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A novel method for ultra-deep desulfurization of liquid fuels at room temperature

Hongya Liu, Shuxiang Bao, Zutong Cai, Tiefeng Xu, Nan Li*, Lulin Wang, Haixiang Chen, Wangyang Lu and Wenxing Chen*

National Engineering Lab for Textile Fiber Materials & Processing Technology (Zhejiang), Zhejiang Sci-Tech University, Hangzhou 310018, China

Abstract

A biomimetic catalytic system composed of iron hexadecachlorophthalocyanine ($FePcCl_{16}$), hydrogen peroxide (H_2O_2), H_2O and pyridine exhibited high activity for ultra-deep removal of dibenzothiophene (DBT) in model oil containing n-octane. The conversion of DBT was up to 100% after 60 min operation at room temperature. In addition, the $FePcCl_{16}$ catalyst could be recycled for more than 23 times without noticeable decrease on the conversion of DBT. Moreover, the activation energy evaluated through Arrhenius' equation was found to be equal to 25.5 KJ/mol. Nitrogen-containing compounds such as pyridine, quinoline, and acridine, naturally existing in many kinds of fuel oil, had previously been considered to inhibit the oxidative desulfurization (ODS) process. Surprisingly, these organonitrogen compounds could actually accelerate the conversion rate of DBT in this catalytic system. Mechanistic studies revealed that the high-valent iron(IV)-oxo species were

the main active intermediate via the heterolytic O-O bond cleavage of the putative

iron(II)-hydroperoxo species. Pyridine binding to iron(II)-hydroperoxo complexes

was demonstrated to facilitate the generation of high-valent iron(IV)-oxo species and

enhance the reactivity of high-valent iron(IV)-oxo species in ODS.

1. Introduction

Many researchers have focused on the removal of polluting compounds from liquid

fuels due to increasing environmental concerns. The sulfur oxyacids (SO_X) produced

by fuels combustion remain a major source of air pollution and acid rain. Therefore,

new regulations implemented by governments around the world are aimed at

reduction of sulfur content in gasoline and diesel, with limits below 15 ppm in many

developed countries [1,2]. Hydrodesulfurization (HDS) is the prevailing technology

for the removal of sulfur-containing compounds in petroleum refining. However, the

operation of HDS requires high temperature and pressure [2,3]. Besides, HDS is

highly efficient for the removal of aliphatic and acyclic sulfur compounds, but not of

aromatic thiophenes and thiophene derivatives [4,5]. In order to achieve ultra-deep

desulfurization, the development of new approaches is necessary.

In recent years, non-HDS methods have been widely explored, including adsorption [6-8], extraction [9,10], biodesulfurization [11], and oxidation [12-16]. Among these methods, oxidative desulfurization (ODS) is considered to be a promising strategy, achieving ultra-deep desulfurization under very mild conditions [17-19]. Peroxyacids have long been used as oxidants for ODS. However, their corrosive nature constitutes a major drawback [20,21]. Oil-soluble oxidants, such as tert-butyl hydroperoxide and cyclohexanone peroxide, were used to remove sulfur-containing compounds in homogeneous environment [22,23]. Nevertheless, their high cost and the by-products generated limit their use in industrial applications. Hydrogen peroxide (H_2O_2), cheap, easily available, and environmentally friendly, is the best option as an oxidizing agent [24-27]. It is well know that liquid fuels are complex mixtures made up predominantly of alkenes and aromatics, which may be oxidized by H_2O_2 in the presence of a catalyst, at high temperature, and with long reaction times [28]. In order to selectively oxidize sulfur-containing compounds under ambient conditions, the use of a biomimetic method for ODS is considered.

