depicted that increasing the reaction period up to 4 h resulted in the increased removal of DBT and further increase in the reaction time beyond 4 h showed no enhancement in the desulfurization (see Fig. 3).

This behavior could be due to the eventual possible decomposition of H_2O_2 when the reaction is conducted for a time that is greater than the optimum. Hence, 65°C was considered as an optimum reaction temperature and 4 h was assumed to be the optimal reaction time, for further study.

Oxidative desulfurization of real diesel fuel

As discussed above, initially, the PS-Fe-salen catalyzed oxidative desulfurization of the DBT was studied with H_2O_2 as a green oxidant. Then, the optimized reaction parameters were used to demonstrate the efficiency of the heterogeneous catalyst for S-content removal from real diesel sample. It was detected that the desulfurization of a real diesel sample was about 72%. This reduction in desulfurization compared to that of the model oil (from 96% to 72%) could be due to the presence of various aliphatic and aromatic substituted sulfur compound such as thiophene, dibenzothiophene (DBT), and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) and benzo-thiophene (BT), in real diesel sample. In summary, these results clearly depict that the sulfur content removal from the diesel fuel can be achieved with PS-Fe-salen- H_2O_2 system. Table 1 presents the comparison of oxidative desulfurization using PS-Fe-salen- H_2O_2 as heterogeneous catalyst in the present study against recent study reported in literature. The result obtained in the present study, i.e. amount of the catalyst, reaction time, and molar proportion of the oxidant to

sulfur, are comparable to those obtained by several other researchers. In fact, the findings of our current study are similar to those obtained by Zhao *et al.*¹¹, owing to the similar structural features of M-porphyrine complex (used by Zhao *et al.*¹¹) and M-salen complex (used in the present study).

Regeneration and recycling of the catalyst

The PS-Fe-salen compound acts as a heterogeneous catalyst. Afterward the end of the reaction, the reaction mixture was cooled to a room temperature, and the heterogeneous catalyst from the aqueous phase was collected by simple filtration. The separated catalyst was washed with methanol (3×5 mL), dried in a oven at 80°C for 2–3 h and recycled for the next run. Catalytic activity of a recycled catalyst was investigated for the elimination of the DBT at an optimized reaction condition. In the 1st and 2nd cycle, it was observed that the removal of the DBT was up to 96%. At the 6th cycle, it was 93% (Fig. 4).

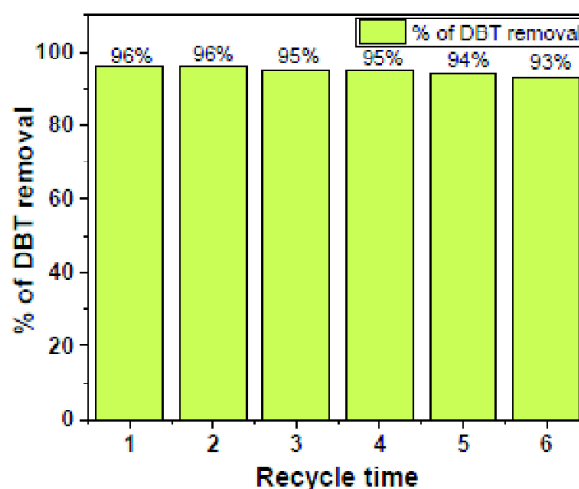


Fig. 4. Reusability of PS-Fe-salen catalyst.

Type of catalyst	Catalyst loading	Temp. ($^\circ\text{C}$)	O/S ratio	Time	% of S removal
[Pmim]FeCl ₄ @SBA-15 ¹⁰	60 mg	RT	5	90 min	95
Fe(III) porphyrins + IL ¹¹	S/C=100	60	4	4 h	100
IMo6@iPAF-1 ¹²	10 mg	90	–	6 h	100
HPW/mpg-C ₃ N ₄ ¹³	100 mg	70	3	150 min	99
PW ₁₂ @TMA-SBA-15 ¹⁴	3 μmol	70	8	130 min	95
SiO ₂ @C-dots/PW5501 ¹⁵	200 mg	50	5	180 min	98
PS-Fe-salen	20 mg	65	4	4 h	96

This slight deterioration in the activity of the catalyst might be due to loss of catalyst during the experimentation. The comparative FI-IR spectra of the fresh and recycled PS-Fe-salen, presented in Fig. 5, display that there is no variation in the heterogeneous complex. This established the catalyst was stable throughout the reaction. The catalyst recycle and regeneration study clearly recognized that the developed catalyst can be recycled for successive cycles without much

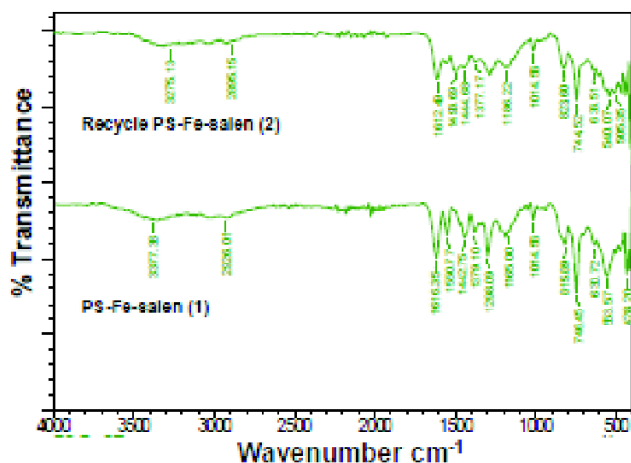


Fig. 5. The comparative FT-IR spectrum of a fresh PS-Fe-salen compound (1) and reused PS-Fe-salen compound catalyst (2).

losing its catalytic activity. This is crucial in economic as well as environmental perspectives.

Conclusions

In summary, PS-Fe-salen was effectively used as a heterogeneous catalyst for S-content removal by desulfurization of DBT using H_2O_2 as a green oxidant.

The catalytic system of PS-Fe-salen- H_2O_2 offers multiple benefits as higher efficacy, small amount of the catalyst, and simple workup procedure for recycling and regeneration of the catalyst. It was observed that the catalyst can be reused up to 6 times with marginal decline in its catalytic action. Oxidative desulfurization was successfully demonstrated by performing the oxidative desulfurization of a actual diesel sample.

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