

The Effect of Coking on Kinetics of HDS Reaction under Steady and Transient States

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ABSTRACT: *A study was made of the coking of a commercial fresh sulfide Ni-Mo/Al₂O₃ catalyst in a fixed-bed reactor. The catalyst was coked using different coke precursors in the gas oil under accelerated conditions at temperatures of 400 to 450°C to yield different deactivated catalysts containing 2-20 wt% C.*

Two cases were studied; crushed catalyst without diffusional resistance and extruded pellets with diffusional resistance. Physical properties and catalytic activities of the coked catalysts were measured using the thiophene sulfur removal in the gas oil.

It is concluded that coking occurs by selective deactivation on hydrotreating catalyst and the experimental results of the catalyst activity under different operating conditions, obey a power law as a function of the coke content.

In the pellet catalyst showed a lower rate of coking and deactivation in comparison to the catalyst without diffusional resistance. It is inferred that high level of coke content (higher than 12 wt% C) affects the tortusity factor of the catalyst,considerably.

In the study of transient deactivation, initial activity of the catalyst was derived by a time variable function, then this equation was used in dynamic model of hydrodesulfurization reaction in a packed bed reactor to determine the activity change of the catalyst in the reactor during actual operational conditions.

KEY WORDS: *Hydrodesulfurization, Coking, Hydrotreating catalyst, Activity function.*

INTRODUCTION

Catalytic hydrotreating is one of the most important processes in oil refining. Although large-scale hydrotreating has been practiced for about sixty years, there is still much incentive for research in this field. The

reason is that the world supply of crude oil has shifted toward heavier stocks with substantial sulfur, nitrogen and heavy metal contents. A major problem in hydrotreating of heavy feedstocks is deactivation of the

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catalyst by coke formation. The properties of the carbon deposit is a function of the feed composition, the type of catalyst and the reaction conditions [1,2].

The coking reaction is a consequence of dehydrogenation-polycondensation reactions which generate coke structures capable of blocking the access of the reagents to the active catalytic sites and progressively closing off the porous structure of the catalyst [3,4].

A great effort in catalytic research has been devoted to the investigation of deactivation parameters in order to reduce their effect and improve the performance of commercial catalysts.

The objective of this work was to investigate the physical properties and the activity of a coked catalyst, Ni-Mo/ γ -Al₂O₃, with different levels of coke content and different coke precursors. Limitations of the hydrodesulfurization rate through particle diffusion resistance as well as deactivation are examined experimentally followed by modeling. The effectiveness factor, effective diffusivity, and relative pellet activity are derived at high and low levels of coke content, from a heterogeneous model of particles in a fixed bed reactor .

EXPERIMENTAL

Catalyst

A commercial hydrotreating catalyst, containing Ni and Mo oxides supported on γ - alumina was used for this research. The shape of the catalyst was that of small extrudate having a diameter of 1.35 mm and average length of 5 mm. Characteristics of the catalyst are presented in Table (1). The sulfur area, pore volume, and pore size distribution of the fresh and coked catalysts were measured by standard N₂ adsorption-desorption methods using ASAP 2000 from U.S. Micrometric Co. The chemical analyses of the catalyst was obtained by atomic absorption spectroscopy. Carbon and hydrogen contents of the coked catalysts were determined by a LECO instrument. The fresh catalyst was sulfided in situ, before being used in the hydrodesulfurization reaction.[5]

Feed

The feed used in the hydrodesulfurization reaction was a medium diesel oil, without any metal compounds, named Isomax gas oil with a trace content of sulfur. This was mixed with thiophene, as a model sulfur carrying molecule, to attain a sulfur content of 2 wt% .The

hydrodesulfurization of thiophene enables us to model HDS of the real feed [6]. Properties of the feed are shown in Table (2). The total sulfur content of the feed and the liquid product are analyzed by X-ray fluorescence (XRF) spectroscopy to obtain the conversion of HDS reaction.

Apparatus

The schematic diagram of the apparatus is presented in Fig. 1. Hydrogen and liquid feeds are mixed at the top of the reactor and, after being preheated, react on the surface of the catalyst under isothermal conditions. The product passes through the condenser and then through a high pressure separator. The remained gas passes through the back pressure regulator and goes out at atmospheric pressure.

Table 1 : Characterization of fresh and presulfided catalyst

| | |
|--|------------------|
| wt % Mo | 10 |
| wt % Ni | 2.2 |
| surface area ,BET (m ² /gr) | 297 - 242 * |
| pore volume (cm ³ /gr) | 0.465 - 0.377* |
| average pore radius (nm) | 3.1 |
| Particle density, ρ_p (gr/cm ³) | 1.37 |
| particle porosity, ϵ_p | 0.44 |
| solid density , ρ_s (gr/cm ³) | 2.74 |
| shape & size | extrudate(1.3mm) |
| bed porosity, ϵ_b | 0.34 |

