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Oxidative desulfurization of dibenzothiophene with molecular oxygen catalyzed by carbon fiber-supported iron phthalocyanine

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Abstract Iron tetranitrophthalocyanine (FePc) was modified and immobilized on carbon fiber ($FePc(NO_2)_3$–CF) by covalent bond to obtain a supported heterogeneous catalyst for the removal of dibenzothiophene (DBT) in tridecane. In the supported catalytic system, the catalyst exhibited an excellent catalytic performance without any sacrificial agents, and the conversion of DBT could reach 92 % at 130 °C and 0.2 MPa of initial dioxygen pressure for 3 h. Compared to unsupported FePc, the introduction of carbon fiber dramatically improved the catalytic activity of FePc and facilitated the reuse of catalysts. The amount of $FePc(NO_2)_3$–CF, temperature and the initial pressure of molecular oxygen were also studied in detail to optimize the reaction conditions. The removal of DBT significantly increased with the increasing of concentration of DBT in model oil. Finally, a mechanism involving high-valent iron oxo species was proposed for the oxygenation. This study provides new insights into industrial desulfurization systems using carbon fiber as catalyst carrier.

Keywords Oxidative desulfurization · Iron phthalocyanine · Carbon fiber · Molecular oxygen

Abbreviations

FePc	Iron tetranitrophthalocyanine
$FePc(NO_2)_3NH_2$	Iron amino trinitro phthalocyanine
CF	Carbon fiber
$FePc(NO_2)_3$–CF	Carbon fiber supported iron phthalocyanine
HDS	Hydrodesulfurization
ODS	Oxidative desulfurization

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DBT	Dibenzothiophene
DBTO	Dibenzothiophene sulfoxide
$DBTO_2$	Dibenzothiophene sulfone

Introduction

Deep desulfurization from fuel oils has attracted wide concerns due to increasingly prominent environmental pollution, thus many governments develop more stringent fuel standards. However, the conventional catalytic hydrodesulfurization (HDS) technology has difficulties in removing dibenzothiphene (DBT) and its derivatives efficiently from diesel [1]. Therefore, an urgent demand for developing feasible non-HDS methods exists to achieve green fuel. Many alternative desulfurization technologies have been attempted based on the principles of adsorption [2], extraction [3], biodesulfurization [4], alkylation [5], oxidation (including photocatalytic [6] and electrochemical oxidation [7] etc.) and their appropriate combinations. With the great advantages of mild reaction conditions, uncomplicated operation and low equipment investment, oxidative desulfurization (ODS) is considered one of the most promising process to dispel the refractory sulfur compounds.

Many catalysts have been developed in several ODS methodologies, such as polyoxometalates [8–10], ionic liquids [11–13], metal oxide [14–16], organic acid [17] and Ti-containing mesoporous molecular sieves [18, 19]. In ODS, hydrogen peroxide and molecular oxygen are most frequently used as oxidizing agents owing to their low-cost and environmental harmony. Despite great recent progress with catalytic oxidation desulfurization technologies, the development of an uncomplicated, low-cost and high-efficiency ODS technology under mild reaction conditions has yet to be achieved. The challenges are to achieve molecule-level dispersion and maximum interfacial interaction between the catalyst and the carrier at low loading.

Metallophthalocyanine (MPc) complexes with a macrocyclic structure resembling that of porphyrin complexes are widely used as catalysts for oxidation by nature in the active sites of oxygenase enzymes, which have been extensively employed in the degradation of organic contaminants, such as dyes [20, 21], pesticides [22], phenols [23, 24] and sulfides [25, 26]. Furthermore, they show better catalytic performance in heterogeneous reaction when supported on carrier materials as fibers [20, 21, 24, 26]. However, there are only a few works concerning metal porphyrin [27–29] and phthalocyanine [30, 31] complexes as effective catalysts for oxidation of thiophenic sulfur to sulfone in oxidative desulfurization. DBT could be removed by iron porphyrin with H_2O_2 or O_2, and two key intermediates (hydroperoxideiron (III) species and porphyrin oxoiron (IV) cation radical) were considered to play a key role in the product selectivity [28], but a mechanism involving a two-step nucleophilic addition rather than a free radical reaction was proposed in the oxygenation of DBT [29]. Iron phthalocyanine (FePc) also showed good catalytic performance in ODS when supported on macroporous polyacrylic cationic exchange resin of D113 [31], while a heavy dosage of the catalyst was used.

