Inhibitory Study for Joint Reactions of Hydrodesulfurization and Hydrodenitrogenation during Hydrotreating of Vacuum Gas Oil

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Abstract— A set of hydrodesulfurization experiments are carried out on vacuum gas oil in a trickle bed reactor to model the effect of inhibition on the joint reactions of hydrodesulfurization, and hydrodenitrogenation. Dibenzothiophene (DBT) is used as a model compound in vacuum gas oil. In absence of nitrogen compounds over the tested catalysts in a trickle bed reactor at (523 to 573 K), 1 to 3 hr⁻¹, and a pressure range of 16 to 20 bar the results show an increase in conversion when temperature increases, a little positive effect on conversions when pressure increases, and a decrease in conversion when LHSV increases. The inhibition model for nitrogen compound is nonlinear and fitted exponent was 0.5 for basic and nonbasic over Platinum catalyst:

Index Terms—Hydrodesulfurization, Joint reactions, Inhibition, Trickle bed reactor

I. INTRODUCTION

HYDRODESULFURIZATION (HDS) of petroleum fractions is one of the most important processes in the petroleum industry to produce clean fuels. In particular, sulfur removal in diesel fuels is now strongly desirable for environmental and technical reasons. For instance, HDS is used to prevent atmospheric pollution by sulfur oxides produced during the combustion of petroleum-based fuels, to prevent poisoning of sulfur-sensitive metal catalysts used in subsequent reforming reactions and in the catalytic converter for exhaust emission treatment, finally, to avoid corrosion problems in engines[1]. The basic nature of these compounds causes them to adsorb onto Lewis acid sites on the catalyst surface, inhibiting the availability of the sites. This poisoning may be reversible or irreversible, depending on the HDS conditions[2]. High concentrations of organic nitrogen compounds can cause significant deactivation for reforming, cracking, hydrotreating, or any other type of hydroprocessing catalysts[3]. The present work aims to study the inhibition effect of nitrogen compounds for HDS of Dibenzothiophene (DBT) in vacuum gas oil (VGO) over a (PtMo/Al₂O₃) prepared catalyst using carbazole and acridine as nonbasic and basic catalysts respectively, this goal was achieved by catalytic converter using carbazole and acridine as nonbasic and basic catalysts.

A. Materials and Chemicals

The feedstock used in this study is non-hydrotreated VGO supplied from North Refineries Company. DBT (99% purity, Sigma) is used as model sulfur compound while acridine (99%, Sigma) and carbazole (99%, Sigma) are used as model nitrogen compounds (basic and nonbasic). Hydrogen gas (99.999%, Al Mansour Gases) is used for HDS of DBT while nitrogen (99.999%, Al Mansour Gases) is used for purging oxygen from the system before each run. The catalyst ((0.5%) PtMo/Al₂O₃) is prepared in this work using incipient wetness impregnation method.

B. Catalyst Preparation

Alumina is dried in a furnace at 393 K for 4 hours, this step is necessary to minimize moisture content in the support before impregnation, the active material (hexachloroplatinic acid, Sigma 8 wt.%) is added to deionized water, pore volume of Mo/Al₂O₃ is equivalent to the volume of deionized water used. The solution is stirred for one hour at room temperature, then it is filtered using a filter paper to get a rid of precipitates, then the solution of active phase is added to Mo/Al₂O₃ particles at a rate of 15-20 drop per minute with continuous stirring till achieving full impregnation. The temperature is kept constant at 373 K through the impregnation by using a water path. Then the particles are washed, dried and calcined for 4 hours in the furnace at 823 K.

C. Catalyst Evaluation

The experiments are carried out in a downward trickle bed reactor consists of a 316 stainless steel tubular reactor, 77cm long, and internal diameter of 1.6 cm. The bed are divided into three main parts; two parts are filled with glass beads and a third part is in the middle loaded with catalyst to provide plug flow conditions for isothermal reactions[4].

Fig. (1) shows the trickle bed reactor rig.