Porphyrin complexes, naturally existing in the active sites of enzymes, were employed as catalysts for the desulfurization of fuel oil by Zhou et al. and Aguiar et al [29,30]. Their use presents two main drawbacks: the difficulty of separating the homogeneous catalyst from the reaction solution and their high cost. Phthalocyanine metal complexes (MPc's), structurally resembling porphyrin complexes, are attractive not only because of their chemical and thermal stability but also due to their convenient synthesis [31,32]. Typically, the activation of the hydroperoxide O-O

bond by MPc's leads to two reaction pathways: homolytic cleavage, causing the production of hydroxyl radical (•OH), which is considered as a poorly selective species; and heterolytic cleavage, producing high-valent iron(IV)-oxo species [33]. Our group found that introducing the fifth ligand is beneficial to O-O bond heterolysis of hydroperoxide, inhibiting the generation of •OH [33]. The choice of the fifth ligand thus emerges as one of the important factors for the performance of ODS. It has been found that both nitrogen-containing and sulfur-containing compounds coexist in many kinds of fuel oil and that organonitrogen compounds have a negative effect on ODS, which results from the poisoning of the active sites [34]. Our interest is to design a biomimetic catalytic system in which we transform organonitrogen compounds, previously considered as waste, into a positive resource for ODS.

In this paper, we constructed a biomimetic catalytic system for the oxidation of dibenzothiophene (DBT) to the corresponding sulfone. Iron hexadecachlorophthalocyanine (FePcCl$_{16}$), attached with strong electron-withdrawing group, was used as catalyst in the presence of H$_2$O$_2$. Pyridine, employed as a model organonitrogen compound, was introduced as the fifth ligand. We also investigated other nitrogen-containing compounds, such as quinoline and acridine, which were also found to strongly promote ODS. The biomimetic catalytic system showed excellent activity under very mild conditions. Effects of operating conditions and the possible reaction mechanism were studied and analyzed.

2. Experimental

2.1. Materials

Benzothiophene (BT), DBT and 4,6-dimethyldibenzothiophene (4,6-DMDBT)

were purchased from J&K Scientific Ltd. Hexadecane (AR), n-octane (CP, 96%),

quinoline (99%) and acridine (98%) were obtained from Aladdin Industrial

Corporation. H_2O_2 (9.7 M) was purchased from Sinopharm Chemical Reagent Co.

Ltd. The spin trapping reagent 5,5-dimethyl-pyrroline-oxide (DMPO) was supplied

from Tokyo Chemical Industry Co., Ltd. Pyridine, ammonium molybdate, urea,

isopropanol (IPA), tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO) were of

analytic grade and were used without further purification.

2.2. Preparation of FePcCl$_{16}$

FePcCl$_{16}$ was synthesized according to literature methods [35]. Urea (70 g),

tetrachlorophthalic anhydride (48 g), FeCl$_2$·4H$_2$O (8.5 g), and ammonium molybdate

(0.2 g) were finely pulverized, poured into 150 ml of 1,2,4-trichlorobenzene and

heated to 190°C for 5 h while stirring. After cooling, the suspension was diluted with

ethanol, and filtered. The crude products were purified by boiling in 1% HCl and 1%

NaOH solutions. Further purification was carried out by sequential extraction with

acetone and trichloromethane, and finally dried. The structure of synthesized FePcCl$_{16}$

was investigated using ATR-FTIR and UV-vis. The results are shown in Fig. S1 and

Fig. S2, which were consistent with related records [35]. More details are given in the

Supporting Information.

2.3. Oxidation of sulfur-containing compounds with FePcCl$_{16}$

Model oils were prepared by dissolving DBT, BT and 4,6-DMDBT in n-octane.

