

## SELECTIVITY OF METAL, ADSORBENT, OXIDE, HETEROPOLYACID CATALYSTS FOR S-HETEROCYCLES DURING NON- HYDRODESULFURIZATION OF DIESEL FUEL

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### Abstract

An analysis on various catalysts was performed to determine their activities and selectivity for the non-Hydrodesulphurization (Non-HDS) technique using diesel fuel. Catalysts studied included well characterized Silica-Alumina on Al<sub>2</sub>O<sub>3</sub> and Activated Carbon supports, salt-acid supports, Organic Mesoporous Carbon, Woodcoat carbides, Mg/Mo/Zn oxide supported catalysts which were prepared by various reactions. The diesel fuel consists of 2-3.5 wt% of sulfur compounds (thiophene and dibenzothiophene) with approximate amounts of aliphatic, alkylaromatics and N-heterocyclic compounds. With oxygen as the oxidant and some metal oxides and adsorbents type catalyst are used in the oxidation-Adsorption reaction process reveals that the metal induced and adsorbent-oxide induced catalyst shows the best selectivity for oxidizing the S-heterocycles. Except for thiophene, there was only a small dependence of observed rates on catalyst ratio, temperature which suggests the reactions were partially diffusion controlled. The optimal catalyst (MoSiI, Si-Al/Mo/Al<sub>2</sub>O<sub>3</sub>, and CsHPW-SiO<sub>2</sub>) showed high activity for conversion of S-heterocycles. This work includes further investigation of the better catalysts, full characterization of the products by GC-MS, ICP-AES to provide a hydrodynamic environment.

**Keywords:** Oxidation; Adsorbent; Catalyst; S-heterocycles; Selectivity.

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### 1. Introduction

Analysis on achieving higher removal of sulfur from non-HDS techniques are booming at a faster pace which will prove more competitive to existing HDS technique [1]. There are some inherent problems for HDS techniques in converting heterocyclic sulfur containing compounds such as methylated derivatives of DBT, 4-methyldibenzothiophene and 4,6 dimethyldibenzothiophene (4,6-DMDBT) [11]. These compounds are sterically hindered in dehydrogenation and also C-S bond energy is almost equal to C-H bond energy, which makes them hard to desulfurize by HDS techniques [6].

Several new processes as alternatives to HDS have been proposed such as selective sulfur adsorption, Isotherming technology, and biodesulfurization etc [2]. Lot of researches on non-HDS techniques are going on, but oxidation with adsorption is the mostly preferred technique by many researches. The reason to prefer non-HDS techniques are firstly they do not require hydrogen and secondly the process can be carried out at relatively mild conditions from 50°C – 90 °C and at atmospheric pressure [13]. The oxidation of sulfur containing compounds in the fuel leads to the formation of corresponding sulfoxides / sulfones, which are highly polar and separated by extraction with polar solvents (Acetonitrile, Methanol, N, N-dimethylformamide etc.) [13]. Third, the most aromatic sulfur containing molecules such as derivatives of DBT are more easily converted to their sulfones that are thiophenes. Several studies on both oxidants and other type of catalysts has been published and some catalysts show significant activity for the oxidation-adsorption of DBT, benzothiophene (BT), and other sulfur containing organic compounds.

## 2. Material and methods

### 2.1 Batch reactor experiments

The reaction was carried out in 500 mL round bottom flask. The flask was placed on a thermostat with condenser and stirrer fitted to it. A typical catalyst load was 0.2 g. Some catalysts were pretreated in situ under atmospheric pressure before the reaction. After that diesel fuel was added with (75 wt% hexadecane, 12 wt% ethylbenzene, 12 wt% 1-methylnaphtahlene, 0.04wt% carbazole, 0.03 wt% acridine, 0.5 wt% thiophene and 0.65 wt% DBT was added in the reactors. Then the system was flushed with the reaction being started with stirrer speed at 400 rpm. When the final time was reached, the stirrer was stopped and the sample was removed and cooled. (Figure 1)