* property for the pretreated catalyst

Table 2 : Physical property of the feed (Iso Max Gasoil)

| | |
|--------------------------------|-------|
| Sp. gravity @15.56 °C | 0.83 |
| Mw (g/gmol) | 269 |
| Kinematic viscosity(CS) | |
| @ 40 °C | 5.12 |
| @ 100 °C | 1.82 |
| Distillation (°C) | |
| I.B.P. | 161.2 |
| 10 vol% | 276.6 |
| 50 vol% | 329.2 |
| 90 vol% | 373.3 |
| F.B.P. | 387 |
| Carbon content | |
| Aromatics(C%) | 5.74 |
| Paraffins (C%) | 71.7 |
| Naphthens(C%) | 22.56 |
| Total sulfur*(%wt) | 2% |

* by thiophene added to gas oil

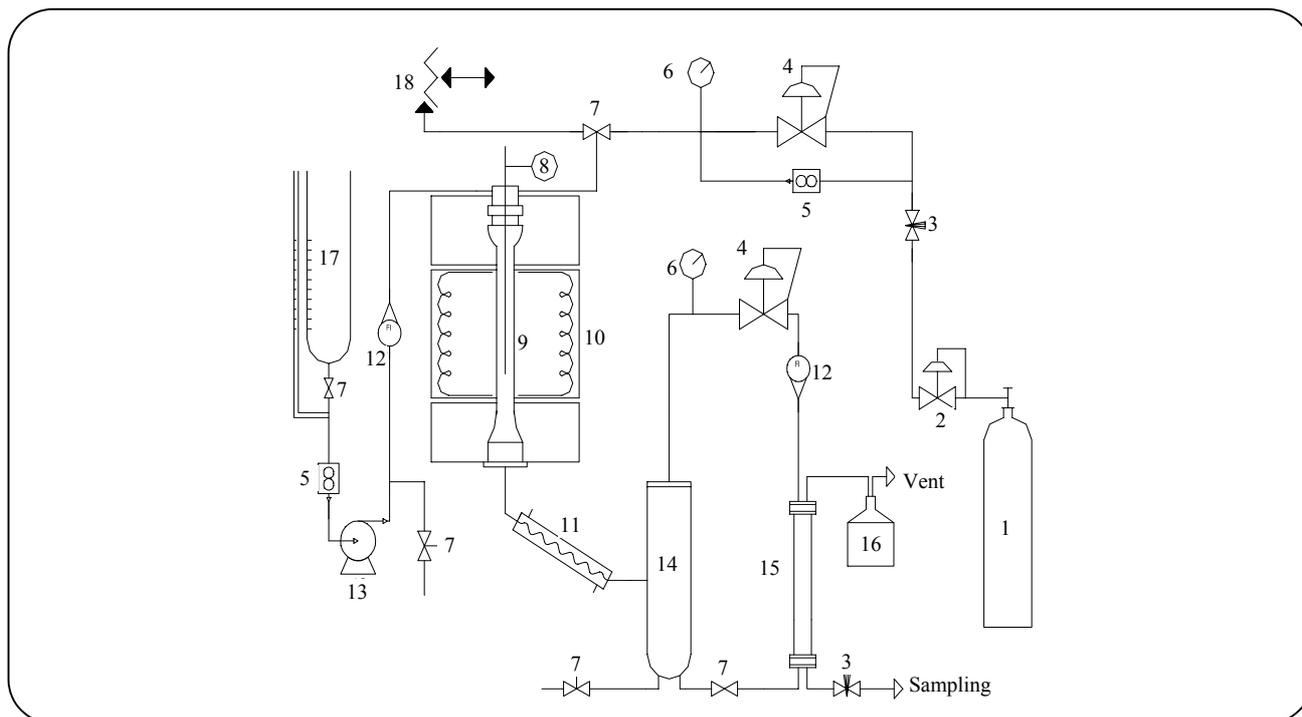


Fig. 1:Diagram of the apparatus

1:Hydrogen cylinder, 2:pressure regulator, 3:needle valve, 4:pressure controller, 5 :flow meter, 6:pressure gauge, 7:valve, 8:thermowell and thermocouple, 9:tubular reactor, 10:heating jacket, 11:condenser, 12:rotameter, 13:liquid pump, 14:high pressure separator, 15:low pressure separator, 16:H₂S trap

Accelerated coking

Coked catalysts were prepared on a fresh-pretreated catalyst by using an accelerated coking reaction at temperatures varying from 400 to 450°C. The hydrogen pressure was reduced, and the feed mixed with some coke precursors, like *o*-xylene, methyl-cyclopentane or thiophene, and flow rate of the feed reduced to accelerate the coke formation. By this procedure, some coked catalysts with different coke contents were obtained and their physical properties, carbon content and activities in hydrodesulfurization reaction, analyzed. The study of coked catalyst was carried out on both crushed and pellet catalysts under steady state conditions. Crushed catalyst was used to study the activity versus the coke content, while pellet catalyst was used to study the diffusional limitations of the catalyst.

Dynamic coking

The other part of the experiments was to study the initial activity as a function of time. Fresh presulfided crushed catalyst was used under atmospheric pressure at two different temperatures, 300 and 340°C, for 40 hr

HDS reaction and the conversion of the feed was determined as a function of time.

The activity function derived from the above experiments, were compared with a heterogeneous model of the reactor.

MATHEMATICAL MODEL

Activity function

The activity function, ζ , of the coked catalysts in the absence of pore diffusion resistance, is defined as follows and used for crushed catalysts,

$$\zeta = \frac{(\text{rate})_C}{(\text{rate})_{C_0}} \quad (1)$$

The activity function is defined relative to the fresh-pretreated catalyst with initial coke content of C_0 . The term ; $(\text{rate})_C$, is used for the coked catalysts.