The aim of the present work is to develop a promising oxidative desulfurization system in a model diesel. Iron phthalocyanine with amino ($FePc(NO_2)_3NH_2$) was immobilized on carbon fiber ($FePc(NO_2)_3$–CF) according to the reference method that substituted aniline compounds were grafted onto single-walled carbon nanotubes by covalent bond [32], and $FePc(NO_2)_3$–CF was employed as the catalyst for the direct oxidation of DBT with O_2 in hydrocarbon solvent. As a result, the introduction of the carbon fiber as carrier significantly improved the catalytic performance so that the extremely low level of FePc could convert DBT to DBT sulfone ($DBTO_2$) efficiently without any sacrificial agents. The effects of different conditions such as temperature, initial O_2 pressure and the concentration of catalyst were investigated, and the possible reaction mechanism was discussed.

Experimental

Materials

DBT (analytical grade reagent, AR) was purchased from J&K Scientific Ltd. Tridecane (AR) and hexadecane (chromatographic grade) were obtained from Aladdin Industrial Co. Carbon fiber was obtained from Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Science. Dioxygen was provided by Zhejiang Hangzhou Dazhong Zhiyang Qiti Co., Ltd. Other reagents were of AR and used without further purification.

Preparation of $FePc(NO_2)_3$–CF

Iron tetranitrophthalocyanine (FePc) was synthesized from 4-nitrophthalic acid, iron dichloride tetrahydrate and urea following the procedures described in Ref. [33]. In a similar way that metal tetraamine phthalocyanines were done by reduction of the nitro derivatives using sodium sulfide reported previously in the literature [34], $FePc(NO_2)_3NH_2$ was prepared by using one-fourth of stoichiometric amount of sodium sulfide for partial reduction of $FePc(NO_2)_4$ [31] in dimethyl formamide at 60 °C for 24 h. With minor modification of the method in Ref. [32], the chemical grafting process of $FePc(NO_2)_3NH_2$ loaded by carbon fiber was carried out as follows (Fig. 1): $FePc(NO_2)_3NH_2$ (0.06 g) dissolved in dimethyl sulfoxide and carbon fiber (2 g) were added to a flask with condenser and stirrer in oil bath, then heated to 85 °C. After 30 min, 1 ml isoamyl nitrite was added, retained stirring with N_2 inlet for 24 h in 85 °C. The solution was cooled to room temperature and filtered, then the carbon fiber was washed by dimethylformamide and deionized water until the filtrate was fully clear, and dried at 80 °C overnight.

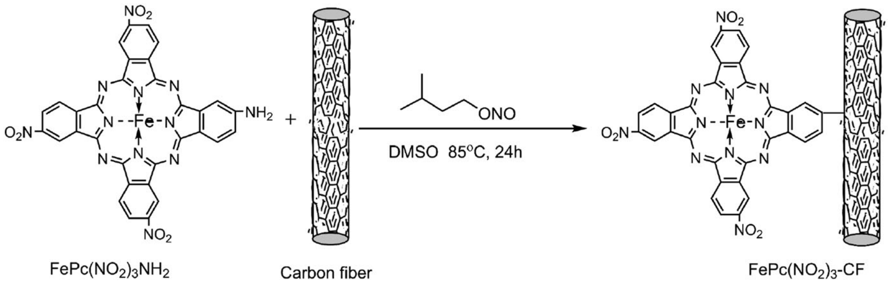


Fig. 1 Synthesis routine of supported iron phthalocyanine by covalent bond

Characterization of catalyst

The infrared spectrum of catalyst, diluted with KBr and pressed into a pellet, was recorded on a Nicolet 5700 FTIR spectrometer. IR (ν/cm^{-1}): (a) $FePc(NO_2)_4$, 733 and 761 cm^{-1} (Pc ring), 1,098 cm^{-1} (C–H, Pc), 1,143 cm^{-1} (Fe–N, Pc), 1,254 and 1,614 cm^{-1} (C=N, Pc), 1,335 and 1,546 cm^{-1} (N=O, NO_2); (b) $FePc(NO_2)_3NH_2$, 749 cm^{-1} (Pc ring), 1,094 cm^{-1} (C–H, Pc), 1,337 cm^{-1} (N=O, NO_2), 1,610 cm^{-1} (C=N, Pc), 3,442 cm^{-1} (N–H, NH_2). The content of FePc loaded on CF was given by atomic absorption spectrometer (Sollar M6) with recording the concentration of metal ion, and the final graft rate was calculated to be 0.23 wt%.