The sulfur content for all three of the tested model oils was 200 ppm. The

desulfurization process is described in Scheme 1. In a typical experiment, a mixture

including 15 mg FePcCl$_{16}$, 0.089 mL H$_2$O$_2$, 10 mL H$_2$O and 5 mL model oil

containing DBT in a 40 mL sample bottle was stirred vigorously at 30°C, and a turbid

H$_2$O/oil emulsion immediately formed. FePcCl$_{16}$ and organosulfur compounds were

present in the oil phase while H$_2$O$_2$ was located in the aqueous phase. Catalytic

reaction was carried out at the interface between the oil and aqueous phases. As

shown in Fig. S3, the model oil after reaction was analyzed by GC-MS (MS: Agilent

5973i; GC: Agilent 6890 N, OV1701 capillary column, 30 m long×0.25 mm inner

diameter (id) ×0.25 μm film thickness). Analysis conditions were as follows:

chromatogram column: DB-5ms; injection volume: 1 μl; injection port temperature,

280°C; detector temperature, 265°C; column temperature: heating from 100°C to

265°C at 30°Cmin^{-1}. The concentration of DBT was measured using hexadecane as

the internal standard.

3. Results and discussion

3.1. Effect of the amount of catalyst on DBT removal

The amount of catalyst was found to be an important factor in the desulfurization

process. As can be seen from Fig. 1, when the amount of FePcCl$_{16}$ was increased from

5 mg to 10 mg and 15 mg, the DBT removal also increased from 96% to 97% and

100%. The positive trend of DBT removal stabilized when the amount of FePcCl$_{16}$

increased to 20 mg. This observation indicates that the active species produced by the

catalyst had reached saturation. When the amount of catalyst increased, the reaction

rate was greatly increased, which may be resulted from the production of more active

species. However, MPc's are highly conjugated macrocyclic compounds, which are

usually prone to aggregation at a relative high concentration, negatively resulting in

catalytically inactive dimers [36]. 15 mg of catalyst was therefore identified as the

optimal amount for the desulfurization system being studied.

3.2. Effect of the H_2O/oil volume ratio on DBT removal

The oxidative desulfurization was carried out at the interface between the oil and

aqueous phases. Since H_2O and oil are immiscible, the desulfurization efficiency can

be affected by the mass transfer rate. As shown in Fig. 2, when the H_2O/oil volume

ratio was changed from 1 to 4, the desulfurization efficiency reached its maximum

value for a ratio of 2. The result may be influenced by two factors. On the one hand,

the increase of H_2O may help in the formation of the H_2O-oil emulsion; on the other

hand, the concentration of H_2O_2 decreases with excess water. Therefore, the H_2O/oil

volume ratio played an important role in the desulfurization.

3.3. Effect of temperature on DBT removal

The conversions of DBT at different temperatures are shown in Fig. 3. The reaction

activity increased with temperature in the range of 30°C to 45°C. The conversion of

DBT reached 96.8% in just 16 min when operating at 45°C. The strong positive effect

of a temperature increase on the conversion of DBT is due to the improvement of

mass transfer in the biphase at higher temperatures. However, the decomposition rate

of H_2O_2 is prone to acceleration with increasing temperature. In addition, room

temperature is beneficial for industrial applications. Therefore, the appropriate

reaction temperature was set to 30°C.

The desulfurization kinetics of DBT at various temperatures were also investigated.

The oxidation of DBT followed pseudo-first-order kinetics [37]. The equations were

as follows:

$$-dC/dt = kC \qquad (1)$$

$$\ln(C_0/C_t) = kt \qquad (2)$$

$$k = k_0\exp(-Ea/RT) \qquad (3)$$

$$\ln k = -Ea/RT \qquad (4)$$

In these equations, C_0 and C_t were the sulfur concentration at 0 (min) and t (min),

while k and Ea were the rate constant (min^{-1}) and the activation energy. The plots of

$\ln(C_0/C_t)$ versus reaction time at different temperatures are given in Fig. 4 (a) and

Table 1. As can be seen from Fig. 4 (b), Ea was 25.5 KJ/mol calculated by Arrhenius'

equation, indicating that this catalytic system allowed the reaction to happen with a

low energetical input.

3.4. Effect of H_2O_2/sulfur molar ratio on DBT removal

To study the influence of the amount of H_2O_2 on the oxidative properties, different

H_2O_2/sulfur (O/S) molar ratios on the conversion of DBT were investigated, and the

results obtained by working with different O/S values at 30°C are given in Fig. 5.