To relate the activity function to the carbon content, a model of coke deactivation was developed with respect to the site coverage mechanism [7].

In this model, activity is a linear function of the fractional coverage of poisoned sites, θ_c , thus

$$\zeta = 1 - \theta_C \quad (2)$$

The fractional coverage of poisoned sites is defined by;

$$\theta_C = \frac{N_P}{N_S} \quad (3)$$

Where N_P is the number of coke sites covered and N_S is the total number of active sites. The average number of carbon atoms on a poisoned site at a given carbon content is given as:

$$\gamma_C = \frac{N_{C,a}}{N_P} \quad (4)$$

where $N_{C,a}$ is the total number of carbon atoms on the poisoned sites. The ratio of carbon atoms deposited on the inactive support, $N_{C,i}$, to the number of carbon atoms on the active sites is defined as:

$$a = \frac{N_{C,i}}{N_{C,a}} \quad (5)$$

Combining Eq. (3) with Eq. (5) gives:

$$\theta_C = \frac{N_C}{N_S(1+a)\gamma_C} \quad (6)$$

Where N_C is the total number of carbon atoms. Eq. (6) can be rewritten in terms of carbon content,

$$\theta_C = \frac{C}{12n_S(1+a)\gamma_C} \quad (7)$$

Where C is g. of carbon/ g. catalyst and n_S is mole number of active sites/g. catalyst. Variation of γ_C with carbon content according to a power law equation takes the form:

$$\gamma_C = \alpha C^m \quad (8)$$

where α is a proportionality constant and m is a constant. Eq. (7) then becomes:

$$\theta_C = \beta C^n \quad (9)$$

where $\beta = \frac{1}{12n_S(1+a)\alpha}$ and $n=1-m$. Combination of

Eq. (2) and (9) yields:

$$1 - \zeta = \beta C^n \quad (10)$$

It is thus concluded that intrinsic catalyst activity can be explained by a power law function of the coke content.

In this research, we have used the presulfided- fresh catalyst as the reference activity of 100% and we will use

the following normalized equation with three parameters, to model the activity function versus coke content.

$$1 - \zeta = \left(\frac{C - C_0}{C_{tot} - C_0} \right)^n \quad (11)$$

C_0 , is the carbon content of presulfided-fresh catalyst and C_{tot} is the maximum carbon content that causes a complete deactivation, and n is a constant. If it becomes unity, it is inferred that coking is a nonselective reaction in hydrotreating of the catalyst [8]. In this research both linear and nonlinear models, will be examined for fitting of the experimental results to find out the best correlated model.

Relative Pellet Activity

The relative pellet activity is defined as the ratio of molar flux of reactant to the catalyst at coke levels of C and C_0 , respectively, [9] as follows:

$$\langle a \rangle = \frac{(N_{th})_C}{(N_{th})_{C_0}} \quad (12)$$

It can be related to the rate of reaction by effectiveness factors

$$\langle a \rangle = \frac{\mu_C (\text{rate})_C}{\mu (\text{rate})_{C_0}} \quad (13)$$

Where μ_C is the effectiveness factor of the coked pellet catalyst, and μ is the effectiveness factor of the fresh catalyst. Inserting Eq. (1) in Eq. (13), it can be related to the activity function

$$\langle a \rangle = \frac{\mu_C \zeta}{\mu} \quad (14)$$

The relative pellet activity, $\langle a \rangle$, is determined by using the experimental results of coked catalyst with respect to the fresh- sulfided catalyst in integral model of reactor.

Heterogeneous Model

The heterogeneous model of the reactor used in this paper, takes the diffusional limitation of the pellet catalyst in a tubular fixed bed reactor, into account during the HDS reaction with coke formation [9-11].

Assumptions

1- The catalyst pellets are assumed as infinite cylinder

with radial dispersion, because the ratio of d_p/l is less than 1/4.

2 - The external resistance of the pellet is negligible in comparison to the internal resistance, because of the high rate of gas flow [12]

3 - The intra-particle diffusional resistance of coke formation is negligible, because of the low rate of coking reaction in excess of hydrogen.

4 - The change in activity is accounted as a separate function in kinetic reaction. For the systems with a low rate of coking, one can use a separable activity function [8].

5 - The coking reaction model obeys the Voohris Equation [13].

6 - The HDS activity is expressed by a pseudo first order kinetic equation in an integral reactor. The first order of HDS reaction and its kinetic parameters are derived using the integral model of the reactor based on the experimental results of conversion on fresh-presulfided crushed catalyst [14,15].

7 - The reactor is a fixed bed tubular reactor with negligible axial and radial dispersion because of low ratio of d_p/L ($<1/40$)

8 - The model is written for both steady state and transient conditions. At steady conditions, the prepared coked samples are studied to derive diffusivity and tortusity factor of the pellet catalyst at different levels of the coke content. Under transient conditions the activity changes of pellet catalyst in the reactor versus time is calculated.

Formulation

The dynamic model is written and solved by using the reaction parameters derived from [14,15] to monitor the degree of conversion during the process.

