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# Oxidative Desulfurization of Hydrotreated Gas Oil using $Fe_2O_3$ and Palladium Loaded over Activated Carbon as catalyst

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## ABSTRACT

This paper describe preparation of catalysts $Fe_2O_3$/ Ac and Pd/ Ac by precipitation method according to the ratio cat : Ac (20:80) and evaluates their catalytic activity to remove sulfur compounds from hydrotreated gas oil. The chemical structure of the prepared catalysts were examined by X- ray diffraction (XRD) analysis, atomic absorption spectroscopy (AAS), surface area and pore volume, and thermal gravimetric analysis (TGA). X-ray fluorescence spectrometer used to determine the content of sulfur in gas oil before and after the treatment. The catalysts in this study showed an efficient removal of sulfur compounds from light gas oil reaches to more than 60%

**Keywords:** Oxidative desulfurization, Hydrotreated gas oil, Ferric oxide over active carbon catalyst, Palladium over active carbon catalyst.

## INTRODUCTION

Refining factories play an important rule to transfer coat oil to more valuable products such as liquid petroleum gas, jet fuel, gasoline, and diesel by using various techniques like distillation, extraction, reforming, hydrogenation, and cracking[1].

Millions of barrels of fuels are consumed daily in the worldwide road transportation therefore; increasing attention is being focus to the composition of fuel processing. The big challenge that faces the refineries is the harmful sulfur oxides which liberate to the environment from the combustion of petroleum fuel that contained high sulfur[2,3]. Sulfur exists in hydrotreated petroleum as hydrogen sulfide, disulfides, organic sulfides, benzothiophene, dibenzothiophene, and their alkylated derivatives[4,5]. These compounds are unwanted and detrimental pollutants that converted to gaseous sulfur oxides ($SO_X$) upon fuel combustion which causes an acidic rain and the contamination of the atmosphere [6].

Oxidative desulfurization (ODS) is a very effective and considers a promising method for removing the dibenzothiophene derivatives from liquid fuel under moderate conditions, as low temperature, pressure and the cost of operation is less compared to HDS[7,10]. The OSD method is a kind of technology using oxidants to oxidize organic sulfur in two steps: the first step; oxidation of the sulfur atoms to strong polarity species and these polar products can be effectively separated by liquid extraction in the final step. In OSD the sulfur containing compounds in fuels are oxidized using different oxidizing agents such as nitric acid, nitrogen dioxide, organic hydro peroxides, hydrogen peroxide, peroxy acids, and ozone in the presence of a catalyst to produce sulfoxides and sulfones compounds respectively[9,14]. By that means, the oxidation of sulfides to sulfoxides and sulfones is generally accomplished by reaction with peroxy acid which generated by the reaction between peroxide and appropriate carboxylic acid. These oxidized molecules due to the strong polarity of them compared to the respective sulfides and the liquid extraction can be more efficient way to remove selectively the oxidized sulfur compounds from oil layer[15,16].This work contributes to a growing interest to produce low or no sulfur containing compounds in gas oil. The oxidation of gas oil by hydrogen peroxide using the catalysts ferric oxide $Fe_2O_3$/ Ac, palladium Pd/ Ac prepared in this work.

## EXPERIMENTAL

### Chemicals and reagents

The analytical grade chemicals and reagents used in this study are ferric nitrate $Fe(NO_3)_3.9H_2O$, sodium hydroxide, and hydrochloric acid purchased from Fluka, palladium chloride $PdCl_2$ and charcoal from Sigma company. Also, barium chloride $BaCl_2$, sodium bicarbonate $NaHCO_3$, sodium carbonate $Na_2CO_3$, and acetonitrile $CH_3CN$ were supplied from BDH. In addition, the oxidizing agent for ODS procedure is hydrogen peroxide $H_2O_2$ (30%w/w) and glacial acetic acid $C_2H_4O_2$ 16N, nitric acid $HNO_3$, 12N, were equipped from Scharlau. While, the hydrotreated gas oil used in this study provided from Midland Refineries Company in Iraq which analyzed using X-ray fluorescence to determine total sulfur content (wt (%)) equal to 1.477 (1477 ppm), API-Gravity= 31.9, and specific gravity= 0.85, distilled water used prior the experiments.

