

## Desulfurization of liquid fuels by air assisted peracid oxidation system in the presence of Fe-ZSM-5 catalyst

Waqas Ahmad<sup>†</sup>, Imtiaz Ahmad, and Muhammad Yaseen

Institute of Chemical Sciences, University of Peshawar, 25120, Peshawar, Khyber Pukhtunkhwa, Pakistan

(Received 10 August 2015 • accepted 14 April 2016)

**Abstract**—Catalytic oxidative desulfurization of the model oil or synthetic sulfur oil (SSO) and the different real/industrial oil fractions was investigated using air assisted hydrogen peroxide and formic acid oxidation in the presence of Fe-ZSM-5 as catalyst. The reactivity of the different model sulfur compounds increased in the order of thiophene < dibenzothiophene (BT) < 4-methyl dibenzothiophene (4-MDBT). The desulfurization yield in case of the model oil was increased in the presence of Fe-ZSM-5 and the sulfur content of the model oil was reduced from 1275 to less than 50 ppm in 60 min at 60 °C temperature. The catalyst also performed efficiently in ODS of real industrial oil fractions, i.e., untreated naphtha (UN), light gas oil (LGO), cooker derived combined heavy gas oil (HGO) and Athabasca oil sands derived bitumen (At. Bit.), and sulfur removal of 80, 78, 62 and 60% was attained, respectively. Kinetic investigation revealed that the ODS catalyzed by Fe-ZSM-5 followed the first-order kinetics.

Keywords: Catalytic Oxidative Desulfurization, Ion Exchange, ZSM-5, Iron Catalyst, Air Oxidation

### INTRODUCTION

Oxidative desulfurization (ODS) is rapidly gaining popularity as an alternative technique to hydrodesulfurization (HDS) for liquid fuels because of its mild operation, cost effectiveness and promising efficiency [5,12]. The process involves the selective oxidation of sulfur compounds present in petroleum to respective sulfones, which are then removed through extraction or adsorption process owing to their increased polarity [2,11,21]. Selective oxidation of the sulfur compounds is effectuated by using proper oxidants, which adds to the overall efficiency of the process. In the literature, different types of oxidants have been employed for ODS, the most common include nitric acid [31], nitric oxide [32], sodium perchlorate [28], Ozone [25], tert-butyl hydroperoxides [35], amyl hydroperoxides [39], and organic peracids [2,24]. Organic peracids are extensively studied for this purpose as they provide an efficient route for selective oxidation of sulfur compounds, but due to their explosive nature, these are mostly generated in situ by reaction of hydrogen peroxide with organic acids like formic acid and acetic acid. However, in order to attain deep desulfurization, excess amounts of H<sub>2</sub>O<sub>2</sub> and organic acid are required. A number of catalysts are employed to assist this oxidation system and to enhance the ODS efficiency with minimum consumption of peracid. As reported elsewhere, ODS of fuel oil using hydrogen peroxide and formic acid without the use of a catalyst caused about 60% sulfur removal, which was increased up to 95% by using activated carbon as catalyst [37]. The other catalysts used include EDTA, sodium and magnesium silicates [15], metal oxides loaded on molecular sieves [7], transition metal salts [9], silica gel [6], and sodium bicar-

bonate [10]. Raid et al. reported the ODS of light gas oil using H<sub>2</sub>O<sub>2</sub> as oxidant in the presence of Zn/hydroxy apatite prepared by ion exchange method; results showed that a maximum of 68% of sulfur was removed. However, such type of catalyst (i.e., transition metal cation exchange) has not been reported for the ODS of heavy oil [26].

It was inferred from such studies that these catalysts actually promoted the formation of peroxy species which further increased the oxidation of the organosulfur compounds giving high desulfurization yields. Molecular oxygen, O<sub>2</sub>, has also been used as a preferred inexpensive oxidant in combination with the various initiators like aldehydes in the presence of a variety of catalysts in ODS with promising results [14,22,34,40]. It is obvious that in case of feed containing high levels of sulfur, the desulfurization efficiency using these reported catalysts is very poor. The desulfurization of heavy feed stocks such as atmospheric residue and bitumen, etc., by ODS process has been paid very little attention so far. Few reports show the non-catalytic ODS of some heavy oil such as Athabasca bitumen, but the sulfur removal attained is very small (up to 50%) [17, 18]. The ODS efficiency of heavy fractions is hindered by a number of factors, such as their high sulfur content, high density and viscosity, as well as the phase transfer limitations during the process.

It has been shown that in heavy fractions the sulfur present is mostly in the form of complex alkylated benzothiophenes; the treatment of these compounds by commercial HDS process is difficult due to the steric hindrance posed by the alkyl side chains around the sulfur atoms due to which these are called refractory sulfur compounds. However, the reactivity of these compounds towards oxidation is high because of the electron-donating effects of the alkyl groups which increase the electron density on the sulfur atom, thereby facilitating the electrophilic attack of S on oxygen atom during oxidation [5]. Therefore, in the presence of a proper oxidation system the sulfur compounds in heavy oil can be removed by ODS process at less cost than the expensive HDS process.

<sup>†</sup>To whom correspondence should be addressed.

E-mail: waqasawati@yahoo.com

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In the present work, we carried out ODS of model as well as real industrial oil fractions using air assisted performic acid oxidation system in the presence of Fe/ZSM-5 catalysts. The reaction conditions (temperature, time and concentration of oxidants, i.e., H<sub>2</sub>O<sub>2</sub> and formic acid) were optimized. The ODS of real industrial fractions including untreated naphtha, light gas oil, heavy gas oil and Athabasca bitumen was studied under the optimized experimental conditions.