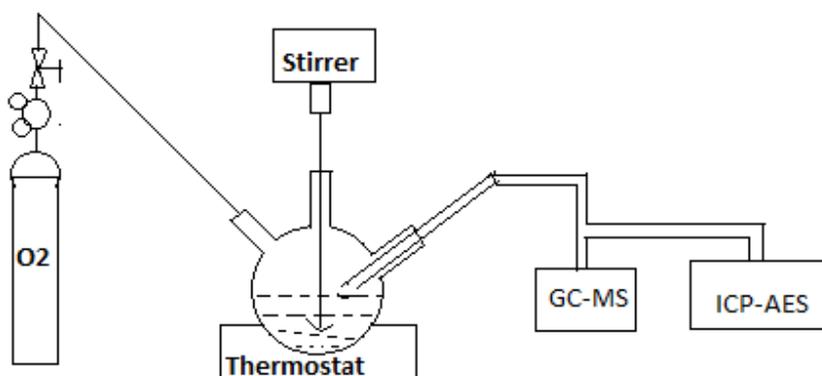


Fig. 1 Schematic representation of batch reactor experiment

### 2.2 Catalyst preparation

Eight supported Si-Al, Mg, C catalysts were synthesized. These were nominal compositions wt %) EFX1 (11.2 % Mg/Mo/ Al<sub>2</sub>O<sub>3</sub>), EFX2 (8.5% MgO/AC), EFX3 (11.1% MgO/AC), EFX4 (6.5% WC/ Al<sub>2</sub>O<sub>3</sub>), EFX5 (3.8% Si-Al/ Al<sub>2</sub>O<sub>3</sub>), EFX6 (5% Si-Al/ Al<sub>2</sub>O<sub>3</sub>), EFX7 (4% Si-Al/ OMC)

EFX1 was prepared according to Mariadassau et.al [12]. Here instead of Pd, Mg/Mo is used. Mg was oxidized at 60°C for 4 hours in 300 mL/min air. The temperature was ramped from room temperature to 90°C at 1°C/ 5 minutes. This is impregnated with aqueous solution drop wise (0.457 mL/g support) then dried at 92 °C overnight in air and oxidized to desired temperature, and the drying temperature was then repeated.

EFX2 was prepared according to Mariadassau et.al [7] and Hercules et.al [14]. The carbon pretreatments for EFX2 and EFX3 were adapted from Rao.et.al [3], Furmanek et.al [8], Rao and Weigert. Activated Carbon was washed with 1-M HNO<sub>3</sub>, overnight with gentle stirring, then with distilled water until the pH of the washings were >4; then the previous two steps were repeated until the pH of the washings was >5. The carbon was dried at 70°C, then calcined at 80°C for 6 hours in the air, then impregnated with aqueous AMH solution (0.300 g/mL) drop wise, while stirring with Teflon rod. The sample was dried in static air at 70°C overnight, and then calcined at 80°C for 4 h.

EFX3 was prepared with reference from EFX2 [7]. Here the drying time takes to 48 hours followed by washing with distilled water until the pH of the washings >5. The carbon was then dried at 50°C and calcined at 70°C for 4 h in static air. It was then impregnated with AMH solution (0.302 g/mL) drop wise while stirring with a Teflon Rod. The sample was then dried, calcined in the same way as EFX2.

EFX4 was synthesized according to the literature [16]. WC was calcined at 60°C for 3h. It was then treated with ammonium metatungstate. The material was stirred and dried at 80 °C for 6 h.

EFX5 was synthesized according to the literature [4]. Alumina was added drop wise with stirring with Teflon rod along with Silica. A separate aqueous hydrazine solution of 0.15mg/L of 81% hydrazine was then added to the impregnated material to reduce and deposit of WC on the support, while evaporating excess water. The sample was then dried at 50°C overnight

and calcined at 90°C in 40mL/min of air for 3 hours, then cooled to 40°C and finally to 35°C in 2h.

EFX6 was prepared according to Rahaman and Vannice [15]. The Al<sub>2</sub>O<sub>3</sub> was dissolved in HCl and evaporated to near dryness twice; adding distilled deionized water to obtain the required volume of solution (6.5%) salt. Si-Al was added and it was stirred with Teflon rod. The sample was then dried at 60 °C and calcined at 50°C for 1 h.