Pellet

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \bar{C}_p}{\partial r} \right) - \varphi_c^2 \bar{C}_p = \varepsilon_p \frac{d\bar{C}_p}{dt} \quad (15)$$

$$\mu_c = \frac{2}{\varphi_c^2} \left(\frac{\partial \bar{C}_p}{\partial r} \right)_{r=1} \quad (16)$$

$$\varphi_c^2 = \frac{\zeta D_{\text{eff}}}{D_{\text{eff},C}} \varphi^2 \quad (17)$$

$$\varphi^2 = R^2 \frac{K_0 \rho_p}{D_{\text{eff}}} \quad (18)$$

$$D_{\text{eff}} = \frac{\varepsilon_p D_M}{\tau} \quad (19)$$

$$\text{at } t = t_0 \quad \bar{C}_p = \bar{C}_{p,\text{fresh}} \quad (20)$$

$$\text{at } \bar{r} = 0 \quad \frac{\partial \bar{C}_p}{\partial \bar{r}} = 0 \quad (21)$$

$$\text{at } \bar{r} = 1 \quad \bar{C}_p = 1 \quad (22)$$

Activity function:

$$\zeta = \alpha^{-\beta} \quad (23)$$

Bed

$$\varepsilon_b \frac{d\bar{C}}{dt} = -u \frac{d\bar{C}}{dz} - \mu_c \zeta \rho_p (1 - \varepsilon_b) K_0 \bar{C} \quad (24)$$

$$\text{at } t = t_0 ; \bar{C} = \bar{C}_{\text{fresh}} , \zeta = 1 , \mu_c = \mu , \varphi_c = \varphi \quad (25)$$

$$\text{at } z = 0 \quad \bar{C} = \bar{C}_0 \quad (26)$$

The kinetic model and rate constant (K_0) is taken from other's [14]. Thiele modulus (ϕ), effective diffusivity (D_{eff}) and tortusity factor (τ) of the pellet catalyst in fresh-presulfided sample are taken from other's [14]. The particle density (ρ_p), particle porosity (ε_b) and bed porosity (ε_b) are shown in table 2. The parameters of coked pellet catalyst as μ_c , ϕ_c , $D_{\text{eff},c}$ and τ_c are taken from reference [15]. The parameters of intrinsic activity (α , β) are taken from reference [15] and that obtained in this work. The model parameters and operational conditions are presented in table 4.

By solving the above model we found the profile of conversion along the catalyst bed as a function of time accompanied by deactivation of catalyst. The change of outlet conversion and total relative activity were compared with experimental results.

RESULTS AND DISCUSSION

The first part of the results are focused on crushed catalyst, with average size of 0.7 mm, without diffusional resistance. The absence of mass transfer resistances, with this size, have been examined by others [12,14].

Table 3: Physical properties of the fresh and deactivated catalyst

| Catalyst | Coke precursor | wt % C | Surface area BET, m ² /gr | Pore volume cm ³ /g | Mean pore radius, nm |
|-------------|---------------------|--------|--------------------------------------|--------------------------------|----------------------|
| Fresh | --- | 0.0 | 297 | 0.465 | 3.14 |
| Presulfided | di-methyl disulfide | 2.1 | 242 | 0.358 | 2.96 |
| Coked (1) | o-xylene | 5.5 | 241 | 0.334 | 2.78 |
| Coked (2) | o-xylene | 7.5 | 208 | 0.290 | 2.79 |
| Coked (3) | m-cyclopentane | 13.9 | 173 | 0.225 | 2.60 |
| Coked (4) | Thiophene | 16.1 | 159 | 0.202 | 2.55 |
| Coked (5) | o-xylene | 16.9 | 151 | 0.197 | 2.61 |
| Coked (6) | o-xylene | 18.9 | 105 | 0.125 | 2.39 |

Table 4: Model parameters and operational conditions

| | |
|------------------------------------|--|
| K_0 (m ³ /hr.Kgcat) | $1.26 \times 10^{13} \text{Exp}(-11539/T)$ |
| D_1 at 320 °C, m ² /s | 1.84×10^{-8} |
| τ | 6.1 |
| α | ~1 |
| β | -0.045 |
| C_0 , kmol/m ³ | 0.55 |
| T, K | 593 |
| P, Mpa | 1.2 |
| WHSV, l/hr | 5.76 |

The equation of intrinsic rate of HDS reaction and its parameters are also taken from the same articles.

The physical properties of the fresh, presulfided and coked catalysts, such as surface area, pore volume, mean pore radius and carbon content are presented in table 3. The differential pore size distribution of the catalysts is presented in Fig. 2. It is observed that, within 2 to 17 % carbon content, the mean pore radius doesn't change significantly and pore size distributions show that pore coverage is almost uniform in this type of catalyst. The effect of carbon content on the fractional pore coverage is observed in Fig. 3. It shows that pretreating of the fresh catalyst causes almost 20% pore coverage. At high levels of coke content, higher than 17% C, there is a sharp increase in pore coverage. The coked catalysts presented in this figure are prepared with different coke precursors like o-xylene, methyl-cyclopentane and thiophene. Within 2 to 17wt% C, pore coverage shows a linear change against weight fraction of

carbon on the catalyst, so it is inferred that coking of the catalyst doesn't depend on the kind of precursor. The experiments represented in Fig. 2 show that coke formation at 18.9% C makes almost complete deactivation of the catalyst.