D. Catalyst Characterizations

A D8 advanced X-Ray Diffractometer manufactured by Bruker AXS (Germany) is used to analyze crystallographic conditions of the bulk phase of catalyst samples. Data collection and manipulation is under automatically control of EVA software, which contains database of the JCPDS powder diffraction files. operated under 40 kV and 40 mA and the scan was from 10° to 80° in a 20-angle with a scan speed of 0.04° per second. Scanning
Electron Microscopy images of the catalyst surface are obtained using an high resolution FEI Quanta 200F Field Emission Scanning Electron Microscope (FESEM) manufactured by with EDX system (INCA Energy 400,US) manufactured by OXFORD. To characterize the basic properties of catalytic samples, temperature programmed desorption (TPD) is used with carbon dioxide as the absorbate molecule, CO2. Temperature programmed desorption (TPD) experiments are carried out in a system supplied by Ohkura Riken Co. Ltd., (model TP-200). The equipment is developed to enable user to obtain data related to desorption characteristics of basic site present on catalyst. The Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size measurements of catalysts are determined using Quanta Chrome Autosorb 6B system supplied by Quanta chrome Corporation (USA). The adsorption and desorption isotherms used in the evaluation of BET surface area were obtained at the boiling temperature of liquid nitrogen (78 °K) and the results are shown in Table (1).

### TABLE I

| Property             | Method | Mo | PtMo |
|----------------------|--------|----|------|
| Total surface area, m²/gm | BET    | 265.7 | 224.3 |
| Pore volume , cm³/gm | BET    | 0.73 | 0.64 |
| Average pore diameter , Å | BJH    | 56.72 | 67.24 |

E. High Performance Liquid Chromatography (HPLC)

DBT content in feedstock and product were determined using a computerize HPLC DIONEX (UV (JYNKOTYK)/VIS160S) .A C18 reverse phase column (Philips, 5 µm x 0.4 cm) was used as a chromatography column. The mobile phase was high purity normal hexane flows at 1 ml / min. DBT concentration can be calculated by comparing the HPLC recorded area with the calibration curves of DBT.

### III. MATHEMATICAL MODELING

#### A. Reaction Kinetics

The rate equation DBT conversion is divided into two stiochematric equation:

1- Hydrogenlysis rate equation:
\[
DBT + 2H_2 \rightarrow BiPh + H_2S \quad (1)
\]

2- Hydrogenation rate equation:
\[
DBT + 5H_2 \rightarrow CHB + H_2S \quad (2)
\]

Numerous researchers concluded that hydrodesulphuization reaction is first order with respect to DBT concentration

\[
r_{HDS} = \frac{k_{DBT}}{C_{DBT}} \quad (3)
\]

Where: \( k_{DBT} \) is reaction rate constant, \( C_{DBT} \) is concentration of DBT.

General Stiochematric equation reaction:
\[
DBT + N\text{-compound} \rightarrow H.C + H_2S \pm NH_3 \quad (4)
\]

Where: N-compound is nitrogen compound, which is carbazole or acridine in the present work and H.C is a hydrocarbon. Nitrogen compounds competitive with sulfur compound on the surface of catalyst, by substitution the fractional occupation of the DBT:
\[ r_{DBT} = k_{DBT} f(P_H) \frac{K_{DBT} C_{DBT}}{1 + K_{DBT} C_{DBT} + K_N C_N} \]  
(5)

\[ f(P_H) = \frac{K_H P_H^n}{(1 + K_H P_H^n)} \]  
(6)

Sub. eq. (6) into equation (5):

\[ r_{DBT} = k_{DBT} \frac{K_{DBT} C_{DBT}}{1 + K_{DBT} C_{DBT} + K_N C_N} \frac{K_H P_H^n}{(1 + K_H P_H^n)} \]  
(7)

For first order reaction respect to hydrogen:

\[ r_{DBT} = \frac{k_{DBT} K_{DBT} C_{DBT}}{1 + K_{DBT} C_{DBT} + K_N C_N} \]  
(8)

This equation is close to the general form of Langmuir-Hinshelwood.