Synthesis of the Organic Mesoporous Carbon (OMC) was adapted from Dai and co-workers [10]. To equal weights of resorcinol was added to 4.09mg/L ethanol and 4.09 kL/g 3.0 HCl. Then 37% aqueous formaldehyde was added in a 1.18 wt ratio with stirring until phase separation (<40 min). After phase separation, the gel was centrifuged, stirred for another 40 min, and then dried at 60 °C for 24 h.

To prepare EFX7 [9-5], Al<sub>2</sub>O<sub>3</sub> was dissolved in 0.1M HCl with gentle heating. After cooling, the appropriate amount of the solution was added to dry OMC carbon to get 5% nominal loading of Si-Al with stirring. Then 0.1M NaOH was added to bring the pH to 12, stirring for 3h. The material was filtered, washed with water several times until the pH of the washings was <9 dried at 58 °C , then finally reduced at 65°C for 3h with a 1°C/10 min.

### 2.3 Analysis of product samples

Two samples were removed for each reactor. One sample was used for quantitative GC analysis to find out how much of the initial compounds has reacted and the other sample was used for GC-MS analysis. These samples were injected into GC fitted with flame ionization detector.

An Alltech compounds was used to separate the compounds. A few samples were analyzed using GC fitted with MS. Based on the molecular fragmentation pattern; we identified principal oxidation products from certain feed compounds. It is clear from the analysis that oxidation and together adsorption reaction takes place in the experiments. There were traces of DBT sulfoxide which was formed either from either acridine or carbazole. There was also evidence of Sulfoxide which can be formed by adsorption of DBT compounds. Typically sulfur concentration is  $6.23 \times 10^{-3}$  mol/L compare to total catalyst adsorption site concentrations of  $7.2 \times 10^{-3}$  mol/g. It is reported that the concentration of acidic adsorption sites on the surface of activated carbon is 0.847 meq/g. Even if all the S-heterocycles in the feed stream has been converted into sulfones ( $6.23 \times 10^{-5}$  mol), and if other sites participated in the adsorption the S/site ratio is smaller for carbons and still <1 for other supports (e.g., 0.71 for a 100m<sup>2</sup>/g support based on S adsorption).

It is also reported that product sulfones and sulfoxide are adsorbed on the surface of catalysts. Of course, more than just sulfones and sulfoxides can be adsorbed on catalyst surfaces. It was reported that the selectivity of adsorption on the activated carbon (Surface area = 1842 m<sup>2</sup>/g and average pore diameter= 2.76 nm for various organics increased in the order: naphthalene( $a_{j,n} = 1.3$  < DBT( $a_{j,n} = 3.0$ ) < 4,6 DMDBT ( $a_{j,n} = 4.5$ ). In one of our experiments with 1% Si/K/Al<sub>2</sub>O<sub>3</sub>, the conversion of ethylbenzene was 9.5% at 65 °C for 3 h.

Although EBHP was not identified by GC-MS in the product sample, it is known to be unstable and typically decomposes to 1-phenylethanol in a heated injection port of GC. Also, it is well known that organic peroxides can oxidize DBT and thiophene to sulfoxides and sulfones even at room temperature with various catalysts. .

### 2.4 Activity and selectivity of the catalyst

With the integration of chromatograms, the ratio of areas between peak i and peak s can be obtained. Thus the conversion of each compound in the sample can be calculated.

$$X_i = [[(C_i^0/C_s^0) - f_1 \cdot (A_i/A_s)] / (C_i^0/C_s^0)]$$

A<sub>i</sub> is the peak area of the compound i, while A<sub>s</sub> is the peak area of interval standard s. C<sub>i</sub><sup>0</sup> is the molar concentration of compound i and C<sub>s</sub><sup>0</sup> is the molar concentration of internal standard s. The f<sub>1</sub> is the calibration factor of compound i. (Table 1 )