Typical procedure of oxidation desulfurization

The adsorption experiments were investigated at room temperature, the detection with GC–MS demonstrated no reduce for the concentration of DBT. Then the typical oxidative desulfurization experiments were carried out in a 100 mL closed reaction axe with magnetic stirrer, a pressure gage and a gas three-way valve, 0.25 g of catalyst and 25 mL model oil containing 500 μg/g DBT and 500 μg/g hexadecane (as internal standard for GC quantifying) were added. The autoclave was closed and the dioxygen flow was continued for 2 min, deflated and repeated the operation for three times to remove the air in autoclave completely, then heated to 130 °C and the initial oxygen pressure was set at 0.2 MPa. Stirring at 300 rpm was continued during 1–3 h at 130 °C. After the completion of the reaction, the autoclave was cooled to ambient temperature in water bath, depressurized slowly to atmospheric pressure, and then opened. The catalyst was filtered in vacuum, washed with anhydrous ethanol and then dried.

Analysis of sulfur compounds

The identification and quantification of sulfur compounds were analyzed by gas chromatography/mass spectrometry (MS: Agilent 5973i; GC: Agilent 6,890 N equipped with an OV1701 capillary column (30 m × 0.25 mm × 0.25 μm). Analysis conditions were as follows: injection port temperature, 280 °C; detector temperature, 250 °C; oven temperature program, 295 °C, hold for 3 min; split ratio, 1/100; carrier gas, ultra-purity nitrogen; column flow, 1.0 mL/min; reagent gases, air flow of 104 mL/min, hydrogen flow of 75 mL/min; the injection volume of sample was 1 μL.

Results and discussion

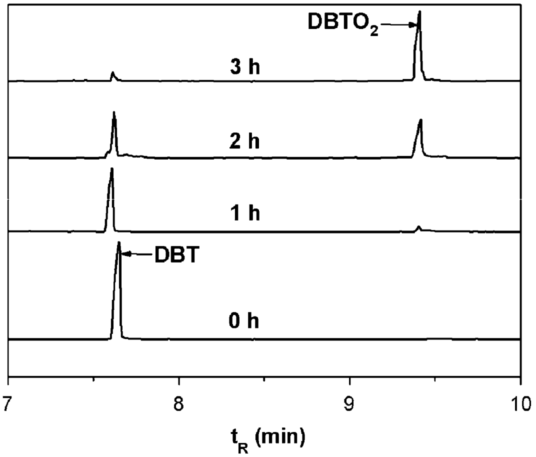
Catalytic performance of FePc supported by CF

Oxidation of DBT in tridecane using O_2 in the presence of $FePc(NO_2)_3$–CF was investigated at 130 °C and 0.2 MPa of initial dioxygen pressure, the peak of DBT gradually stepped down and a new peak appeared in the high retention time (Fig. 2), the conversion of DBT in 3 h reached 92 %. The result indicates that the oxidation of DBT can be effectively performed using $FePc(NO_2)_3$–CF and dioxygen. Meanwhile, the conversion of DBT with 10 g/L different catalysts ($FePc(NO_2)_3$–CF (containing FePc, 0.23 wt%), $FePc(NO_2)_4$, $FePc(NO_2)_3NH_2$) were given in Fig. 3. It is clear that the catalytic activity of $FePc(NO_2)_3$–CF is apparently higher than the unsupported catalyst of $FePc(NO_2)_4$ and $FePc(NO_2)_3NH_2$, and the activity of catalyst decreases in the order of $FePc(NO_2)_3$–CF > $FePc(NO_2)_4$ > $FePc(NO_2)_3NH_2$. It is known that the nitro substituent is an electron acceptor group, and the electron density of Pc ring is less than the Pc with amino group so that it is more convenient for the electron transfer. Furthermore, the dosage of FePc in heterogeneous supported system was almost 1/400 of that in unsupported system. Obviously, the introduction of carbon fiber significantly improved the catalytic activity of FePc, it seems that the method of preparation of the supported catalyst has influenced the catalyst structure in terms of distribution of the active sites on the surface and their accessibility and of the state of the complex [35]. Here, FePc on a molecular level is well dispersed on carbon fiber by covalent bond, and the large specific surface area of carbon fiber dramatically increases the number of catalytic active sites. In addition, we note that both carbon fiber and FePc have unique conjugated π electron structures, which facilitates the electron transfer in the catalytic reaction process. Therefore, $FePc(NO_2)_3$–CF presented well catalytic performance in the oxidative desulfurization of DBT.