According to the stoichiometry of the reaction, 2 mol of H_2O_2 are consumed for the

oxidation of 1 mol of DBT to the corresponding sulfone. When O/S molar ratios were low (below 3:1), the actual conversion of DBT approached the theoretically expected values within 5 h. The results demonstrate that $FePcCl_{16}$ can effectively activate H_2O_2. In other words, the utilization efficiency of H_2O_2 is high. When the O/S molar ratio increased from 1 to 40, the reaction time for 100% conversion of DBT decreased to 60 min. Further increasing the O/S molar ratio to 80 did not change the time for 100% conversion of DBT. The experimental results indicate that the O/S molar ratio has a strong effect on the reaction rate. In order to effectively oxidize DBT to the corresponding sulfone in a short reaction time, the O/S molar ratio of 40 was chosen as the optimal value.

3.5. Effect of different substrates on sulfur removal

In order to study the desulfurization performance of $FePcCl_{16}$ on different substrates, experiments on BT, DBT, and 4,6-DMDBT were carried out under the same conditions. As shown in Fig. 6, complete conversion of DBT and 4,6-DMDBT could be achieved in 60 min, while the time for 100% conversion of BT increased to 80 min. These results demonstrate that $FePcCl_{16}$ can treat various refractory sulfur-containing compounds. The catalytic activity for different substrates decreased in the order of 4,6-DMDBT>DBT>BT. The results agree well with the electron density on the sulfur atoms which is 5.760 for 4,6-DMDBT, 5.758 for DBT and 5.739 for BT, as calculated by Otsuki et al [38].

3.6. Selective oxidation of DBT

It is well known that liquid fuels are very complex mixtures, which contain alkanes, alkenes, and aromatics. In our study, the new model oil was prepared with decalin, 1-octene, toluene, and n-octane using the 1:2:3:4 volume ratios. Experiments were carried out in the same conditions as those described above, with the exception of the model oil. As shown in Fig. S4, the result indicates that the conversion of DBT is not effected by alkanes, alkenes, cycloalkanes, and aromatic hydrocarbons. Therefore, $FePcCl_{16}$ has strong anti-interference capacity. Because of the nitrogen-containing and sulfur-containing compounds coexist in many kinds of fuel oil, we investigated the effect of the nitrogen-containing compounds on ODS. Figures S5-7 show the results of DBT oxidation in the presence of pyridine, quinoline, and acridine. The presence of the different nitrogen-containing compounds, even in very low concentration, still had a positive effect on the oxidative removal of DBT. The result may be a consequence of the coordination of these nitrogen-containing compounds to the central Fe, which in turn promotes ODS.

3.7. Recycling of FePcCl₁₆

To investigate the stability and circulation properties, a small amount of high concentration model oil was added directly into the original reaction bottle, ensuring that the concentration of sulfur was 200 ppm as the first run, we also added H_2O_2 in order to go back to the initial concentration of H_2O_2, without adding $FePcCl_{16}$, H_2O, and pyridine. The data shown in Fig. S8, indicates that the desulfurization system can be recycled up to 23 times without a noticeable decrease in activity. The catalytic

system exhibited excellent performance in the recycling experiment, showing the

positive prospects of its application in industry.

3.8. Mechanism analysis

There are two possible reaction pathways for the activation of the hydroperoxide

O-O bond, which leads to the production of either •OH or high-valent iron(IV)-oxo

active species. In order to investigate whether •OH played the key role for ODS, IPA,

a typical •OH scavenger, was employed. If •OH had positive effect on the catalytic

oxidation of DBT, the conversion of DBT would decline sharply with excess IPA

[39]. As shown in Fig. S9, the conversion of DBT was almost the same with excess

IPA, suggesting that •OH is not the effective active species in the catalytic oxidation

of DBT. As we can see from Fig. 7, pyridine, the fifth ligand, obviously promoted the

conversion of DBT, which means that pyridine is beneficial to another reaction

pathway, namely a non-radical mechanism.