The effect of carbon content on the intrinsic activity is observed in Fig. 4. The activities of the coked catalysts were determined using model compound, thiophene in gas oil, for HDS reaction under different operational conditions as follows;

Pressure: 1.2 to 3 MPa, temperature: 250 to 320 °C and space velocity: 4 to 7.5 hr⁻¹.

Two models were fitted to the results; a nonlinear model, equation (11), and a linear model, using the same equation but n=1, which are presented in Fig. 4. The constants of equation (11) for nonlinear model are derived as follows;

$$C_0 = 0.02 \quad C_{\text{tot}} = 0.21 \quad n = 0.72$$

In this model a complete deactivation occurs at 0.21 grC/gr,cat (at $\xi=0$),

The linear model, equation (27), is represented by:

$$1 - \xi = \left(\frac{C - C_0}{C_{\text{tot}} - C_0} \right) \quad (27)$$

$$C_0 = 0.011, \quad C_{\text{tot}} = 0.19$$

In this model a complete deactivation occurs at 19 wt% C (at $\xi=0$)

Mean relative deviation of the results is presented by the following equation;

$$\text{MRD} = \frac{1}{N} \sum_i^N \frac{\text{ABS}(Y_{i,\text{act}} - Y_{i,\text{cal}})}{Y_{i,\text{act}}} \quad (28)$$

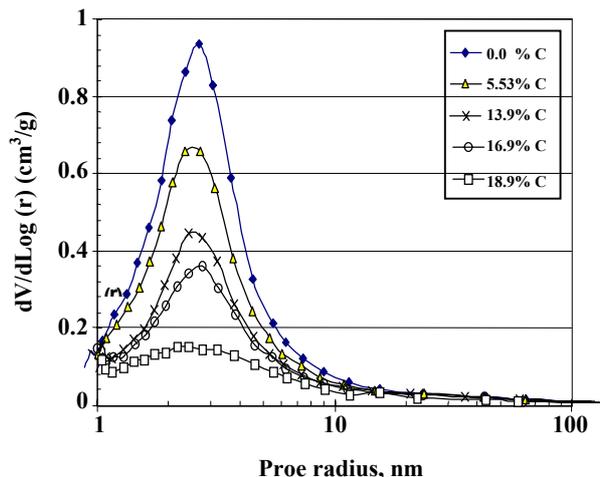


Fig. 2: Differential pore size distribution of fresh and coked catalyst.

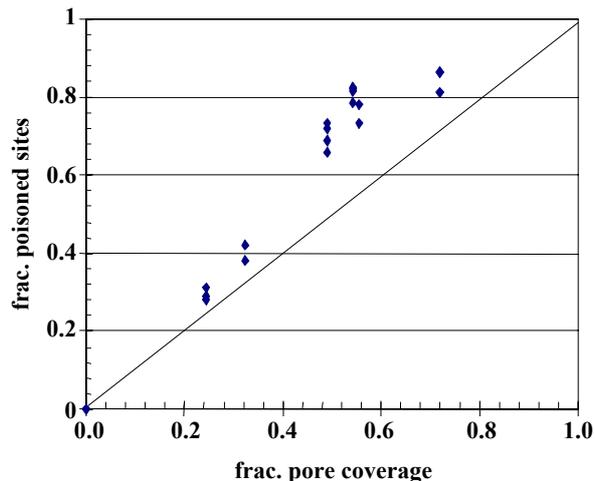


Fig. 5: Fractional poisoned sites vs. fractional pore coverage.

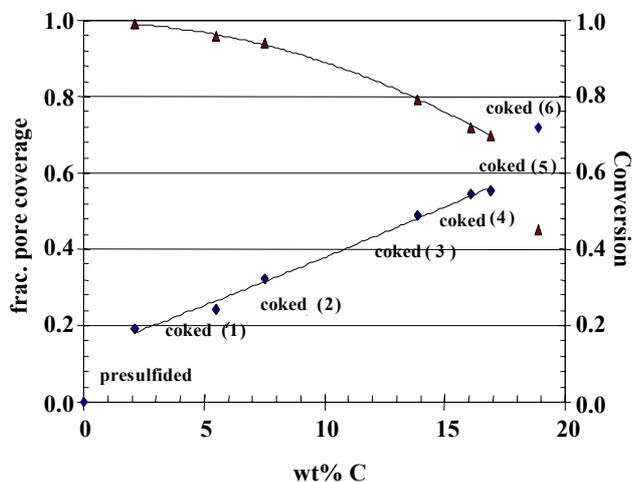


Fig. 3: Fractional pore coverage with various coke contents.