## EXPERIMENTAL

### 1. Chemicals and Reagents

All chemicals used were of analytical grade and used as such without further purification.

#### Chemicals used:

Thiophene (99%), Sigma Aldrich	CoCl <sub>2</sub> , Sigma Aldrich
Dibenzothiophene (98%), Sigma Aldrich	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, Sigma Aldrich
Hydrogen peroxide (30%), Fluka	MnCl <sub>2</sub> , Sigma Aldrich
n-Heptane (97%), Sigma Aldrich	CuCl <sub>2</sub> , Sigma Aldrich
FeCl <sub>3</sub> , Sigma Aldrich	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, Sigma Aldrich
4-Methylthiobenzothiophene (97%), Sigma	Formic acid (99%) Sigma

Model oil or Synthetic Sulfur oil (SSO) containing 1,275 ppm S was prepared by dissolving model S compounds in n-heptane (97%). Commercial zeolite NH<sub>4</sub>-ZSM-5 having surface area of 400 m<sup>2</sup>/g and Al/Si ratio of 280 was purchased from Zeolyst International USA. NH<sub>4</sub>-ZSM-5 was converted to H-ZSM-5 by heating at 350 °C for 3 hours.

The industrial oil samples used included untreated naphtha (UN), light gas oil (LGO), heavy gas oil (HGO) and Athabasca bitumen (At. Bit.).

### 2. Synthesis and Characterization of Catalysts

The catalysts used in the study were Fe-ZSM-5, Co-ZSM-5, Zn-ZSM-5, Mn-ZSM-5, Cu-ZSM-5 and Ni-ZSM-5, which were synthesized in the laboratory by ion exchange method. For preparation of Fe-ZSM-5, about 3.24 g of FeCl<sub>3</sub> was dissolved in 100 ml of de-ionized water to prepare 0.2 M solution. The solution was transferred to a 250 ml beaker and added 3 g of H-ZSM-5, the suspension was stirred at 70 °C for 5 hours. The catalyst was recovered by vacuum filtration, washed three times with de-ionized water and dried in an oven at 90 °C for 24 hours. The Co-ZSM-5, Zn-ZSM-5, Mn-ZSM-5, Cu-ZSM-5 and Ni-ZSM-5 catalysts were prepared by the same method from their respective salts, i.e., CoCl<sub>2</sub>, ZnNO<sub>3</sub>, MnCl<sub>2</sub>, CuCl<sub>2</sub>, and NiNO<sub>3</sub> as metal precursor.

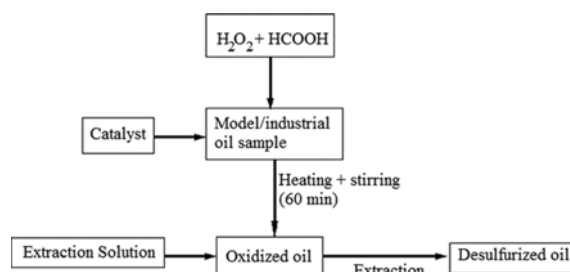
Active metal concentration of each of the catalysts was determined by X-ray fluorescence (XRF) analysis, using Bruker AXS S2 Ranger XRF machine, operated by computer software. The instrument was calibrated by standard copper disc and quality check disc with standard concentration of Si, Cu, Mn, As, Mo and Sb. The sample was mounted in sample cup on a MYLAR polymer membrane and analyzed in a stream of He gas. The surface area, pore volume and pore diameter of the catalysts were determined by

surface area analyzer (Quantachrome Nova station A), using BJH model and nitrogen gas as adsorbent. The morphology of each of the catalyst was examined by scanning electron microscope Model No. JEOL-Jsm-5910; Japan.

### 3. Oxidation of SSO and Industrial Oil

The oxidation of the model oil or SSO and industrial oil was studied in a 250 ml three neck flask mounted on a temperature controlled oil bath, fitted with a condenser and magnetic stirrer. In a batch experiment, 20 ml of the model oil was taken in a flask, added 2 ml of hydrogen peroxide and 2.5 ml of formic acid, then about 0.005 g of the catalyst was added. Dried air was bubbled through the reaction mixture using a Pyrex glass air bubbler at a flow rate of 150 ml·min<sup>-1</sup>. The reaction was carried out at 80 °C for 60 min. After termination of the experiment, the oxidized (residual) model oil was extracted with methanol-water (80 : 20) mixture.

The reactivity of different sulfur compounds was investigated by carrying out reaction at different temperatures and withdrawing small aliquots from the reaction sump at different time intervals. Oxidation kinetics was also studied. Concentrations of performic acid and hydrogen peroxide were optimized. Effect of extraction number on total desulfurization yields was also investigated.



Schematic of the ODS process

The oxidation of industrial oil samples was carried out at 60 °C for 45 min. In case of the heavy fractions, i.e., the HGO and the At. Bit., about 5 ml of benzene was also added as a solvent to reduce the viscosity and to facilitate mixing of the reagents. After oxidation, the oil was extracted twice.