### Preparation of palladium, and ferric oxide loaded over activated carbon

The catalysts in this study were prepared according to the ratio cat : Ac (20:80). $Fe_2O_3$/ Ac catalyst was prepared as reported by Hussein H. A.[17] as follow: a calculated weight of $Fe(NO_3)_3.6H_2O$ was dissolved individually in 40 ml distilled water. The precipitation of metal achieved by adding 1.0M $NaHCO_3$ to the solution gradually until pH of the solution reached to 8-9 and the content was continuously stirred at 60 °C for 3 hours. After that, the mixture was filtered through a Buchner funnel in vacuum and washed using distilled water to get rid of sodium ions. To make sure that the precipitate was free of sodium ions few drops of 0.1M $BaCl_2$ was added to the filtrate as filtrate turbidity means the presence of sodium ions so continued in the washing with water until it is free from sodium ions. The precipitate cake was dried in an oven at 120 °C for 24 h to remove water.

The required weight of active carbon to achieve the ratio of cat : Ac (20:80) dried at 120 °C for 24 h and then wetted with 10 ml of distilled water. The calculated weight of the catalyst prepared earlier dissolved individually in (5 ml concentrated HCl: 40 ml distilled water) and mixed with continuous stirring with the calculated weight of active carbon and the mixture left for 24 h at room temperature to allow the most of metal solution to be loaded on the activated carbon. The dried catalyst is calcinated for 2 h at 400 °C in muffle furnace and the purpose of this step is to load the metal salts on the active carbon and converted them to their corresponding metal oxides leading to deposit of active metal oxide over the support. Also, in the calcination step generate strong interaction between metal oxide and the support (Activated carbon). While, the preparation of Pd/C include dissolving of a calculated amount of $PdCl_2$ in hydrochloric acid ($PdCl_2$ doesn't dissolve in water).

The impregnation step of Pd on carbon has been done by adding (10 ml) of formaldehyde $CH_2O$ to $PdCl_2$ solution to reduce palladium ions $Pd^{+2}$ to Pd as metal precipitated on active carbon. After that, neutralization the solution by adding sodium hydroxide with continuous stirring and remove chlorides ions by washing the precipitate with distilled water. The drying step was important to get rid of water and moisture at 120 °C. Before the impregnation of $Fe_2O_3$ and Pd on activated carbon, charcoal was mixed with nitric acid $HNO_3$ at room temperature for 24 h to increase reactivity and porosity of carbon. After 24 h the resultant active carbon filtered, washed many times with distilled water to remove the residual of acid in its pores and then dried at 120 °C for 2 hours.

### Procedure of oxidative desulfurization experiments

The ODS experiments were performed in a water bath at 40 °C with 5 ml of glacial acetic acid, 10 ml of $H_2O_2$ mixed with 100 ml of gas oil and 3 g of the catalyst in a three necks round bottom flask with. The mixture was stirred for 3 h using a mechanical stirrer at 1000 rpm, during the stirring process a solution of 2 g $Na_2CO_3$ dissolved in 20 ml of distilled water was added drop by drop to the mixture. After the oxidation was finished the mixture attained phase separation, the oxidized sulfur was extracted with acetonitrile at room temperature. The acetonitrile and gas oil ratio was 1:1 by volume then the gas oil phase was separated and analyzed using X-ray fluorescence spectrometer ARL 8410 (ASTM D4294 method). The removal efficiency of sulfur compounds is calculated using the following equation.