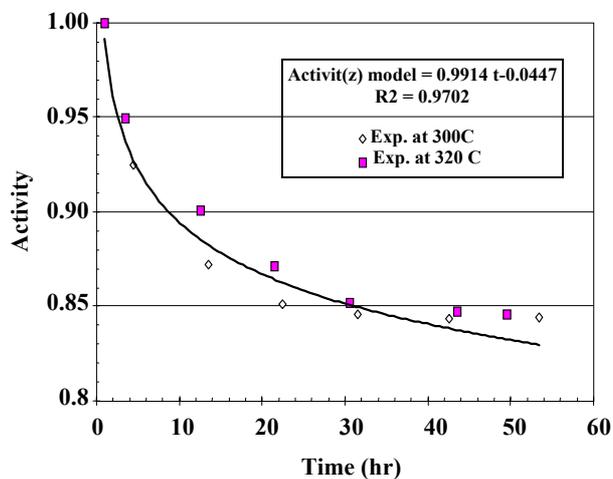


Fig. 6: Intrinsic activity change of catalyst vs. time.

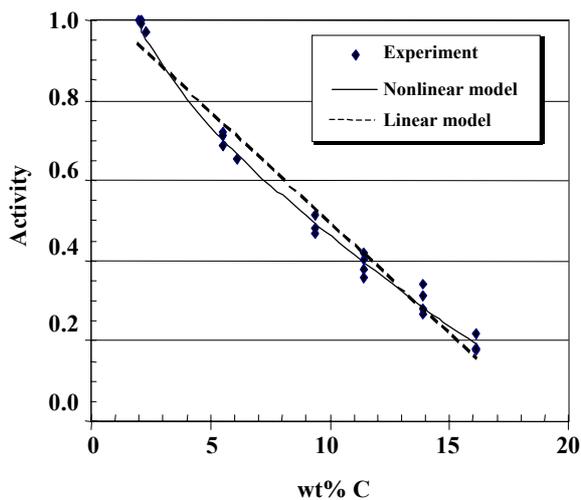


Fig. 4: Comparison of nonlinear and linear model with experimental results.

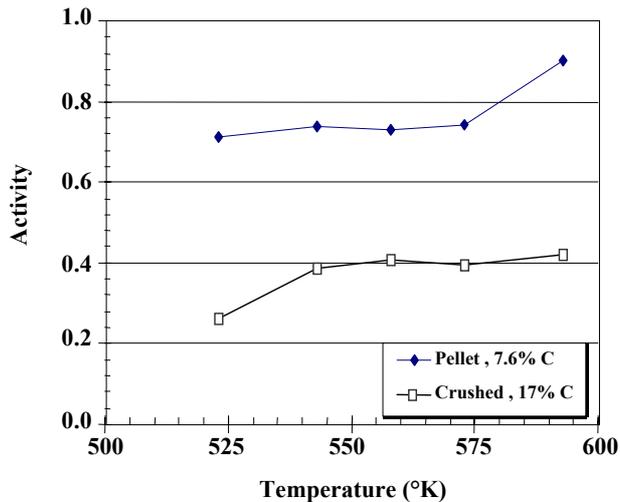


Fig. 7: Comparison of the activity of pellet and crushed coked catalyst.

MRD is calculated 4.8% and 9% for nonlinear and linear models, respectively. It is inferred that the nonlinear model, equation (11), has a higher correlation with the actual conditions, although the linear model can better describe the complete deactivation.

To investigate the selectivity of the coking, the experimental results of fractional poisoned sites, $1-\zeta$, are plotted versus fractional pore coverage in Fig. 5. It is observed that the experimental points are above the bisector. It can thus be inferred that the active sites are more affected by coke than the other sites. The power law model as well as Fig. 5 prove that coking of the hydrotreating catalyst is selective [7].

To derive the function describing the initial activity versus time, the crushed catalyst is treated with a mixture of thiophene as reactant and 4wt% *o*-xylene, as coke precursor, in gas oil, with hydrogen at atmospheric pressure at temperatures ranging from 300 to 340°C. The results of activity vs time are plotted in Fig. 6. It shows that after almost 32 hr. the system becomes stable with a relative catalyst activity of about 85%. The coke deposited in this condition is obtained 5 to 6 wt% C. Treating the experimental data on by the Voorhies' equation, the following equation is obtained for intrinsic activity as a function of time;

$$\xi = (t)^{-0.045} \quad (29)$$

Where t is time in hr., at initial condition, $t_0=1$, the relative activity of the fresh- presulfided catalyst is considered unity. The above activity function is used in Eq. (23) in heterogeneous model of catalyst pellet in fixed bed reactor.

As the industrial catalysts are in the pellet form, we tried to investigate the effect of diffusional resistance on the catalyst deactivation and relative pellet activity. So, two different forms of the catalyst, crushed and pellet, are compared with each other in Fig. 7. They are deactivated under the same conditions and in the same period of time. The coke deposited on the pellet catalyst was 7.6 wt% C, and 17wt% C on the crushed catalyst. In this figure, the relative activities are exhibited at different temperatures. It is inferred that diffusional resistance lowers the rate of deactivation.

To figure out how pellet resistance affects the deactivation of the catalyst, the experimental relative activities of the coked pellet catalysts are plotted versus

fractional poisoned sites, $1-\zeta$, derived from the model equation 11, in Fig. 8. These results are similar to anti-selective poisoning [8]. It is inferred that the resistance against coke formation or deactivation in the pellet form is much higher than the catalyst without pore diffusional resistance. This figure shows that smaller fraction of the active sites are deactivated in the pellet and the activity of the catalyst is maintained at higher level.