### 4. GC Analysis

The concentration of the sulfur compounds in the model oil was determined by an Agilent 7890A gas chromatograph (GC) equipped with a flame ionization detector (FID) and autosampler. Analysis was performed with 1 : 100 split ratio of hydrogen and injection temperature of 250 °C. The oven temperature was in the range 85-300 °C, with a ramp of 6 °C/min for 85-120 °C, 15 °C/min for 120-170 °C and 20 °C/min for 170-300 °C. During each analysis 0.5 μl of sample was injected and separated on a PIONA capillary column with internal diameter of 0.25 μm and length of 25 m. Calibrated values were employed for the sulfur compounds to correct for the FID response. The change in concentration of model compounds was calculated as % conversion using the following equation.

$$\% \text{ Conversion} = \frac{(C_o - C_t)}{C_o} \times 100 \quad (1)$$

where C<sub>o</sub> is the initial concentrations and C<sub>t</sub> the final concentra-

tion after time  $t$ .

The change in concentration was used to investigate the kinetics of the oxidation for model sulfur compounds. In  $C_o/C_t$  was plotted against  $t$  using the first order kinetics equation, as given below. The rate constant was obtained from the slope of the linear plot at respective temperature.

$$\ln \frac{C_o}{C_t} = -kt \quad (2)$$

The activation energy for oxidation of different sulfur compounds was determined by plotting  $\ln K$  against  $1/T$ , using the Arrhenius equation, where  $T$  is the temperature (K).

$$k = -\frac{E_a}{RT} + \ln A \quad (3)$$

## 5. Total Sulfur Analysis

Total concentration of sulfur in the samples was analyzed by SN analyzer (Antek by PAL) equipped with chemiluminescence and vacuum UV detector. The instrument was operated with argon as a carrier gas and pure oxygen gas as oxidant. Analyses were performed in triplicate and the average result was reported for each  $5 \mu\text{l}$  of the sample that was injected. The desulfurization yield of the model oil was calculated as % desulfurization using the following relation:

$$\% \text{ Desulfurization} = \frac{(S_o - S_t)}{S_o} \times 100$$

where the  $S_o$  is the sulfur concentration of the original oil and  $S_t$  is the sulfur concentration of the treated oil.

## RESULTS AND DISCUSSION

### 1. ODS of Model Oil

Oxidative desulfurization of the model oil was investigated using air assisted performic acid oxidation system in the presence of different transition metals exchanged ZSM-5 catalysts. Our initial experiments indicated that optimum temperature and time for the ODS of the model oil in the absence of the catalyst was  $80^\circ\text{C}$  and 1 h, respectively; therefore, catalytic ODS of the model oil was investigated under the same set of experimental conditions. After catalytic oxidation, the oxidized model oil was extracted with methanol-water solution (80:20). We have previously reported that the use of air in the presence of  $\text{H}_2\text{O}_2$  and formic acid is synergistic and sufficiently increases the desulfurization yield of the SSO [16]. It has been reported that during oxidation of sulfur compounds by  $\text{H}_2\text{O}_2$  and  $\text{HCOOH}$  system, the transition metals promote the formation of peracid, which effectuates the selective oxidation of sulfur compounds [7,9,15]. The results of the current study showed (Table 1) that among the different catalysts (Co, Ni, Mn, Zn, Fe and Cu exchanged ZSM-5), maximum desulfurization (more than 96%) was attained with Fe/ZSM-5 followed by Zn/ZSM-5 and then by Ni/ZSM-5, whereas in case of reaction catalyzed with the rest of the catalysts, the desulfurization yield was less than 91%. The highest desulfurization yield of 96% was shown by Fe/ZSM-5, which may be attributed to the high ability of  $\text{Fe}^{+2}$  cation to decompose  $\text{H}_2\text{O}_2$  and thereby enhancing the formation of peracids [13]. The formation of peracid by the metal cations depends upon its

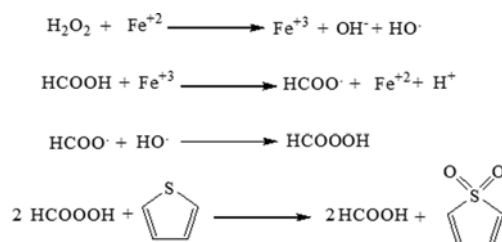
**Table 1. Oxidative desulphurization of model oil using metal exchanged ZSM-5 catalyst**

Catalyst	Sulfur content ( $\mu\text{g}\cdot\text{g}^{-1}$ ) $\pm$ SD	Desulphurization (%)
Co/ZSM-5	109.31 $\pm$ 0.38	91.43
Ni/ZSM-5	56.79 $\pm$ 1.62	95.55
Mn/ZSM-5	116.77 $\pm$ 0.55	90.84
Zn/ZSM-5	63.22 $\pm$ 1.62	95.04
Fe/ZSM-5	50.24 $\pm$ 0.52	96.06
Cu/ZSM-5	119.86 $\pm$ 0.36	90.60
ZSM-5	142.77 $\pm$ 0.90	88.80
No Cat	154.32 $\pm$ 0.62	87.90

redox cycles. During the oxidation process, the metal cation is reduced to oxidize the substrate. The reduced catalyst is then re-oxidized by the oxidant present in the medium. It has been previously reported that among the various metals cations, iron showed a balance between the reduction and oxidation rates [29]; therefore, Fe/ZSM5 showed high desulfurization efficiency in the present case.

In the current oxidation system, air was used as a co-oxidant in combination with  $\text{H}_2\text{O}_2$  and  $\text{HCOOH}$ , which could enhance the oxidation of organosulfur compounds by regeneration of the performic acid during the reaction. We have previously reported that in  $\text{H}_2\text{O}_2/\text{HCOOH}$  oxidation system, the conversion of thiophene and DBT was increased by 32 and 10%, respectively, when air was used as co-oxidant [16]. Transition metals have been reported to increase the efficiency of oxidation using molecular oxygen or air. For ODS of DBT using molecular oxygen and aldehydes, the presence of the transition metal salts of Co, Mn and Ni was found to be very active, leading to 99% conversion of DBT at  $40^\circ\text{C}$  temperature [22]. It was shown that transition metals activate the autoxidation of aldehyde, forming peroxy radical which oxidizes DBT to respective sulfones. However, it may also be suggested that in the present oxidation system, air helped in recycling the catalysts, i.e., by oxidizing  $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$ .