\[ \frac{K_{H_2} C_{H_2}}{1 + K_{H_2} C_{H_2}} \approx 1, \quad (K_{H_2} C_{H_2} \gg 1) \]  
(9)

Neglect the self-inhibition for DBT because the constant concentration for DBT therefore no self-inhibition which meaning:

\[ r_{DBT} = k_{DBT} \frac{K_{DBT} C_{DBT}}{1 + K_N C_N} \]  
(10)

Let: \( k_{DBT} = k_{DBT} K_{DBT} \)

\[ r_{DBT} = k_{DBT} \frac{C_{DBT}}{1 + K_N C_N} \]  
(11)

For nonlinear inhibition effect, Let (n) is exponent fitting the inhibition.

\[ r_{DBT} = k_{DBT} \frac{C_{DBT}}{1 + K_N C_N^n} \]  
(12)

\[ r_{DBT} = k_{DBT} \frac{C_{DBT}}{1 + K_N C_N^n} \]  
(13)

\[ r_{DBT} = k_{DBT} C_{DBT} \]  
(14)

Where: \( r_{DBT} \) is rate of reaction with inhibition of nitrogen compound, \( k_{DBT} \) is rate reaction constant with inhibition.

\[ k_{DBT} = \frac{k_{DBT}}{1 + K_N C_N^n} \]  
(15)

The inhibition features can be formulated as:

B. Inhibition Effect

Inhibition effect representation by finding the (n) which is the fitting exponent for the inhibition effect of nitrogen compound.

\[ k'_{DBT} = \frac{k_{DBT}}{1 + K_N C_N^n} \]  
(16)

\[ k'_{DBT} = \frac{1}{1 + K_N C_N^n} \]  
(17)

\[ k_{DBT} = 1 + K_N C_N^n \]  
(18)

B.1 Adsorption equilibrium constant

The adsorption constant is an indicator of force to adsorption on the surface of catalyst with competitive of sulfur compound. When the adsorption constant is high this means that nitrogen compound is highly competitive with sulfur compound and highly adsorbed on the surface of catalyst.

\[ a = K_N \]  
(19)

B.2 Reaction rate constant for inhibition

Reaction rate constant for inhibition can calculate from previous equation:

\[ k_{DBT} = \frac{k_{DBT} - k'_{DBT}}{k_{DBT}} \]  
(20)

B.3 Inhibition factor

The inhibition factor (\( \phi \)) is a function of behavior nitrogen compound and show degree of inhibition, which increase when the initial concentration of nitrogen compound increase. The inhibition factor (\( \phi \)) can calculate from:

\[ \text{Inhibition factor } \phi = \frac{k_{DBT} - k'_{DBT}}{k_{DBT}} \]  
(21)

IV. RESULTS AND DISCUSSION

A. Catalyst characterizations

Figures (2) shows a good active material distribution (PtMo) which appear as small particle size while the alumina support appear like large particle or surface contain small particle.

The XRD pattern of homemade catalyst (PtMo) is shown in the Fig. (3), this figure indicates that calcination temperature does not change the crystalline structure of the catalyst. Fig. (4) and Table (1) show the textural surface of homemade (PtMo) catalyst. The homemade catalyst has high surface area, so it has high macroporous particles and low mesoporous particles which mean more voids between particles therefore an increase in pore volume of catalyst. It can be shown a reduce in surface area, pore volume, and pore size distribution after incorporation of platinum (Pt) for prepared catalyst these results agree with Zden’ek Vit[5] and Vishwakarma[6] who found a reduction of surface area for (Mo/ alumina) deposited with different metals. The TPD pattern of PtMo/Al2O3 catalyst is shown in Fig. (5). It is clearly seen that there is a no fully individual peaks and they are broad because CO2 is adsorbed weakly on the catalyst surface and this caused by little amount of basic sites. Weak basic site on the hydrotreating catalyst very important point because these catalysts are acidic catalyst, for typical hydrotreating catalyst there two function, acidic support for cracking heteratom bonds and metals for hydrogenation[7],[8] so strength of hydrotreating base to acidity. These result show strength of basic very weak and strength of acidic very high therefore these result are very excellent.
Inhibition effect can be represented by exponent factor \((n)\) which is a power of inhibition effect for nitrogen compound. For the present study \((n)\) is found by fitting the nitrogen compound data, Figs.(6-9) show that procedure. The adsorption constant for carbazole and acridine can be calculated by equation (20). The adsorption constant for carbazole is (367.87) at a concentration range of (0-200 ppm) over (PtMo) catalyst respectively at 20 bar, 1 LHSV and 573K. The adsorption constant for acridine is (564.537) at concentration (0 to 200 ppm) over (PtMo) catalyst respectively at 20 bar, 1LHSV and 573K. At large value of adsorption constant nitrogen compound is highly competitive with sulfur compound and highly adsorbed on the catalyst, also when the adsorption constant is low nitrogen compound is highly adsorbed on the catalyst. These results agree to Laredo[9] who found that the adsorption constant for carbazole is (328.2), indole (1834.9) and quinoline (661.2) also Laredo[10] and Laredo[11].