To determine the effect of coke content on effective diffusivity and tortuosity factor of the catalyst, the model of the pellet was solved under steady conditions for the fresh and coked catalysts. In this case, equations (15) to (22) are solved numerically by trial and error, under steady conditions. After predicting a value for Thiele modulus, ϕ , and solving the equations, the calculated effectiveness factor, μ , is compared with experimental results, until they converge. For coked catalyst it is necessary to use activity function versus coke, ζ , from equation (11). By this procedure, it is possible to find out Thiele modulus, effective diffusivity and tortuosity factor of the fresh and coked pellet. The results are presented in Fig. 9. It is inferred that at low level of coke, the diffusivity and tortuosity factor are not affected significantly. At carbon contents, higher than 12 wt% C, pore blockage causes a decrease in diffusivity and increase in tortuosity factor.

After determination of the above parameters, the heterogeneous model under transient conditions was studied. The operational conditions were; 320°C and 1.2 MPa, using catalyst pellets. The model equations are presented by Eq. (15) to (26). They are solved numerically by implicit finite difference method using experimental parameters derived from the previous section. The results of the model are presented for 100 hr. in Figs. 10 to 12. Fig. 10 shows the outlet conversion versus time in comparison with experimental results. Total relative activities derived from outlet conversion are presented in Fig. 11 and compared with those of the experimental. These figures show a good agreement between model and experiment. Fig. 12 presents results of activity changes and coke deposition by dynamic model. It is obvious that the rate of coking and activity reduction are important in the first hours. It is observed that, after almost 60 hr., a stable condition is reached, for the pellet catalysts, with relative activity of 85%.

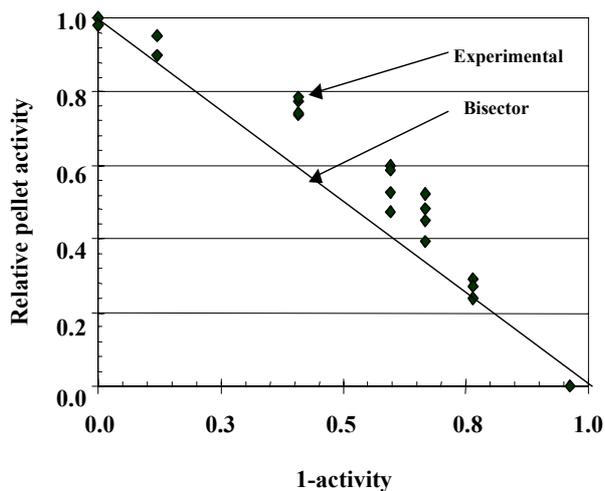


Fig. 8: Pellet activity from experiment vs. fractional poisoned sites from model.

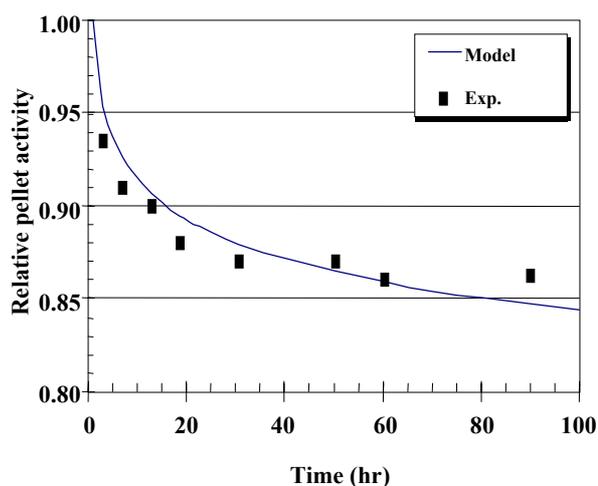


Fig. 11: Comparison of transient activity changes from model and experiments, at $T=320\text{ }^{\circ}\text{C}$.

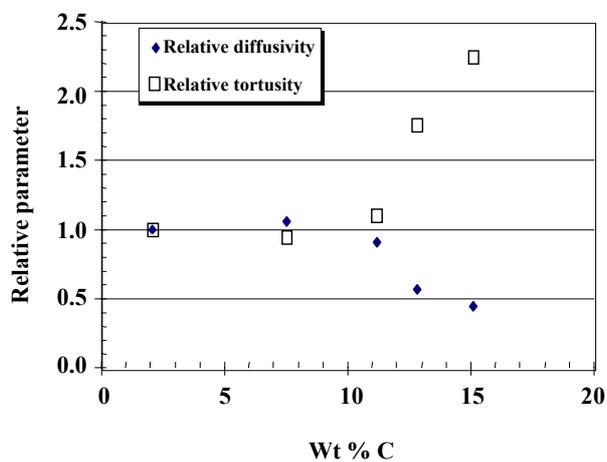


Fig. 9: Comparison of diffusional parameters of pellet-coked catalyst.