To verify the role of metal species, oxidation of the model oil was carried out in the absence and presence of ZSM-5 without any metal cation. It was found that the desulfurization yields without catalysts and un-loaded ZSM-5 were very low; 88 and 87%, respectively. These results show that ODS of the model oil in the presence of Fe/ZSM-5 increased the sulfur removal by almost 9%, as compared to an uncatalyzed run. Thus, the catalyst has offered a clear advantage in the ODS of model oil over non-catalytic ODS. Hence, one could postulate that the Fe/ZSM-5 promoted the formation of peroxyacid by decomposition of hydrogen peroxide via Fenton-like system [13], depicted as below:



**Reaction Scheme 1. Oxidation of thiophene by peracids in the presence of Fe/ZSM-5.**

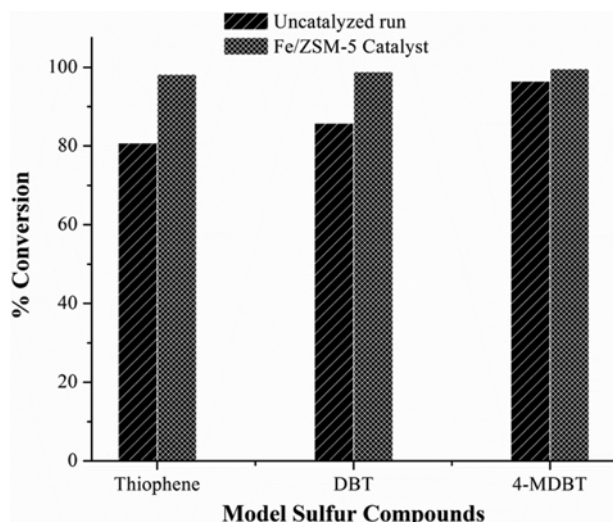


Fig. 1. Conversion of model sulfur compounds in the presence and in the absence of Fe/ZSM-5 catalyst.

The conversion of the individual sulfur compounds in the presence and in the absence of Fe/ZSM-5 catalysts was also studied. Results indicate that (Fig. 1) in the presence of Fe/ZSM-5, the conversions of thiophene, BT and 4-MDBT were increased by 18, 14 and 3%, respectively. There was very little increase in the conversion of 4-MDBT, because of its high reactivity even in the absence of the catalyst; however, in case of thiophene and BT, the conversion was markedly increased by the catalyst.

## 2. Catalyst Characterization

The catalyst used in the current study was prepared by exchange of transition metal cation on commercial ZSM-5 zeolite via ion exchange method. The active metals concentration was determined by XRF analysis. Results show that the cation exchange of all metals was not same on the ZSM-5 zeolite (Table 2); the concentration of different metals exchanged on ZSM-5 ranged from 1.15 to 3.47 wt%. In case of Co-ZSM-5, the metal concentration was the minimum of 1.15% whereas in case of Zn/ZSM-5, the metal concentration was the maximum of 3.47%. As all ion exchange sites are not equal [27], besides various metals exchange differently depending upon its size on different ion exchange sites. However, during the diffusion of the metal ion in the pores of the zeolites, the transport limitation arising due to electrostatic forces between the metal ion and the walls of the zeolites may overshadow the size effects

Table 2. Active metals concentration of transition metal supported ZSM-5 catalysts

S. no.	Catalysts	Active metals concentration (wt%)
1	Co/ZSM-5	1.15
2	Mn/ZSM-5	1.44
3	Ni/ZSM-5	1.43
4	Zn /ZSM-5	3.47
5	Fe/ZSM-5	2.59
6	Cu/ZSM-5	2.51

[23]. Also, ion exchange was carried out with dilute solution of metal precursor (0.2 M), which was intended to get low metal loading in order to attain high efficiency. Since during ion exchange the iron precursor used was Fe(III) salt, hence the exchanged ZSM-5 also contained Fe(III); this has been revealed in a number of literature reports [19].

As Fe/ZSM-5 was found to be the most active catalyst, therefore, its SEM and surface area analysis was compared with the original HZSM-5. The surface area of the Fe/ZSM-5 was found to be 350 m<sup>2</sup>/g, whereas that of the commercial ZSM-5 was 420 m<sup>2</sup>/g. The decrease in the surface area of the Fe/ZSM-5 may be attributed to the incorporation of Fe metal cations on the zeolite surface in the micropores and channels. The SEM micrograph of the commercial NH<sub>4</sub>-ZSM-5 (Fig. 2(a)) shows fine particles of regular shaped granular structure; the individual particles have uniform and smooth surfaces. The micrographs of the fresh Fe-ZSM-5 (Fig. 2(b)) exhibit similar morphology as the parent zeolite but the granules are rarely agglomerated. The micrographs of the spent Fe-ZSM-5 (Fig. 2(c)) show that the catalyst particles are more agglomerated, and the individual granules have rough and corroded surfaces, which may be due to attrition of the particles during the reaction as well as settling of the reacting materials on the catalyst surface.