The EPR spin-trap technique was widely used to detect the generation of •OH [39].

DMPO is one of the most commonly used trapping reagents. The EPR spectrum can

characterize the spin adduct. For example, the signals of a relative peak ratio of

1:2:2:1 were observed from the EPR spectrum of the •OH radical adduct. As shown in

Fig. 8, the DMPO-OH signals were exhibited without pyridine, while the introduction

of pyridine resulted in the disappearance of the DMPO-OH signals. If •OH was the

main active species in our catalytic system, the introduction of pyridine would greatly

inhibit ODS. But, in fact, pyridine obviously promoted the conversion of DBT. This

result indicates that •OH is not the effective active species in the catalytic oxidation of

DBT and pyridine helps the heterolytic cleavage of the peroxide O-O bond, which is beneficial for ODS.

A sensitive method was developed for the determination of Fe(IV)=O in the catalytic oxidation process [39,40]. DMSO can be oxidized to $DMSO_2$ via a two-electron transfer step by Fe(IV)=O (reaction 1), while the products oxidized by •OH are markedly different from $DMSO_2$ (reaction 2). As shown in Fig. 9, the result reveals the generation of high-valent iron(IV)-oxo species involved in the catalytic oxidation of DBT.

$$Fe(IV) = O + (CH_3)_2SO \rightarrow (CH_3)_2SO_2 \qquad (1)$$

$$2 \cdot OH + 2 (CH_3)_2SO + O_2 \rightarrow 2 CH_3SO_2H + HCHO + CH_3OH \qquad (2)$$

In conclusion, the possible mechanisms of ODS in this catalytic system are illustrated in Scheme 2. Without pyridine, high-valent iron(IV)-oxo species (**3**) generated by the reaction pathway (**1**-**2**-**3**) may be the active species for ODS. Pyridine binding to high-valent iron(IV)-oxo species (**6**) may be formed via O-O bond heterolysis of **5** whose optimized structure can be seen from Fig. 10, which have been proposed as the reactive species for ODS in the presence of pyridine. Pyridine was demonstrated to facilitate the generation of high-valent iron(IV)-oxo species and enhance the reactivity of high-valent iron(IV)-oxo species in ODS process.

4. Conclusions

The present work focused on the developed biomimetic catalytic system for the selective and direct oxidation of DBT to the corresponding sulfone, in the absence of

co-reductants or sacrificial agents and under very mild conditions. The reaction

conditions were as follows: V(model oil) = 5 mL, V(H_2O) = 10 mL, n(O/S) = 40,

m(catalyst) = 15 mg, n(catalyst/pyridine) = 1:100, T = 30°C. Under the above

conditions, the conversion of DBT could reach 100% for 1 h, and was not influenced

by the presence of alkenes, cycloalkanes, and aromatic compounds. The removal

efficiency of BT, DBT, and 4,6-DMDBT by catalytic oxidation followed the order of

4,6-DMDBT > DBT > BT, and the reaction rates were dependent on the electron

density on the sulfur atom. The idea that organonitrogen compounds can be

transformed from a waste to a resource for ODS were proposed in this paper.

Nitrogen-containing compounds, such as pyridine, quinoline, and acridine, are unique

in that they are naturally found in many kinds of fuel oils, strongly promoting the

oxidation of DBT in our catalytic oxidation system. We have provided strong

evidence that the high-valent iron(IV)-oxo species were the main active intermediate

in the biomimetic catalytic system. The role of pyridine was proposed to facilitate the

formation of the high-valent iron(IV)-oxo species.

Author information

Corresponding author

*(N. Li) E-mail: linan@zstu.edu.cn; Phone: +86 571 86843611; Fax: +86 571

86843611.