Efficiency of desulfurization= $(s_{\circ} - s_1/ s_{\circ})*100$

Where $S_0$ is the initial S-content and $S_1$ is the final S-content after (ODS). The results indicate that the catalyst is efficient to remove sulfur from gas oil with the catalyst

### Instruments used in the Structural Characterization

Crystalline structure of the catalysts was examined by X-ray diffraction (Shimadzua-XRD-6000, Japan) equipped with Cu Ka radiation ($\lambda$=1.5406A°) with a scanning speed 8° per min. 40Kv and 30mA, $2\theta$ from 10° to 80°. Atomic absorption spectroscopy type (Shimadzu Europe AA-6300) used to determine the percentage of elements Pd and Fe in the prepared catalysts Pd/Ac and $Fe_2O_3$/Ac respectively. HORIBA/SA9600 series was used to measure the surface area and pore volume.

Also, thermal gravimetric analysis was performed to determine the thermal stability of oxide was performed by TGA-4000 instrument from Perkin-Elmer/Holland.

X-ray fluorescence analyzer (Lab X-300) used to calculate the content of sulfur in gas oil before and after treatment.

## RESULTS AND DISCUSSION

### X-ray Diffraction

X-ray diffraction (XRD) gives crystallographic and amorphous information of the prepared catalysts loaded over an active carbon. Fig. 1 and 2 show the XRD patterns for the supported catalysts prepared in this work. The diffractogram of the calcined $Fe_2O_3$/ C at 400 °C shows the main diffraction peaks at 33.34°, 35.68°, 49.44°, 54.12°, and 62.54° which are related to Iron oxide in the form of hematite $Fe_2O_3$ and magnetite $Fe_3O_4$. It is assumed that the Iron oxide in the form of magnetite particles are formed mainly inside the support pores in the calcination step after the impregnation of ferric nitrate over the support. The formation of magnetite is attributed to the reduction some of $Fe^{+3}$ to $Fe^{+2}$ by carbon particles in the presence of high temperature (calcination step). Reduction agent in the carbon is the carbon monoxide CO resulting from burning of the activated carbon, carbon monoxide dose not has the ability to access to inside of the catalyst so, magnetite is formed on the surface. Therefore, the final result particles formed are hematite the central part surrounded by magnetite[18].

The XRD investigation for Pd/ C reveals three diffraction peaks at 40.32°, 46.6° and 68.3° related to the Pd face-centered cubic crystal structure as in Fig. 2. Also, there is a characteristic values for $2\theta$ at 24.25° and 25.13° attributed to carbon particles which supported $Fe_2O_3$ and Pd respectively. These results match with the earlier studies with simple variation due to the difference in the calcination temperature[19,21].

The peaks of the patterns of $Fe_2O_3$/C and Pd/C catalysts are in good agreement with those of the standard XRD JCPDS data: PDF number 39-1346 and PDF-number 046-1043 respectively.