## 3. Reactivity of Sulfur Compounds

Experiments were conducted to analyze the oxidation products of sulfur compounds which are shifted to solvent phase during extraction. Each of the model sulfur compounds was dissolved in n-heptane solvent and oxidized individually, including thiophene, dibenzothiophene (DBT), and 4,6-dimethyl dibenzothiophene (4,6-DMDBT). The oxidation products was liquid in case of thiophene and white precipitates (insoluble in oil phase) in case of DBT and 4,6-DMDBT, which was readily soluble in the extraction solution. The oxidation products isolated individually were characterized by

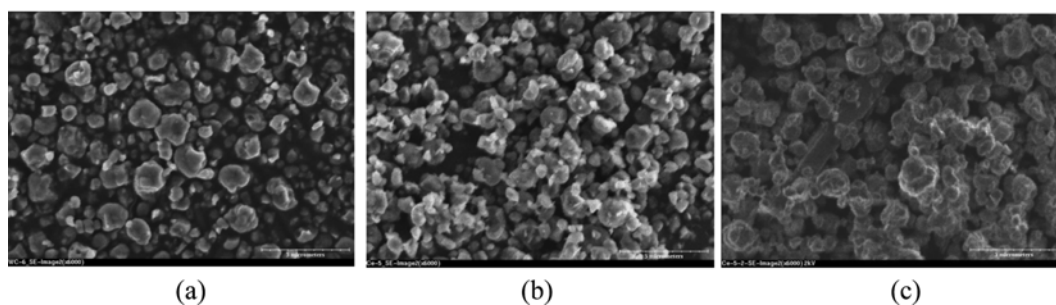


Fig. 2. SEM micrographs of (a) H-ZSM-5 (b) Fe/ZSM-5 (c) Spent Fe/ZSM-5.

GC-MC analysis. The oxidation product of the thiophene was identified to be thiophene sulfone having first peaks appearing with mass to charge ratio of 117  $m/z$  and 118  $m/z$ . The oxidation product of DBT gives a molecular ion peak with mass to charge ratio of 216  $m/z$ , which was identified to be DBT sulfone. Similarly, the oxidation product of 4,6-DMDBT was identified to be 4,6-DMDBT sulfone, which gave the molecular ion peak with mass to charge ratio of 246  $m/z$ . In this part of the study we used 4,6-DMDBT instead of 4-MDBT, since both have similar molecular structure with only the difference of a methyl group which does not take part in the reaction; therefore, both have the same reactivity towards oxidation. The electron impact mass spectra of oxidized sulfur compounds are given in Fig. S1 to S3 in supplementary information.

To view the role of Fe/ZSM-5 catalysts on the oxidation reactivities of different model sulfur compounds, different temperatures (25, 40, 60 and 80 °C) and different reaction times (15, 30, 45, 60 and 90 min) were considered for oxidation of model sulfur compounds in the presence of Fe-ZSM-5 catalyst. Results indicated that the oxidative conversion of thiophene was very slow at low temperature; however, it increased with the increase in the reaction time (Fig. 3(a)). At 25 and 40 °C, maximum conversion of 78 and 89% was attained in 90 min. At higher temperature, the oxidative conversion is fairly fast; at 60 °C oxidation is nearly completed in

90 min, whereas more than 93% conversion is attained in 60 min. Similarly, at 80 °C temperature above 90% conversion of thiophene occurs in 30 min, while oxidation is near to completion within 45 min reaction time.

Similarly, the reactivity of DBT also increased with the increase in temperature and reaction time (Fig. 3(b)). At low temperatures, 25 and 40 °C, maximum conversion of 78 and 88% was attained in 90 min reaction time. At high temperatures, the oxidative conversion of DBT was very rapid, at 60 and 80 °C, more than 90% conversion occurred in 45 min and 30 min, respectively. The oxidation reactivity of 4-MDBT is analogous (Fig. 3(c)); at low temperatures, 25 and 40 °C, oxidation does not complete even in 90 min, but reaches to a maximum of 79 and 90%, respectively. At higher temperatures, 60 and 80 °C, more than 90% conversion occurs in 45 and 30 min, respectively, whereas near complete oxidation is attained before 60 min at these temperatures. These results show that near complete oxidative conversion of all model sulfur compounds occurs at 60 °C and 60 min reaction time, in the presence of Fe-ZSM-5 catalyst. It may be concluded that in the presence of Fe/ZSM-5 catalyst, the reactivities of different sulfur compounds have increased, and the same level of conversion of all model compounds occurs at 60 °C, which occurred at 80 °C in the absence of the catalyst.