Table 1 : Reactant conversion by experiments – analyzed by GC-MS

	Run1 %	Run2 %	Run3 %	Run4 %	Run5 %	Run6 %	Run7 %	Run8 %
Ethylbenzene	3.03	3.64	4.57	5.34	5.01	9.26	5.63	8.84
1-methylnaphthalene	2.78	4.65	6.11	5.54	5.42	9.65	5.59	10.80
Carbazole	12.56	11.92	20.68	14.65	13.60	30.74	15.62	19.45
Acridine	8.54	7.33	11.43	16.54	16.77	14.56	12.00	26.65
Thiophene	9.34	11.18	17.14	13.84	13.43	16.83	15.11	15.96
DBT	7.83	9.00	9.55	13.21	11.23	14.73	10.54	14.65
	Run9 %	Run10 %	Run11 %	Run12 %	Run13 %	Run14 %	Run15 %	Run15 %
Ethylbenzene	2.46	4.15	4.86	4.05	7.01	9.03	4.70	9.43
1-methylnaphthalene	1.76	2.66	3.98	6.24	4.52	10.50	5.87	10.43
Carbazole	6.18	8.76	11.72	11.75	14.65	30.65	14.76	16.34
Acridine	3.40	3.55	7.34	13.65	16.54	10.54	12.94	26.86
Thiophene	14.74	14.65	13.65	11.87	26.74	21.87	17.34	15.74
DBT	5.31	5.76	6.75	9.51	10.24	12.64	10.83	17.43
	Run16 %	Run17 %	Run18 %	Run19 %	Run20 %	Run21 %	Run22 %	Run23 %
Ethylbenzene	5.13	10.67	0.22	1.98	9.68	8.20	8.33	8.43
1-methylnaphthalene	5.93	10.29	0.65	3.43	9.85	4.95	6.76	5.43
Carbazole	22.54	27.87	6.45	16.53	17.15	8.22	12.54	6.50
Acridine	27.53	11.45	0.75	25.34	21.01	12.61	21.84	9.40
Thiophene	13.67	22.95	4.63	22.94	13.40	23.65	23.1	21,80
DBT	16.78	12.54	3.15	34.76	15.65	7.72	8.96	12.22

Elemental analysis was performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). A known amount of catalyst was dissolved in nitric / sulphuric acid under reflux for three times and then diluted with distilled water. (Table 2)

Table 2 Elemental Analysis by ICP, ICP-AES

## ICP CALIBRATION

Sample Name	Expected Concentration	Si-Al (0.5wt %)	Si-Al (1 wt %)	MgO	ZnO	WC
		ppm				
Std 1	0	0.1	0.054	0.043	0.02	0.084
Std 2	1	0.954	0.931	0.923	0.912	0.954
Std 3	5	4.232	4.195	4.175	4.056	4.017
Std 4	30	30.65	30.45	30.34	30.13	30.02

## CATALYST LOADINGS BY ICP-AES

Sample Name	ICP Measurement (ppm)	Catalyst (g)	Catalyst loading wt%
EFX7 – ICP1	410.23	1.0345	4.65
EFX7 – ICP2	256.23	0.5874	4.56
EFX7 – ICP3	312.55	1.0343	4.35
EFX7 – ICP4	117.93	0.9843	1.64

### 3. Results

#### 3.1 Base metal catalysts

The base metal catalysts used in the experiments were MgSil (11.2% Mg / SiO<sub>2</sub>), MoSil(10.8% Mo/ SiO<sub>2</sub>) , (5.4% CaO/ SiO<sub>2</sub>) and ZnO exchanged with Cu<sup>2+</sup>. These are all catalysts for hydrocarbon oxidation. We can conclude that (5.4% CaO/ SiO<sub>2</sub>) and ZnO exchanged with Cu<sup>2+</sup> are almost inactive for oxidation of S-heterocycles and alkylaromatics. It is concluded that MgSil and MoSil behaved similarly in the oxidation of S-heterocycles. The point at the far right was taken at much higher wt% than normal for these runs. The same trend is followed for all experiments. The curve for MgSil is slightly above MoSil and below that of MoSil. Therefore MoSil is slightly more selective for the oxidation of S-heterocycles, while for both catalysts the oxidation of the alkylaromatics inhibits the oxidation of S-heterocycles. (Fig. 2)