Effect of catalyst concentration, reaction temperature, initial oxygen pressure

The oxidative desulfurization experiment without catalyst was performed before examining the efficiency of catalyst. As shown in Fig. 4, the conversion of DBT was 26 %. When 2.5 g/L of $FePc(NO_2)_3$–CF was added to the ODS system, it indicated an excellent catalytic performance that the conversion of DBT remarkably increased to 69.3 %, continued to increase the dosage of catalyst to 10 g/L and the removal of DBT reached 92 %. However, the conversion of DBT moved upward slightly with the increase of the catalyst, it might be due to the features that fiber was lightweight and unconsolidated. Because of the stirring in the reaction process, the fiber became fluffier and part of them was exposed to the surface of solution, as a matter of fact,

Fig. 2 GC-FID chromatograms of the oxidation of DBT



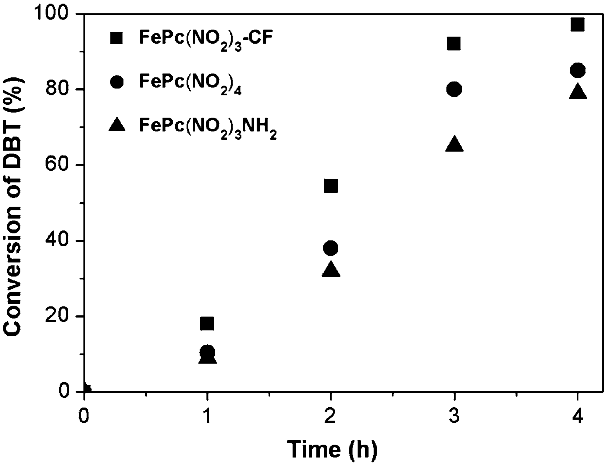


Fig. 3 Conversion of DBT with 10 g/L different catalyst: $FePc(NO_2)_3$–CF (containing FePc, 0.23 wt%), $FePc(NO_2)_4$ and $FePc(NO_2)_3NH_2$. Conditions: initial oxygen pressure, 0.2 MPa; temperature, 130 °C; DBT 500 μg/g in 25 mL tridecane

not all of the catalyst could be fully utilized, while appropriate stirring could promote the flow of solution and accelerate the catalytic reaction. Therefore, the concentration of catalyst was set at 10 g/L and stirring speed was 300 rpm in the text, taking into account of efficiency and utilization rate of catalyst.

The removal of DBT from model diesel from 60 to 140 °C are shown in Fig. 5, a sharp increase of DBT conversion appeared when changing the temperature from 120 to 130 °C, and the conversion of DBT was 24 and 92 %, respectively. When the temperature was increased to 140 °C, the conversion of DBT could reached 100 %, whereas the stability of solvent was to be challenged that infinitesimal alkanes were oxidized, and the peak of oxidation product closed to internal standard substance.