*(W. Chen) E-mail: wxchen@zstu.edu.cn; Phone: +86 571 86843611; Fax: +86 571

86843611.

Author Contributions

The manuscript was written through contributions of all authors. All authors have

given approval to the final version of the manuscript.

Notes

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Appendix A. Supplementary data

Supplementary data. Supplementary data associated with this article can be

found, in the online version, at

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Figures Captions

Scheme 1. Oxidation of dibenzothiophene in H_2O/oil emulsion droplets.

Fig. 1. Effect of the amount of catalyst on conversion of DBT. Experimental conditions: V(model oil) = 5 mL, V(H_2O) = 10 mL, n(O/S) = 40, T = 30°C, n(catalyst/pyridine) = 1:100.

Fig. 2. Effect of the H_2O/oil volume ratio on conversion of DBT. Experimental conditions: V(model oil) = 5 mL, n(O/S) = 40, m(catalyst) = 15 mg, T = 30°C, n(catalyst/pyridine) = 1:100.

Fig. 3. Effect of temperature on conversion of DBT. Experimental conditions: V(model oil) = 5 mL, V(H_2O) = 10 mL, n(O/S) = 40, m(catalyst) = 15 mg, n(catalyst/pyridine) = 1:100.

Fig. 4. (a) Pseudo-first-order kinetics for oxidation of DBT; (b) Arrhenius activation energies for DBT oxidation.

Table 1. Apparent pseudo-first-order values obtained at different temperatures.

Fig. 5. Effect of H_2O_2/sulfur molar ratio on conversion of DBT. Experimental conditions: V(model oil) = 5 mL, V(H_2O) = 10 mL, m(catalyst) = 15 mg, T = 30°C, n(catalyst/pyridine) = 1:100.

Fig. 6. Effect of different substrates on sulfur removal. Experimental conditions:

V(model oil) = 5 mL, V(H$_2$O) = 10 mL, m(catalyst) = 15 mg, n(O/S) = 40, T =

30°C, n(catalyst/pyridine) = 1:100.

Fig. 7. Effect of pyridine on conversion of DBT. Experimental conditions:

V(model oil) = 5 mL, V(H$_2$O) = 10 mL, n(O/S) = 40, m(catalyst) = 15 mg, T = 30°C,

n(catalyst/pyridine) = 1:100.

Fig. 8. DMPO spin-trapping EPR spectra in aqueous solution with [H$_2$O$_2$] = 15 mM,

[DMPO] = 30 mM, [catalyst] = 0.2 g/L, T = 30°C.

Fig. 9. GC-MS chromatograms of DMSO$_2$, oxidation products of DMSO

catalyzed by FePcCl$_{16}$. The inset shows the MS spectrum of DMSO$_2$.

Scheme 2. Mechanism of catalytic oxidation of DBT.

Fig. 10. Optimized structure of pyridine binding to the putative iron(II)-hydroperoxo