Inhibition factor

Figs.(10-12) show the inhibition factor for carbazole and acridine over PtMo catalyst. The inhibition factor of carbazol is more than that of acridine for both catalyst, the results show that the inhibition factor for carbazol is more than that of acridine for both catalyst.
Fig. 7: Fitting of carbazole inhibition over PtMo/γ-Al₂O₃ catalyst at 20 bar, (1LHSV) and 573K when n= 0.5

Fig. 8: Fitting of acridine inhibition over PtMo/γ-Al₂O₃ catalyst at 20 bar, (1LHSV) and 573K when n= 1

Fig. 9: Fitting of acridine inhibition over PtMo/γ-Al₂O₃ catalyst at 20 bar, (1LHSV) and 573K when n= 0.5

Fig. 11: Inhibition factor of acridine (0 to 200 ppm) over PtMo/γ-Al₂O₃ catalyst at 20 bar, 1 LHSV and 573K

Fig. 12: Inhibition factor of carbazole, acridine (0 to 200 ppm) over PtMo/γ-Al₂O₃ catalyst at 20 bar, 1 LHSV and 573K

Carbazole is (0.537) over PtMo for inhibition 100 ppm of carbazole, while inhibition factor for carbazole is (0.642) over PtMo catalyst for inhibition of 200 ppm. The results show that the inhibition factor for acridine is (0.608) over PtMo for inhibition by 100 ppm acridine, while the inhibition factor for acridine is (0.708) for inhibition by 200 ppm. These results agree with those of [Laredo[11].

**D. Activation energy**  

According to Arrhenius equation, a plot of (ln K) versus (1/T) gives straight line with slop equal to (-E/R), from which the activation energy is calculated as illustrated in figures (13). The obtained values of activation energies are presented in Table (2). Farag[12] found activation energy of DBT over two different types of catalyst MoS₂, CoMo/Al₂O₃ at same conditions is (79.002), (43.89) kJ/mol respectively. Secondly the type of solvent, Kabe[13] found activation energy of DBT in two different types of light gas oil over same type of catalyst CoMo/Al₂O₃ at the same conditions and is (108.68), (112.86) kJ/mol respectively. Thirdly is the type of sulfur compound, activation energy for total sulfur almost higher than individual, Steinner[14] found that the activation energy for total sulfur of light gas oil is (119.966) kJ/mol depending on contains of sulfur compound in oil. For present study these results disagree to Kabe[15] who found (100.32) kJ/mol for DBT, this comparison with the same individual sulfur compound.
concentration of DBT under certain conditions of pressure 16 to 20 bar, 523 to 573K temperature, and liquid hourly space velocity of range 1to 3 hr\(^{-1}\). It is proven by the present study of that HDS of DBT is highly inhibited nonlinearly by basic and non-basic compounds. The inhibition is strongly depends on the concentration of nitrogen compounds, inhibition effect of basic nitrogen compound, acridine, is more significant than nonbasic nitrogen compound, carbazole, for all tested conditions.

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