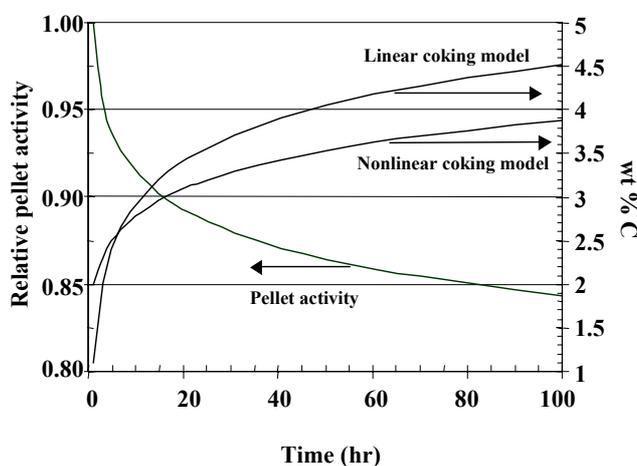


Fig. 12: Results of transient model of total activity and coke formation on the pellet catalyst

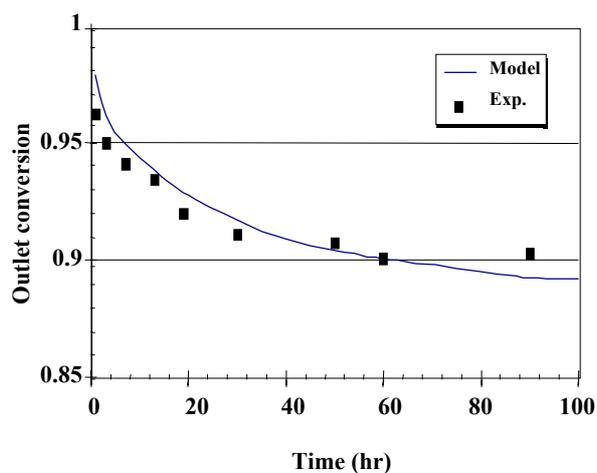


Fig. 10: Comparison of the outlet conversion of the model reactor and experiments at $T=320\text{ }^{\circ}\text{C}$.

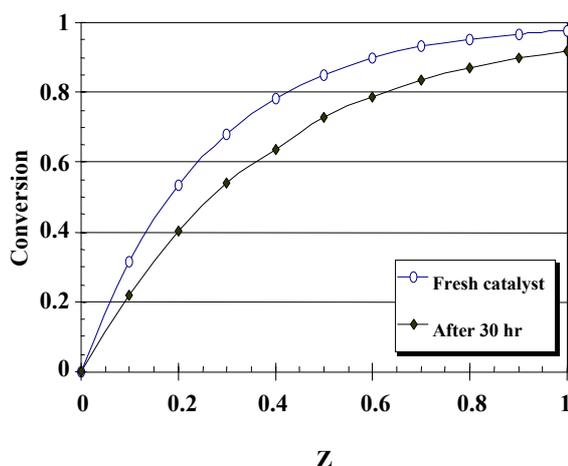


Fig. 13: Results of conversion along the bed derived by model at two periods of time.

At the end of the process, after 100 hr., the coke deposition was determined experimentally from the used catalyst and was determined to be 3.5 % C. In Fig. 12 The amount of coke calculated by linear and nonlinear model at the end of run was 4.5 % C and 3.8 % C, respectively. It is inferred that nonlinear power law model of coking fits better than the linear model in this period of time.

Fig. 13 is the results of conversion predicted along the bed for two periods of time ,one for fresh –presulfided and the other after 30 hr.

By this model one can calculate the change of conversion with respect to the coke deposition along the bed and time.

CONCLUSIONS

The hydrotreating catalysts in the pellet form, with pore diffusion control show a high resistance against coking and deactivation in hydrotreating of the gas oil feeds, free from wax and metal compounds.

Coke deactivation of these catalysts is a combination of site coverage and pore blockage. At low levels of carbon content, up to 12 wt % C, site coverage is dominant whereas at higher levels, pore blockage is the dominant mechanism.

Coking of the hydrotreating catalysts is a selective reaction with respect to the site coverage mechanism. The activity function of the catalyst, versus coke content, is obtained by a power law equation, especially for the initial period of deactivation.

In HDS reaction, the dynamics of the reaction accompanied by deactivation are presented by the mathematical model in a tubular reactor to oversee the change of initial activity against the time under operational conditions of pressure and temperature, to find out the time needed to reach the catalyst stability.

By this procedure one can have a good estimation of deactivation and stability of any synthetic catalysts made in laboratory in comparison with the industrial catalysts.

Acknowledgement

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Nomenclature

| | |
|---------------------|---|
| $\langle a \rangle$ | Relative pellet activity |
| C | Coke content, Kg coke/kg cat |
| \bar{C} | nondimension bed concentraion |
| \bar{C}_p | nondimension pore concentration |
| D_{eff} | Effective diffusivity, m ² /s |
| D_M | Molecular diffusivity, m ² /s |
| d_p | Particle Diameter, m |
| K_0 | Reaction constant, m ³ /hr.Kgcat |
| L | Length of the bed, m |
| l | Length of catalyst, m |
| \bar{r} | nondimension Catalyst radius |
| R | Catalyst radius, m |
| T | Time, hr |
| U | Superficial velocity ,m/hr |
| \bar{z} | nondimension Bed length |

Greek letters

| | |
|----------|---------------------------|
| ξ | intrinsic activity |
| θ | Fractional poisoned sites |
| μ | Effectiveness factor |
| ϕ | thiele modulus |

Subscript

| | |
|---|-----------|
| c | with coke |
| 0 | initial |
| p | particle |
| b | bed |

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