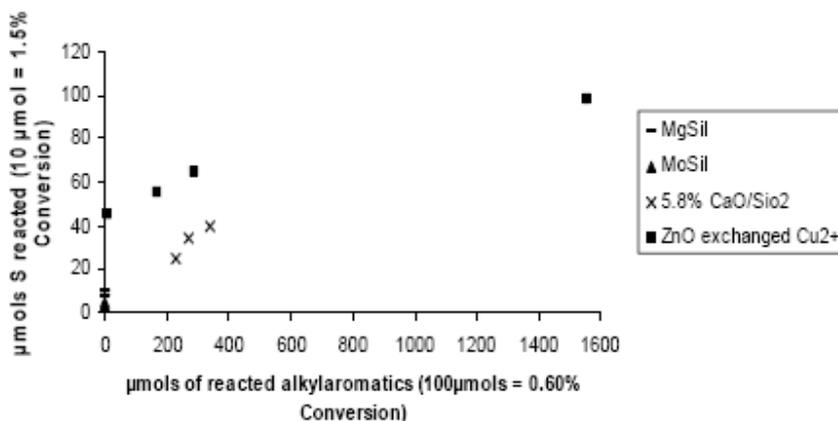


Fig. 2 Selectivity for base metal catalysts for S-heterocycles

#### 3.2 Heteropolyacid catalyst

The heteropolyacid catalysts tested included 0.01g per mL feed of C<sub>5</sub>HPW-SiO<sub>2</sub> (C<sub>S2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O (40 wt%) / SiO<sub>2</sub>), 0.03 g per mL feed of C<sub>S2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub>, 0.03 g per mL feed of (NH<sub>4</sub>)<sub>3</sub>H<sub>2</sub>PMo<sub>12</sub>O<sub>40</sub>, 0.03 g per mL feed of (NH<sub>4</sub>)<sub>3</sub>H<sub>4</sub>PV<sub>6</sub>Mo<sub>12</sub>O<sub>40</sub>. and 0.03 g per mL feed of C<sub>S2.5</sub>Ni<sub>0.08</sub>H<sub>0.34</sub>PMo<sub>12</sub>O<sub>40</sub>. The different weights were used to adjust the catalyst surface areas to more similar amounts. Almost all these experiments were at the same reaction conditions, 70°C for 2h. Two experiments using C<sub>5</sub>HPW-SiO<sub>2</sub> were at 56 °C. The amount of reacted S-heterocycles again increased with the amount of reacted alkylaromatics for the heteropolyacid catalyst, same as for the base metal catalysts. It can be concluded that there are two different types of active sites for the heteropolyacid and supported base metal catalysts. While in general the heteropolyacids are less selective for S-heterocycles oxidation than MgSil and MoSil, the supported C<sub>5</sub>HPW-SiO<sub>2</sub> may be more active for oxidation of S-heterocycles than either the unsupported heteropolyacids or the base catalysts, although evidence is limited. (Fig. 3)

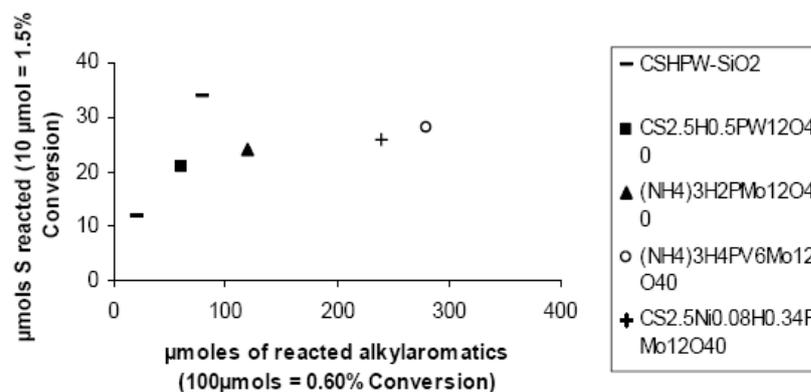


Fig. 3 Selectivity of heteropolyacid group catalyst for S-heterocycles

### 3.3 Si-Al Catalyst

For the Si-Al based catalysts, one experiment each with Zn and 1% Si-Al/Al<sub>2</sub>O<sub>3</sub> are carried at 60°C for 3 h and one experiment with 0.5% Si-Al/Al<sub>2</sub>O<sub>3</sub> was carried out at 70°C for 2h. The Si-Al group behaves similar to base metals in the oxidation of S-heterocycles. In particular there is no apparent inhibition by the alkylaromatic oxidation products. Zn performed slightly better than other two Pt catalyst, probably due to its higher Si-Al loading. (Fig. 4)