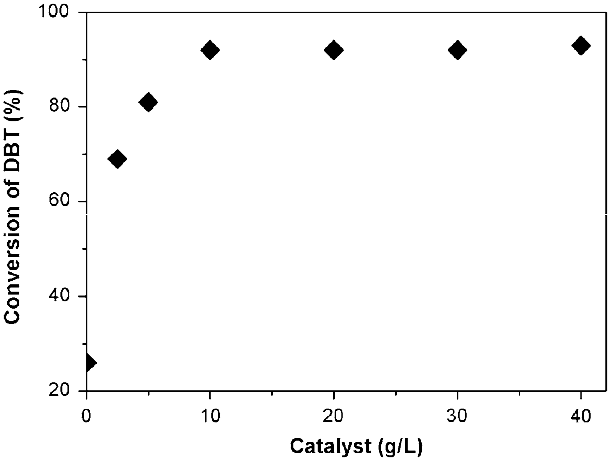


Fig. 4 Effect of the catalyst concentration on the conversion of DBT. Conditions: initial pressure, 0.2 MPa; temperature, 130 °C; time, 3 h; DBT 500 μg/g in 25 mL tridecane

Besides, FePc might tend to be destabilized at a high temperature. Therefore, the appropriate reaction temperature employed for the subsequent studies was set at 130 °C.

Air as oxidant was considered before investigating the effect of initial oxygen pressure. As shown in Fig. 6, the data at pressure of zero indicated the conversion of DBT was 6 % in air. Once the inflow of pure oxygen started, the conversion of DBT rose to 59 % spectacularly and reached to 92 % with increasing the pressure to 0.2 MPa, then climbed slowly to 100 % at 0.5 MPa. These results indicate that the oxygen plays an important role in the reaction and efficient desulfurization can be achieved with the low concentration of oxygen. From the viewpoint of efficiency and safety, 0.2 MPa was adopted as an optimum pressure.

Even though the reaction was performed in alkane solution at 130 °C and 0.2 MPa oxygen pressure, there was no need to be anxious about the security issues. Only a few very small peaks of the GC–MS spectra displayed for the possible oxidation products of tridecane, and the amount of these products were too small to calculate the ratio of the concentration exactly. The reaction conditions were moderate relatively corresponding to the severe conditions of the exploration trial (160 °C, 7 MPa) to confirm the stability of decalin as the solvent by Zhou et al. [29], and tridecane was more stable apparently than decalin in model oil according to our comparison experiments. It seems to be acceptable to the multitudinous high temperature and pressure reactions in chemical industries.

Oxidative desulfurization in model oil with different DBT concentration

In actual diesel, the concentration of sulfur compounds has a wide range and it is higher than 500 μg/g in most cases. In this work, oxidative desulfurization was investigated in the range of concentration of DBT from 100 to 2,000 μg/g. The curve presented in Fig. 7 showed that the conversion of DBT declined with an increase of substrate

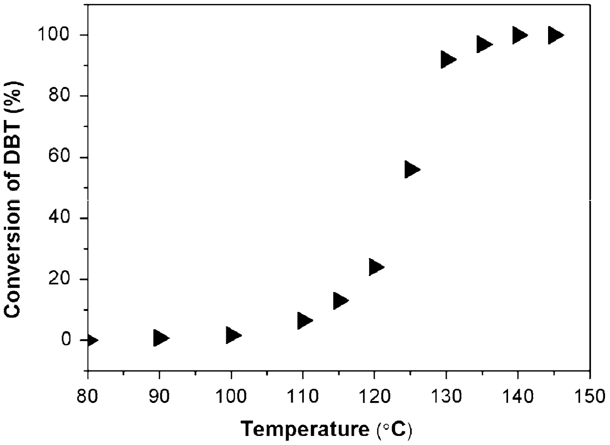


Fig. 5 Effect of temperature on the conversion of DBT. Conditions: FePc$(NO_2)_3$–CF, 10 g/L; initial pressure, 0.2 MPa; time 3 h; DBT 500 μg/g in 25 mL tridecane

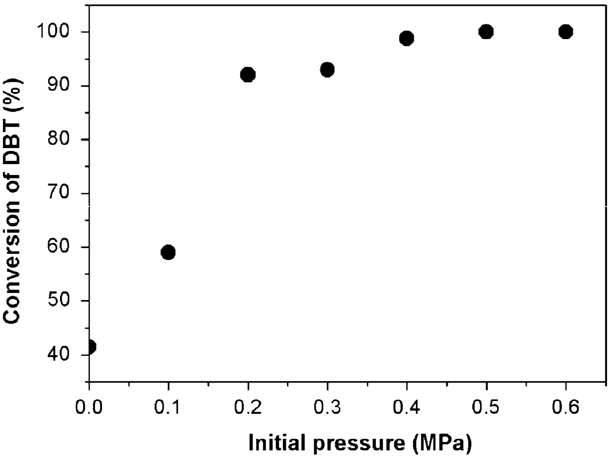


Fig. 6 Effect of initial pressure on the conversion of DBT. Conditions: FePc$(NO_2)_3$–CF, 10 g/L; temperature, 130 °C; time 3 h; DBT 500 μg/g in 25 mL tridecane