To study the kinetics of the Fe/ZSM-5 catalyzed run, a plot of

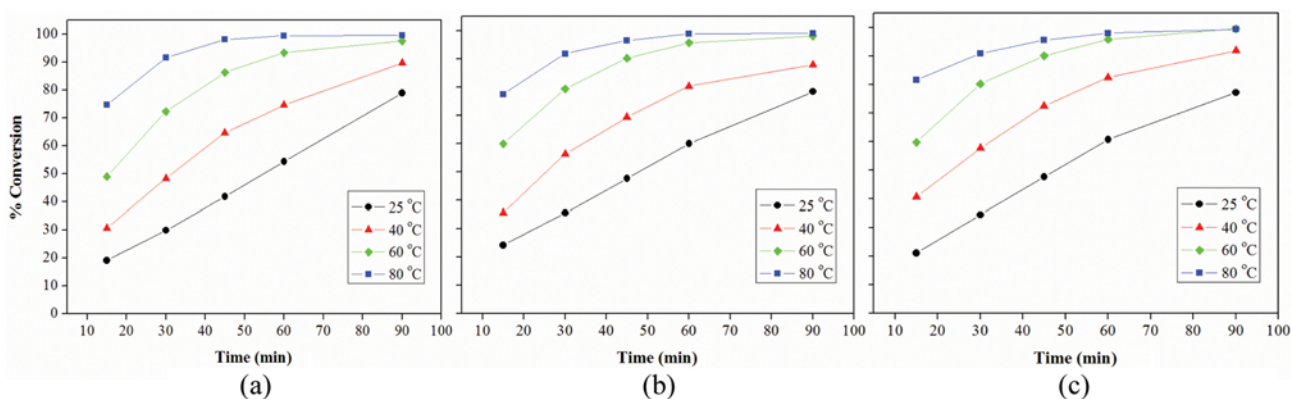


Fig. 3. Effect of temperature and time on oxidation of model sulfur compounds in the presence of Fe/ZSM-5 catalyst (a) thiophene (b) DBT (c) 4-MDBT.

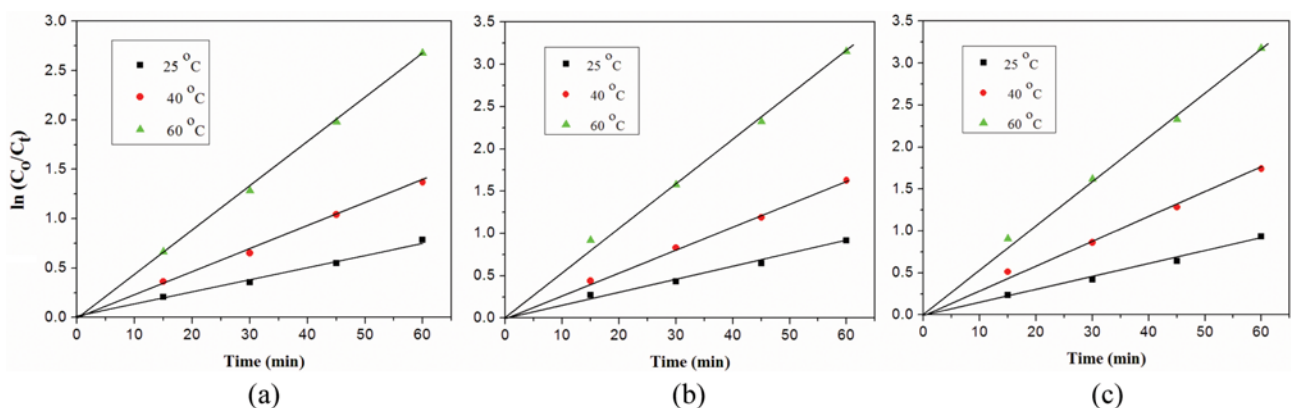


Fig. 4. 1<sup>st</sup> Order kinetics for oxidation of model sulfur compounds in the presence of Fe/ZSM-5 (a) thiophene (b) DBT (c) 4-MDBT.

**Table 3. First order rate constants for oxidation of model sulfur compounds in the presence of Fe/ZSM-5 catalyst at different temperatures**

Sulphur compound	First order rate constant (min <sup>-1</sup> )			Activation energy (kJ/mol)	
	25 °C	40 °C	60 °C	Experimental	Reported
Thiophene	0.012	0.022	0.044	30.60	35-48 [32]
DBT	0.014	0.026	0.049	29.46	53 [33]
4-MDBT	0.015	0.027	0.050	28.32	56 [33]

ln(Co/Ct) against time was constructed for thiophene, DBT and 4-MDBT, which gave a linear relation (Fig. 4(a)-(c)), indicating that the oxidation of model sulfur compounds follows first-order kinetics. First-order rate constants for thiophene, DBT and 4-MDBT at different temperatures are indicated in the Table 3, which shows that the order of reactivity of model sulfur compounds occurs as, thiophene < DBT < 4-MDBT. The reactivity order of the model sulfur compounds in the presence of Fe-ZSM-5 indicated that the oxidation reactivity increases with the increase in the electron density of the sulfur compound, which is in disagreement with some literature reports. For example, Wang et al. reported that the order of ODS reactivity for different sulfur compounds using H<sub>2</sub>O<sub>2</sub>/Ti-HMS system was DBT > BT > 4,6-DMDBT > Thiophene [36]. Caero et al. also obtained similar findings using H<sub>2</sub>O<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> oxidation system [4]. However, Mure et al. reported that in the catalytic oxidation system involving the larger peroxy complex formation, the reactivity of alkyl substituted thiophenes is decreased due to steric hindrance [33].

The apparent activation energy, determined from the Arrhenius plots, was found to be 30.58, 29.17 and 27.86 kJ/mol for thiophene, DBT and 4-MDBT, respectively. The activation energies determined for these compounds in the absence of the catalyst were 33.62, 30.44 and 29.07 kJ·mol<sup>-1</sup>, respectively. This indicates that the catalyst has considerably reduced the activation energies for oxidation of model sulfur compounds. It can also be observed that the activation energies of the model sulfur compounds are smaller than reported in the literature. For example, Caero et al. reported that the apparent activation of different sulfur compounds ranges from 35.3 to 48.4 kJ/mol, using H<sub>2</sub>O<sub>2</sub> in the presence of vanadium oxide catalyst [4]. Mure et al. reported that the activation energies of DBT and 4-MDBT were 53 and 56 kJ/mol in H<sub>2</sub>O<sub>2</sub>/Na<sub>2</sub>PW<sub>12</sub>O<sub>40</sub> oxidation system [33]. Comparing the apparent activation energy values for model sulfur compounds obtained during oxidation in the presence of Fe/ZSM-5 to those obtained in the absence of catalyst, it was found that the activation energy values were sufficiently reduced in the presence of catalyst, which indicated that the catalyst efficiently catalyzed the oxidation of sulfur compounds.