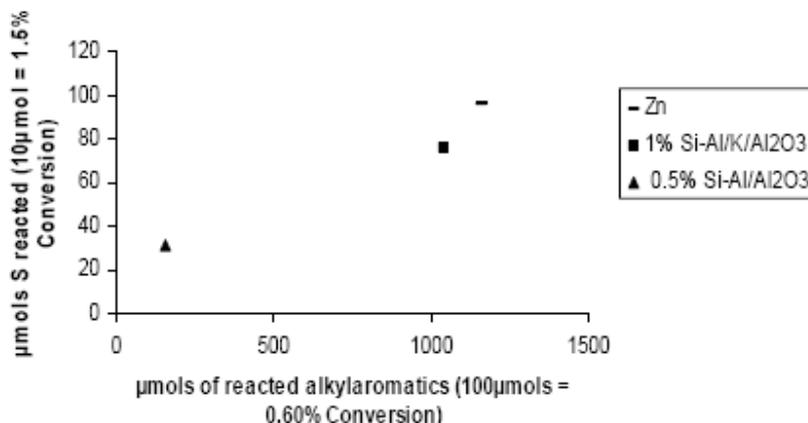


Fig. 4 Selectivity of Si-Al group of catalyst for S-heterocycles

### 3.4 Carbide catalyst

The experiments for carbide catalysts were at 60°C. It is seen that the carbide catalysts behave in a similar manner toward S-heterocycles, and that they are more selective than the base metal catalysts. The HNO<sub>3</sub> pretreated carbon was more active for S-heterocycles oxidation, although they are poorly selective for the latter. A higher reaction temperature led to a decrease in the amount of reacted alkylaromatics, S-heterocycles, but this is based on very limited data. There was a general increase in the oxidation of S-heterocycles vs alkylaromatics. (Fig. 5)

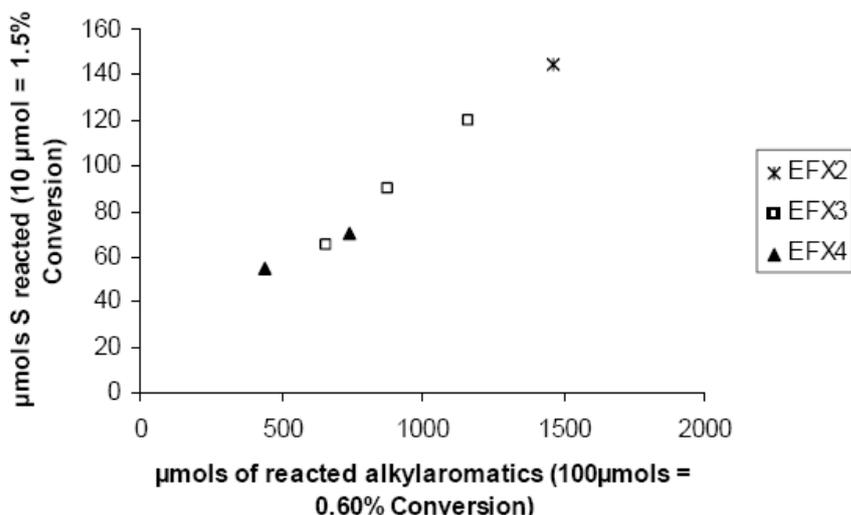


Fig. 5 Selectivity of Carbide group Catalyst for S-heterocycles

### 3.5 OMC catalyst

One run result was discarded because it showed high conversions of ethylbenzene and thiophenes were not repeated using either EFX7 or any other catalyst. As expected, the higher loading catalysts EFX5 and EFX6 are more active. These catalysts are similar in S-heterocycle selectivity to the base metal catalysts but less selective than the carbides. They are similar to the base metals in terms of activity for S-heterocycle oxidation. The difference

in the catalyst dispersion probably led to their different activities for S-heterocycle oxidation. (Figs. 6,7)