concentration, while the removal value of DBT was on the rise, it implied more DBT molecules involved in reaction. The reason is easy to understand: the substrate molecule has more opportunity to contact with the catalyst in a higher concentration solution and it is better utilization efficiency for the catalyst.

Regeneration of catalyst

The principal motivation for the preparation of supported catalysts is the possibility of their easy separation from the reaction system and their reuse for successive

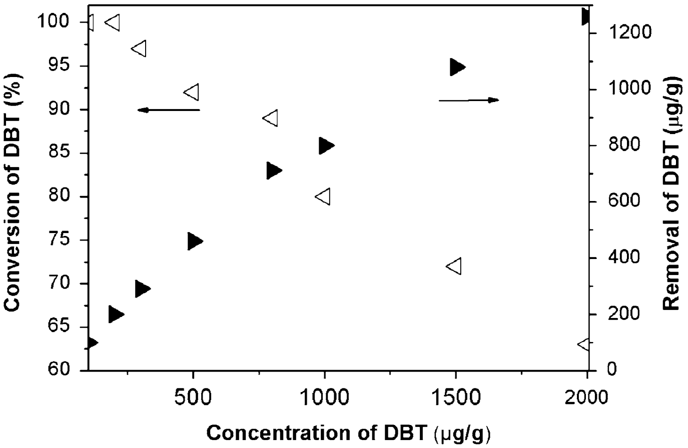


Fig. 7 Oxidative desulfurization with different concentration of DBT. Conditions: $FePc(NO_2)_3$–CF, 10 g/L; temperature, 130 °C; time, 3 h; initial pressure, 0.2 MPa; 25 mL tridecane

reactions, provided that the catalysts retain their catalytic properties as well. So the stability and reusability of catalyst are an indispensable part to consider in catalytic reaction, carbon fiber as carrier of metallophthalocyanine is a superduper solution for this problem in our work. After some simple procedures like filtration, washing and drying, carbon fiber-supported FePc could be reused to remove DBT. $FePc(NO_2)_3$–CF was performed 4 runs in oxidative desulfurization as shown in Fig. 8, correspondingly, the conversion of DBT was 92, 88, 87 and 78 %. The slight decrease of the catalyst activity may be due to the weakened complexation of the center metal iron and Pc ring at the high reaction temperature. As a result, it becomes difficult to form intermediates and active species for FePc interaction with oxygen that its catalytic performance weakens gradually, nevertheless, $FePc(NO_2)_3$–CF still could maintain an impressive removal for DBT.

The possible mechanism

Some mechanisms based on different key intermediates have been proposed for the oxidation hydrocarbon compounds with molecular oxygen catalyzed by mononuclear FePc complexes, many of them tend to produce peroxide iron (PcFe–O–OR) that homolytic and heterolytic cleavages of the peroxide O–O bond are possible ways to form the intermediates:$PcFe^{IV}=O$, $PcFe^{V}=O$ [36–38]. In this paper, FePc supported on CF by covalent bond was used as catalyst without any peroxide existing in the reaction system, it was hard to form the intermediates as the analogous way. Hence, the oxidation of DBT to $DBTO_2$ with O_2 catalyzed by $FePc(NO_2)_3$–CF was speculated on radical-free high valent iron-oxo mechanism (Fig. 9). With the activation at a high temperature, molecular oxygen is favored to interact with FePc to form the peroxideiron radical ($PcFe–O–O^{\bullet-}$), it is desired to capture oxygen from $PcFe–O–O^{\bullet-}$ for the sulfur atom of DBT with two lone pair electrons. Since the bond energy of O–S is much higher than the O–O bond, the