#### 4. Effect of Oxidants Concentration

The oxidative desulfurization of model oil was found to occur with 96% efficiency at temperature of 60 °C and reaction time of 60 min, in the presence of Fe-ZSM-5 catalyst. As mentioned in earlier sections, complete oxidation of model sulfur compounds occurs with H<sub>2</sub>O<sub>2</sub> and HCOOH concentration or volume ratio of 2 : 2.5 ml for 20 ml of model oil. However, to study the effect of Fe/ZSM-5

**Table 4. ODS of model sulfur compounds with different volumetric ratios of oxidants in the presence of Fe/ZSM-5 catalyst**

H <sub>2</sub> O <sub>2</sub> to HCOOH ratio (ml)	% Conversion		
	Thiophene	DBT	4-MDBT
0.5 : 0.75	67.93	74.34	76.31
01 : 01.3	80.23	86.63	89.28
1.5 : 1.75	93.09	94.91	96.76
02 : 02.5	98.23	98.88	99.59

catalysts on the quantity of oxidants required for complete oxidation of model sulfur compounds, reaction was carried out using different volume ratios of H<sub>2</sub>O<sub>2</sub> and HCOOH (2 : 2.5, 1.5 : 1.75, 1 : 1.25 and 0.5 : 0.75, ml) respectively, with 20 ml of model oil. Results indicated (Table 4) that using 2 : 2.5 ml ratio of H<sub>2</sub>O<sub>2</sub> and HCOOH, oxidation of model sulfur compounds was complete, whereas at the ratio of 1.5 : 1.75 ml, the conversion yield was about 93 to 96%. With further decrease in the oxidant ratio by 0.5 ml, 10 to 15% decrease in the oxidative conversion was observed. Hence, it could be concluded the H<sub>2</sub>O<sub>2</sub> and HCOOH volumetric ratio of 1.5 : 1.75 ml is sufficient for near complete oxidation of thiophene, DBT, and 4-MDBT, in the presence of Fe-ZSM-5 catalyst. Thus, in the presence of catalyst relatively less quantity of oxidant is required for the ODS of model oil.

These results show that the quantity of oxidant consumed is more substantial than the stoichiometric quantity required for oxidation of sulfur compounds present in the model oil, which was also reported by other researchers [3,8]. However, the quantity of the oxidant required in the current oxidation system (H<sub>2</sub>O<sub>2</sub>/S=24) is less than the one reported in the literature using H<sub>2</sub>O<sub>2</sub>/S=190 in the presence of H<sub>2</sub>O<sub>2</sub>/HCOOH oxidation system for ODS of model oil [24]. In addition, the excess of aqueous oxidant (H<sub>2</sub>O<sub>2</sub>/Organic acid) not only helps in complete oxidation of sulfur compounds but also in extraction of the oxidized products [38].

#### 5. Extraction of Oxidized Model Oil

A number of polar solvents have been employed for extraction of the oxidized oil, in the ODS process, which include N-methyl pyrrolidone (NMP), dimethyl formamide, dimethylsulfoxide (DMSO), furfural, methanol and acetonitrile, out of which different researchers found different solvents to be more effective for extraction of oxidized oil [30,38]. In the current investigation, methanol water solution (80 : 20) was used for extraction of model oil oxidized in the presence of Fe/ZSM-5. To investigate the extraction efficiency of the methanol water solution (80 : 20), the concentration of the sulfur compounds extracted was studied. The balance of sulfur concentration in model oil extract, before and after the catalytic oxidation, is shown in Table 5. The data reveals that model sulfur compounds could be slightly extracted by the methanol water solution without oxidizing the model oil. However, in case of catalytic oxidation followed by extraction of model oil, about 1,224 ppm of sulfur was removed. During extraction stage all of the oxidized sulfur compounds were shifted to methanol water solution.

The influence of multiple extractions on the removal of the sulfur was also investigated. Results in Table 6 show that the desulfurization yield of 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> extraction stage was 96.05, 97.06 and

**Table 5. Concentration of the sulphur compounds extracted before and after the catalytic oxidation (balance of sulphur in oil and extraction solution)**

Extraction steps	Sulfur content ( $\mu\text{g}\cdot\text{g}^{-1}$ )	
	Model oil	Extraction solvent
No extraction	1275	-
Extraction without oxidation	1245.08	30.02
Extraction after catalytic oxidation	50.424	1223.87

**Table 6. Desulfurization of oxidized model in the presence of Fe/ZSM-5 catalyst by multiple extractions with methanol-water (4:1)**

Extraction cycles	Sulfur content ( $\mu\text{g}\cdot\text{g}^{-1}$ ) $\pm$ SD	Desulfurization (%)
1 <sup>st</sup> Extraction	50.424 $\pm$ 0.52	96.05
2 <sup>nd</sup> Extraction	37.541 $\pm$ 1.46	97.06
3 <sup>rd</sup> Extraction	28.338 $\pm$ 0.77	97.78

97.78% (Table 6). It can be seen from the results that after the second extraction there was little change in the desulfurization efficiency, suggesting that extraction in two stages is helpful in maximum removal of oxidized sulfur compounds. Because of the high polarity of the solvent system, the recovery yield for the model oil was excellent, about 97 to 99%, the minor loss in yield might be due to handling during extraction.