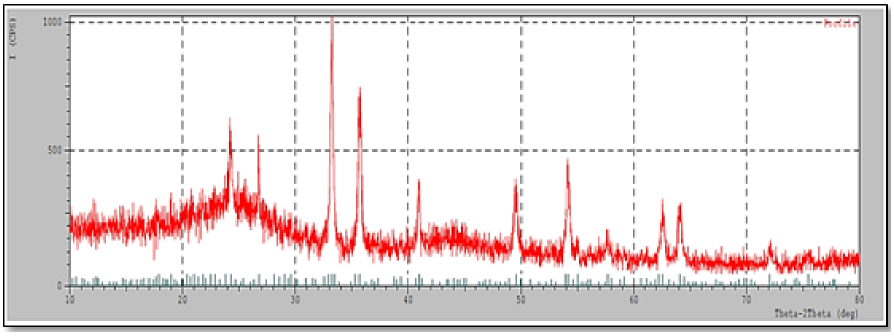

**Fig. 1. XRD of $Fe_2O_3$/ Ac**

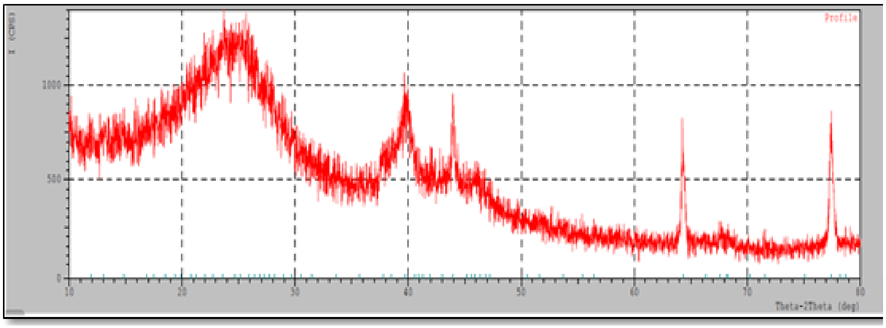

**Fig. 2. XRD of Pd/C**

### Atomic Absorption Spectroscopy

Atomic absorption spectroscopy technique utilizes to determine the percentage of metal ions presented in the catalysts. Table (1) reveals that the prepared catalysts containing on 1.1149% and 5.8708% of Pd and Fe in their composition respectively.

**Table 1: Percent of metal and metal oxide in the prepared catalyst**

| Catalyst | Metal (%) | Metal oxide (%) | Weight of carbon (gm) |
|---|---|---|---|
| $Fe_2O_3$/ Ac | 5.8708 | 16.79 | 16 |
| Pd/ Ac | 1.1149 | - | 16 |

### Determination of surface area and pore volume

Also, determination of the surface area and pore volume of the catalysts are fundamental aspect, since such properties can influence the catalytic activity and mass transport of reactants and products[22]. The data in Table (2) exhibit surface area and pore volume of $Fe_2O_3$/C and Pd/C.

**Table 2: Surface area and pore volume of $Fe_2O_3$ and Pd loaded over carbon**

| Catalyst | Surface Area m²/gm | Pore Volume cm³/gm |
|---|---|---|
| $Fe_2O_3$/ Ac | 44.260 | 0.233 |
| Pd/ Ac | 70.179 | 0.200 |

### Thermal Analysis

Thermal gravimetric analysis studied for $Fe_2O_3$/C as in Fig. 3. The TGA curve showed, there was losing of weight at two points; first one at 271 °C which was around 8.197%. After TGA calculation, the compound suffered losing in weight around 13.4 which could be equivalent to the notional value. The second point occurred at 595.5 and has the percent 13.351% and practical value was 2.57

which is parallel with the theoretical value. The weight losing of ferric oxide at the two points have small value. This can be attributed to loss of water molecules that oxide absorbed it from the surrounding[25]. The second prospect for losing in weight can be represented to transform the oxide from α formula to the more stable formula (α) especially that α formula of ferric oxide is prepared at 700 R C and while in this work (α) formula was prepared at 400C°[11].