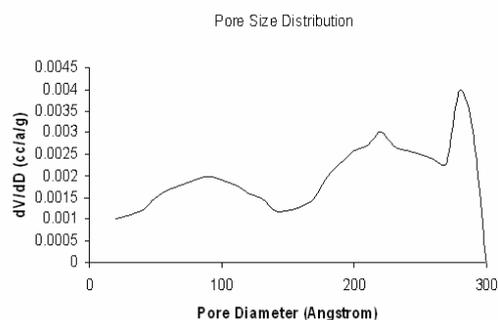
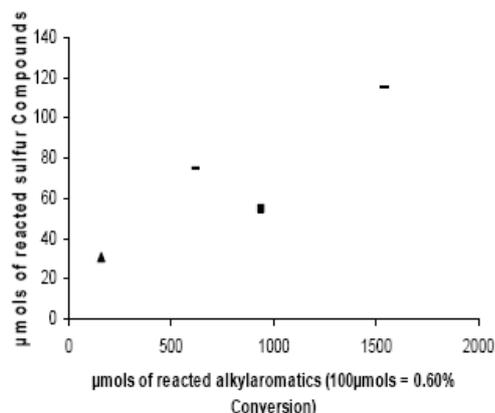


Fig. 6 Selectivity of OMC group catalyst for S- heterocycles Fig. 7 Pore Size Distribution for OMC

#### 4. Discussion

Non-HDS using oxidation and adsorption with several group of catalysts (base metal, heteropolyacid, carbide, supported Si-Al,  $\text{Al}_2\text{O}_3$  catalysts) was studied in this research project. The reaction conditions  $50^\circ\text{C}$ - $90^\circ\text{C}$  under atmospheric pressure are milder than in the Non-HDS process. In addition to advantages of low costs associated with mild reaction conditions, this process avoids danger in handling peroxides or hydrogen peroxide. The parallel oxidation and adsorption of alkylaromatics and S-heterocycles were also investigated, in contrast to most other research in Desulfurization.

Although some researchers have reported higher reaction rate but usage of adsorbents based catalysts reduces reaction rate and reaction temperature. The higher reaction temperatures are undesirable if the selectivity of S-hetero-cyclic oxidation over alkylaromatics oxidation is considered. An optimal catalyst for this process reaction requires not only activity but also selectivity for the oxidation-adsorption of S-hetero-cycles.

The optimal oxidation and adsorption catalysts also showed high activity. This characteristic is very different from the commercial HDS catalysts. The activity of non-HDS catalysts is also decreased by organic heterocompounds and polyaromatic hydrocarbons, for which the order of inhibition has been reported: saturated and monoaromatic hydrocarbons < condensed aromatics  $\approx$  oxygen compounds  $\approx$  hydrogen sulfide < organic sulfur compounds < basic nitrogen compounds. There are at least two reports emphasizing on oxidation of sulfur compounds [1, 17]

#### 5. Conclusion

Compared to other work this work show that ( $\text{MoSi}$ , 1 % $\text{Si-Al/Al}_2\text{O}_3$ ,  $\text{CsHPW-SiO}_2$ ) catalysts type can oxidize S-heterocycles at milder conditions where alkylaromatics oxidation is less of a problem and with reasonable activity for converting S-heterocycles. During the process, some compounds show the reactivity or tendency to form a polymer. NMR studies can provide a better result on polymerization reaction for the above process.

#### ABBREVIATIONS

HDS – Hydrodesulphurization  
 DBT- Dibenzothiophene  
 GC- Gas Chromatography  
 MS - Mass Spectrometry  
 ICP- Inductive Coupled Plasma  
 AES - Atomic Emission Spectroscopy  
 OMC- Organic Mesoporous Carbon  
 AC- Activated Carbon  
 WC- Woodcoat Carbides

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