## 6. ODS of Commercial Oil Samples Using Fe/ZSM-5

The oxidative desulfurization of commercial oil including untreated naphtha, LGO, HGO and At. Bit. was carried out in the presence of Fe-ZSM-5 catalyst, at 60 °C and 60 min reaction time. The oxidative desulfurization of commercial oil was more complicated because of their complex nature. It was observed that only methanol extraction was inefficient for extraction of oxidized commercial oil; therefore, combined extraction of acetonitrile followed by methanol (aq. 80% solutions) was used, which was shown to be an efficient extraction system for oxidized commercial oil by Sobati et al. [30].

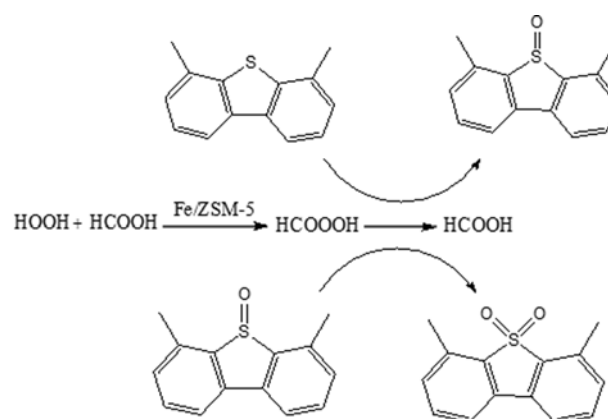
The results indicated that (Table 7) the desulfurization yield of commercial oil samples, i.e., UN, LGO, HGO and At. Bit. oxidized in the absence of catalyst was 62, 63, 45 and 43%, respectively, whereas when oxidized in the presence of Fe-ZSM5 catalyst, the desulfurization yield was 80, 78, 62 and 60%, respectively. The data shows that percent removal of sulfur in the commercial samples was increased up to 20 to 15%, by the catalyst. Thus, as in model

**Table 7. ODS of commercial oil samples with and without Fe/ZSM-5**

Sample	Sulfur content (wt%)		% Desulfurization
	Original	After ODS	
Untreated naphtha	2.30	0.54	79.95
Light gas oil	1.28	0.28	78.28
Heavy gas oil	4.20	1.58	62.32
Athabasca bitumen	4.90	1.94	60.40

oil, the catalyst Fe-ZSM5 also showed its efficiency in case of commercial oil samples, which have hydrocarbons molecules with more complex nature than the model oil. It might be suggested that, due to its high surface area the catalyst disperses evenly in the non-polar medium, and the Fe<sup>+3</sup> cation promotes the formation of peroxy radical, which further carries out the selective oxidation of the sulfur compounds.

It is however depicted from the data that with the increase in the boiling point of the commercial oil samples, the desulfurization yield decreases. This phenomenon may be attributed to the more complex nature of the sulfur compounds occurring in heavier fractions which are difficult to oxidize. As the density of the distillate fractions increases, the structural complexity of the sulfur-bearing molecules also increases, so aromatic thiophenes with multiple alkyl side chains, due to which their oxidation reactivity also decreases. Besides, due to high viscosity and the complex nature of polyaromatic hydrocarbons in the heavy fractions, the phase transfer limitations also retard the oxidation efficiency of the oxidants. During oxidation of heavy fractions, HGO and At. Bit., benzene was also added to reduce viscosity of the oil and facilitate mixing of the reagents, which could be recovered with 95-97% efficiency.

**Reaction Scheme 2. Oxidation of 4,6-DMDBT in the presence of Fe/ZSM-5.**

In literature, very few reports are available on using supported transition metals cations as catalysts for ODS of petroleum fractions. Few researchers describe the ODS of light gas oil, using Zn incorporated on hydroxyapatite as catalysts prepared by ion exchange and impregnation process, in the presence of H<sub>2</sub>O<sub>2</sub> as oxidant [20,26]. Results show that the catalyst prepared by ion exchange process was more efficient than prepared by impregnation method. One study reported the sulfur removal of 68% [1] in case of light gas oil having sulfur content of 1,281 ppm, and in another study the desulfurization of similar feed is shown to be 89%. However, the researchers used oxidation followed by adsorption of oxidized oil on modified bentonite clay, which is a time consuming process. In the current study, sulfur removal of 78% was attained in case of LGO, while using only a two-stage economic extraction process. Additionally, the desulfurization of fractions having high inherent sulfur, UN (2,000 ppm S), HGO (4,000 ppm S) and At. Bit. (5,000 ppm S), was obtained with high efficiency of 80, 62 and

60%, respectively.

## CONCLUSIONS

The efficiency of oxidative desulfurization in case of model oil and different industrial oil fractions using air assisted performic acid oxidation system was sufficiently increased in the presence of Fe-ZSM-5 catalyst. The catalysts enhanced the formation performic acid via Fenton's mechanism. The sulfur content of the model oil was reduced from 1275 to less than 55 ppm in 60 min at 60 °C temperature. Similarly, in case of different industrial oil samples, such as untreated naphtha, light gas oil, coker-derived combined heavy gas oil and Athabasca oil sands derived bitumen, sulfur removal was increased by 20 to 15% in the presence of the Fe-ZSM-5 catalyst.

## ACKNOWLEDGEMENTS

The authors are thankful to Prof. Dr. Arno De Klerk for providing technical support and facilities at the Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Canada. The contribution of Prof. Dr. Muhammad Shakirullah (Late), Institute of Chemical Sciences, University of Peshawar, Pakistan is also acknowledged. The cooperation of HEC for the financial support in the form of IRSIP program is highly acknowledged.

## SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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