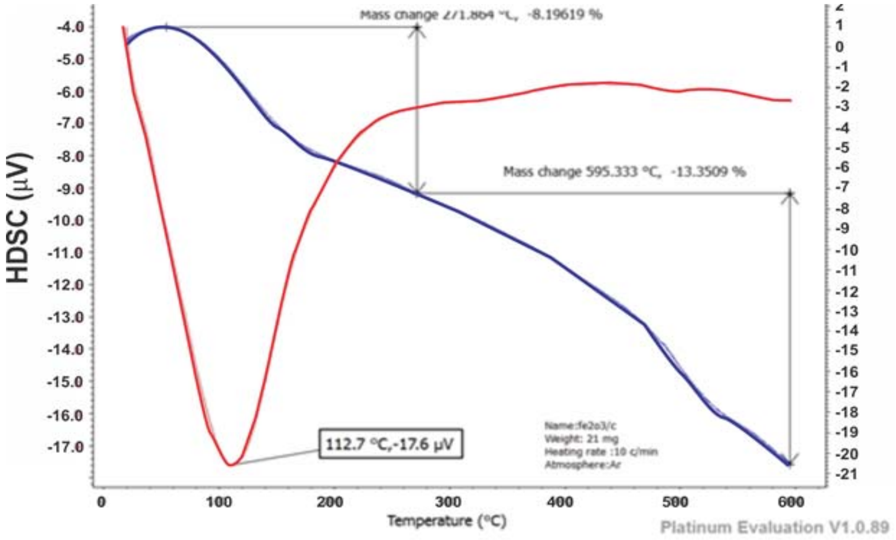

**Fig. 3. TGA curve of $Fe_2O_3$/C**

### Oxidative desulfurization of gas oil using Pd/ C & $Fe_2O_3$/ C

Oxidative desulfurization based on the use of gas oil was conducted as mentioned in literature[20] using hydrotreated gas oil (sulfur content 1477 ppm, 100 ml) with 3 g of the prepared catalyst mixed with 30% $H_2O_2$ as an oxidizing agent followed by adding 5 ml of $CH_3COOH$ as a co-catalyst. The mixture refluxed for 3 h at 40 °C using a mechanical stirrer at 1000 rpm and while stirring 2 g of $Na_2CO_3$ dissolved in 20 ml of DW added to the mixture. At the end of reaction, the mixture left to settle for 30 min. to attain phase separation. The biphasic mixture was separated by extraction with acetonitrile and 2% barium chloride. Clearly a white precipitate of barium sulfate $BaSO_4$ was formed in the aqueous layer.

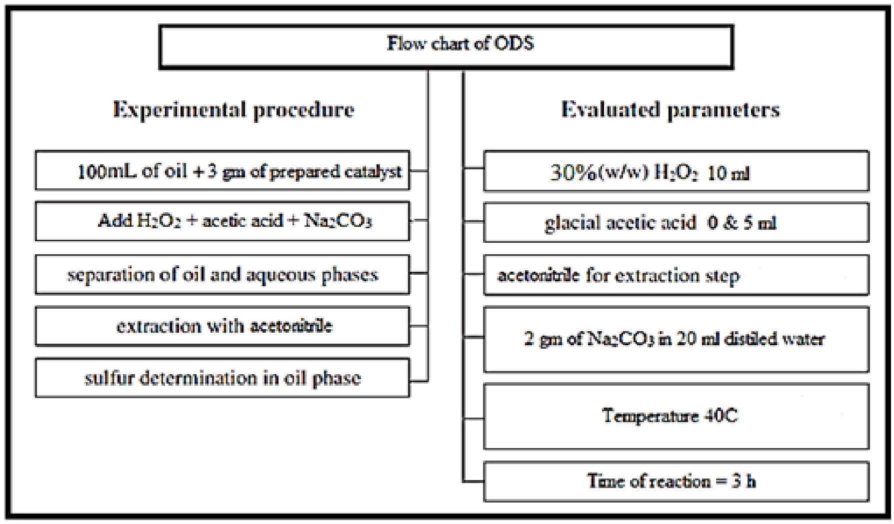

**Fig. 4. Experimental flow chart for desulfurization procedure**

Results of the oxidation of gas oil containing on sulfur compounds in the presence and absence of acetic acid as a co-catalyst are shown in Table (3). It can be seen that the OXD process is more effective in the presence of the acetic acid than without it. In the same table the effect of hydrogen peroxide and $Na_2CO_3$ on the OXD process also studied. The removal of sulfur was 71.20% and 66.0% for $Fe_2O_3$/Ac and Pd/Ac respectively. $H_2O_2$ is considered as a green reagent which is oxidizing organic sulfur compounds to the corresponding sulfones at ambient temperature.