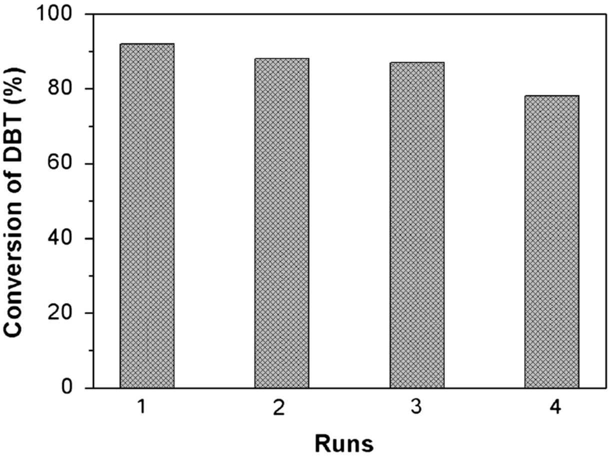


Fig. 8 Recycling of catalyst in model oil of ODS. Conditions: $FePc(NO_2)_3$–CF, 10 g/L; initial pressure, 0.2 MPa; temperature, 130 °C; time, 3 h; DBT 500 μg/g in 25 mL tridecane

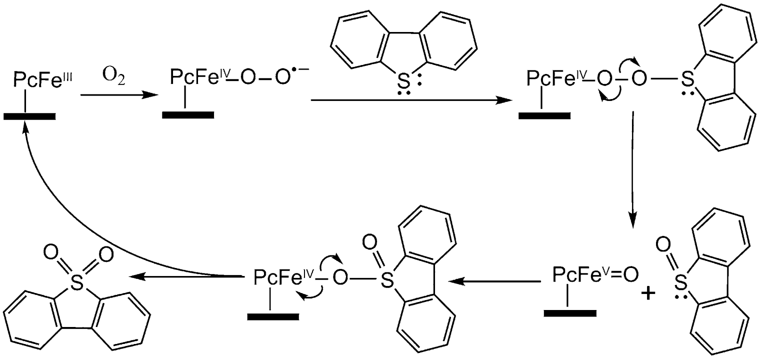


Fig. 9 Proposed mechanism for the oxygenation of DBT

weakened O–O bond breaks up into $PcFe^{V}=O$ and DBT sulfoxide (DBTO). While DBTO cannot exist stably with high activity intermediate $PcFe^{V}=O$, so sulfoxide is oxidized to sulfone rapidly, the oxygenation is a consecutive process, this might illuminate why the peak of DBTO could not be found in the GC–MS detection.

To confirm the radical-free high valent iron-oxo mechanism for the present oxygenation, a radical inhibitor (hydroquinone) was added to model oil before reaction, only infinitesimal $DBTO_2$ was detected and there was not any DBTO in the oxidative products. These results provides direct evidence for the formation of high valent iron oxo free radical species. In the oxygenation of DBT, the species is speculated on high valent iron oxo anion free radical species, which accepts the electron from the sulfur atom of DBT and then turns into unstable intermediate ($PcFe^{V}=O$), these are different from the high-valent iron oxo phthalocyanine cation radical species that can be stabilized and characterized at very low temperatures [39]. Combining the formation of species with the convinced oxidative process in many work that DBT was converted to DBTO and further $DBTO_2$ [6, 16, 29], the speculated involvement of Fe(V)=O species shown in Fig. 9 seems to be supported.

Conclusion

In this paper, an efficient ODS process using carbon fiber-supported FePc as catalysts in the presence of molecular oxygen has been studied. It was found that the oxidative desulfurization of DBT could be achieved with the catalyst of $FePc(NO_2)_3$–CF in the simple ODS system. Compared with $FePc(NO_2)_4$, the use of carbon fiber as carrier vastly reduced the dosage of FePc, while the reactivity of the catalyst increased. $FePc(NO_2)_3$–CF is easily separated from the reaction system and can be recycled without obvious inactivation. A mechanism, involving a high-valent iron oxo phthalocyanine radical species, has been proposed. It may be useful to improve the graft rate of metallophthalocyanine on carbon fiber further and explore the reinforced mechanism of carbon fiber. In summary, this process offers a novel strategy for deep desulfurization.

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