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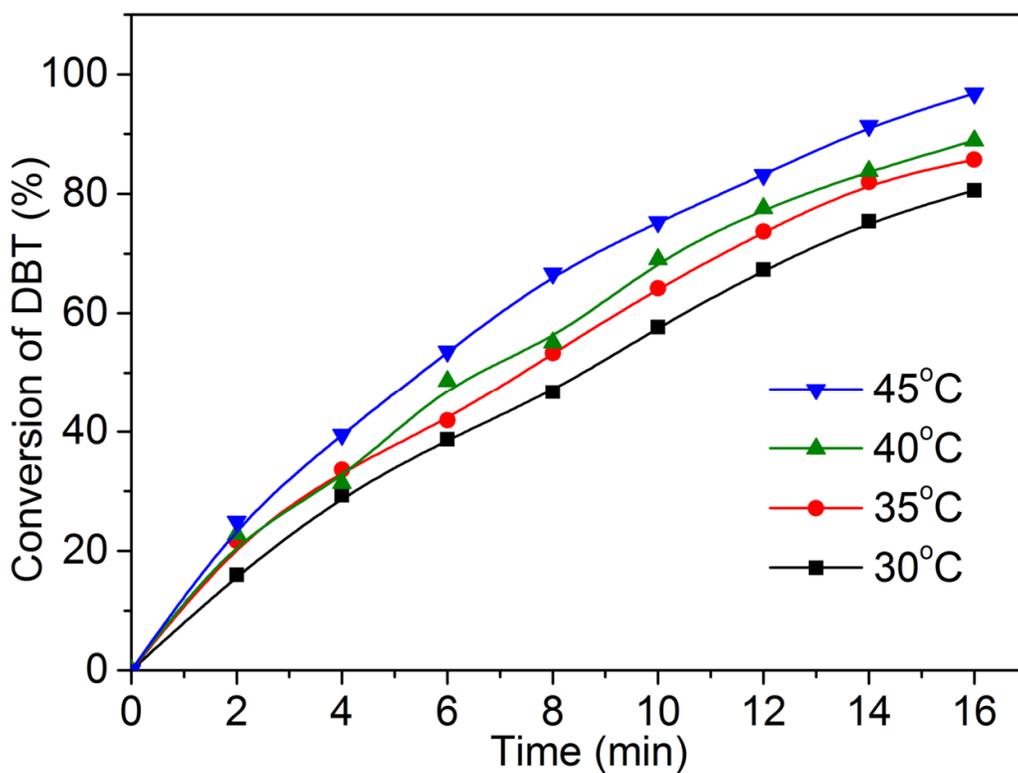
Fig. 3. Effect of temperature on conversion of DBT. Experimental conditions:

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Temperature (K)	App. K_{obs} (min^{-1})	R^2
303	0.0894	0.9865
308	0.1058	0.9810
313	0.1203	0.9762
318	0.1459	0.9922

WATER PHASE

H_2O_2

H_2O

OIL PHASE
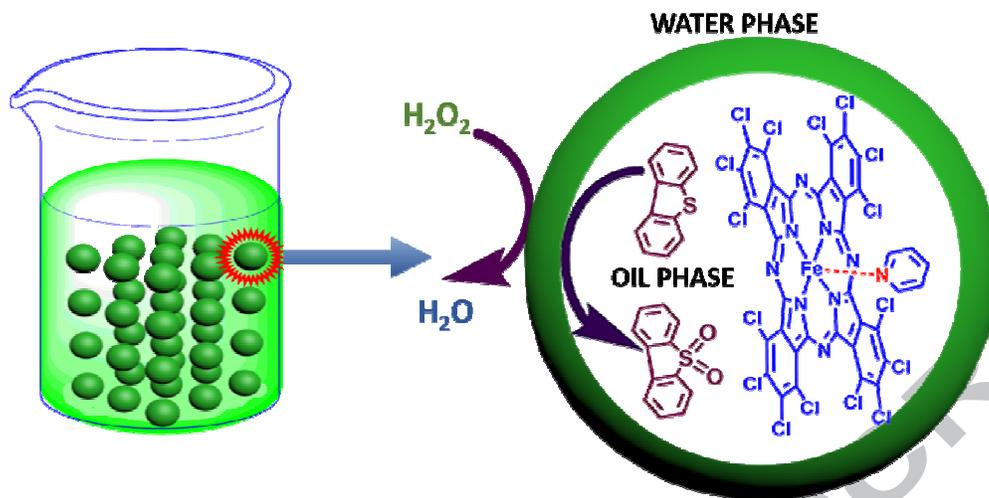
Highlights

◆ A biomimetic catalytic system for oxidative desulfurization was proposed.

◆ $FePcCl_{16}$ exhibited remarkable catalytic activity for sulfides oxidation at 30°C.

◆ $FePcCl_{16}$ catalyst could be recycled for more than 23 times.

◆ High-valent iron(IV)-oxo species were the active species in the catalytic process.