**Table 3: Efficiency removal of sulfur compounds in the presence and absence of $CH_3COOH$ and different amount of $H_2O_2$ and $Na_2CO_3$ at 40C° and 3h the time of reaction**

| No. Exp. | Catalyst | Vol. of $CH_3COOH$ (ml) | Vol. of $H_2O_2$ (ml) | Amounts of $Na_2CO_3$(gm) | Removal Efficiency (%) |
|---|---|---|---|---|---|
| 1 | $Fe_2O_3$/ Ac | 0.0 | 10 | 0.0 | 12.10 |
| 2 | Pd/ Ac | 0.0 | 10 | 0.0 | 10.40 |
| 3 | $Fe_2O_3$/ Ac | 5.0 | 10 | 2 | 71.2 |
| 4 | Pd/ Ac | 5.0 | 10 | 2 | 66.0 |
| 5 | $Fe_2O_3$/ Ac | 5.0 | 15 | 2 | 17.03 |
| 6 | Pd/ Ac | 5.0 | 15 | 2 | 13.24 |
| 7 | $Fe_2O_3$/ Ac | 0.0 | 10 | 0.0 | 16.10 |
| 8 | Pd/ Ac | 0.0 | 10 | 0.0 | 18.24 |

The results in Table (3) indicates that the higher removal efficiency of sulfur from hydrotreated gas oil was achieved when using 10 ml of $H_2O_2$ as oxidizing agent, 5 ml of $CH_3COOH$ as co-catalyst, and 2 g of $Na_2CO_3$.

### Mechanism of the oxidation reaction

A reasonable mechanism of oxidative desulfurization process can be suggested as an active catalyst species can be formed by the nucleophilic attack of hydrogen peroxide on metal atoms of the catalyst. Electrons are evacuated from the peroxyl ions, because of that increasing the electrophilic character of the peroxidic oxygen. The ODS moves by nucleophilic attack of an active catalyst (oxidants) and convert sulfur containing compounds in fuels to form sulfones which are much more polar species. Fig. 5 represents the mechanism of ODS in liquid phase[20,25].

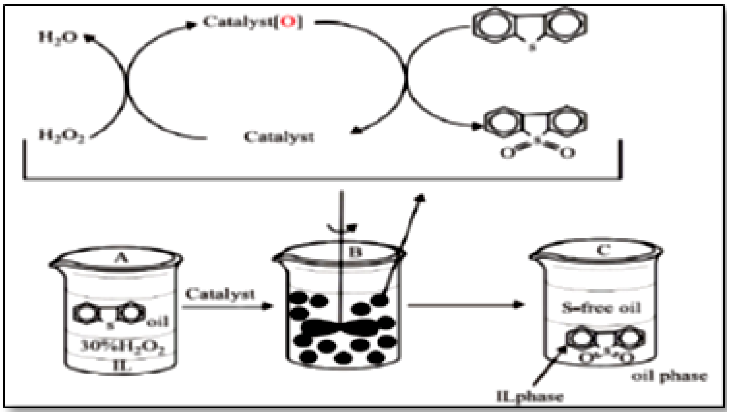

Fig. 5. Mechanism of ODS in liquid phase

## CONCLUSION

In this study, $Fe_2O_3$/ Ac and Pd/ Ac were prepared by precipitation method in ratio Cat : Ac equal to 20:80 and used as catalysts for the oxidation of sulfur compounds in gas oil. It was found that the catalytic activity at selected parameters: 100 ml of gas oil mixed with 3 g of the catalyst in the presence of $H_2O_2$ as oxidizing agent and $CH_3COOH$ and $Na_2CO_3$ as a co-catalyst. Results obtained in this study for gas oil samples showed that the use of the prepared catalysts achieved an efficiently removal of sulfur in gas oil using eco friendly reagents reached to 71.20% and 66.0% for $Fe_2O_3$/ Ac and Pd/Ac respectively.

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