Effect of Catalyst Pore and Pellet Sizes on Deactivation in SRC Oil Hydrotreatment

A reaction-deactivation model based on experimental observations was used to predict catalyst life for hydrotreating a solvent-refined coal oil. The model coordinates catalyst pore and pellet sizes to the quantity of carbonaceous material deposited. The results show that for a parallel fouling mechanism, a larger pore size and/or smaller pellet size catalyst tends to have a longer life as well as higher activity. The model also shows that deactivation due to coke deposition approaches a limit.

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SCOPE

Coal liquids can be upgraded to chemical feedstocks and fuel oils by catalytic hydrotreatment, but rapid catalyst deactivation and high production costs are still problems to be solved. For normally used hydrotreatment catalysts, diffusion of reactants and products inside the catalyst pellets plays an important role in both activity and durability. Although lower diffusional limitation can give better initial activity, there exists disagreement on whether catalysts with or without diffusional resistance can give longer life.

In this work, effects of the intraparticle diffusional resistance, in terms of pore diameter and pellet size, on the catalyst deactivation are given for a solvent-refined coal (SRC) oil hydrotreatment. The predictions of the effect of diffusional resistance are based on a model that employs a concept of active site coverage and pore mouth reduction by coke, and is supported by broad experimental observations.

CONCLUSIONS AND SIGNIFICANCE

The model concludes that the better catalyst for hydrotreating solvent-refined coal oil, in terms of higher activity and longer life, is the one that has lower diffusional restrictions, which can be achieved by increasing the pore size and/or reducing the pellet size, but preferably both. This new prediction is different from that reported by other investigators who suggested that some intraparticle diffusional limitation can benefit the catalyst life. The difference results from the assumptions made and system investigated. In the case where loss of catalyst active sites is the primary deactivation mechanism, as studied by other investigators, some diffusional resistance is beneficial to the catalyst life. However, in the case where pore mouth reduction or blocking plays an important role in deactivation, as in this study, diffusional limitation is detrimental to the catalyst life. Therefore, deactivation mechanisms are a key point in selecting a good catalyst in terms of its life. In addition to predicting diffusion effects on deactivation, the current model also shows that coke deposits and their effects on catalyst activity level off at high values, a commonly observed phenomenon in heavy oils hydrotreatment.

INTRODUCTION

Coal liquids can be upgraded to chemical feedstocks and clean fuels, but certain problems still need to be resolved. Rapid catalyst activity decay is among the most difficult problems confronting hydrotreatment developments. Coke deposit is largely responsible for this rapid decay. As discussed previously by Chang et al. (1982), coke can form from the reactants (parallel fouling), from the products (series fouling), or equally from the reactants and the products (independent fouling).

Diffusion of reactants and products plays an important role in both catalyst activity and durability. Although a lower dif-

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fusional limitation can give better initial activity, there exist disagreements on whether catalysts with or without diffusional limitations can give longer life.

Masamune and Smith (1966) mathematically modeled activity decay of a pellet catalyst for first-order, isothermal reactions in the cases of parallel, series, and independent fouling. The deactivation function of the catalyst was expressed in terms of coke on catalyst. The catalyst activity was presented as an effectiveness factor that is a function of both Thiele modulus and time on stream. They concluded that for parallel deactivation a catalyst exhibiting an intermediate level of intraparticle resistance gives the highest activity, particularly at long process times. Lee and Butt (1973) expanded Masamune and Smith's work to analyze more complicated systems, and gave a similar conclusion. Murakami et al. (1968) experimentally confirmed the theoretical developments by Masamune and Smith. They used the disproportionation of toluene as a sample parallel reaction scheme, and dehydrogenation of primary alcohols as a sample series reaction scheme.

Polinski et al. (1981) and Stiegel et al. (1982) treated catalyst aging as a modified shrinking core model and were able to account for diffusional resistance due to pore clogging. The results indicate that larger-diameter catalysts with a greater diffusional resistance tend to reduce the rate of poisoning and thus increase the catalyst life. They also presented experimental data for a synthesized coal gasification product and catalytic coal liquefaction with different diameter catalyst pellets to illustrate the validity of their model.

Most of the above models and observations were for reaction-deactivations in which increasing diffusional resistance caused by coke or metal was not a main concern. However, in most coal liquids and residual oils hydrotreatment, pore mouth reduction along with reactant exclusion can be important in catalyst deactivation since heavy oils contain substantial quantities of large size, highly condensed compounds that are coke precursors and that have difficulty diffusing into pores of the same order of sizes. In an experimental study, Prasher et al. (1978) reported that used catalyst pellets exhibited severe reduction in intraparticle diffusion. This reduction was attributed to coke and metal deposition during the reactions.

Chiou and Olson (1978) have modified the model of Masamune and Smith to account for pore plugging and geometrical exclusion due to high coke content in aged H-coal catalysts. The correlation of effective diffusivity made by Satterfield et al. (1973) was incorporated. The results demonstrate that physical properties of both catalyst and reacting molecules have a decisive effect on the loss of catalyst life and the nature of coke formation. A model employing a similar concept was developed by Haynes and Leung (1983). Their results show that when pore plugging as well as active site poisoning is considered, the catalysts with lower diffusional resistance are more advantageous than those with higher resistance in terms of activity and life of the catalysts.

Newson (1975) proposed a pore-plugging model to describe hydrotreatment catalyst deactivation in axial flow trickle-bed reactors. In his model he assumed a Maxwellian pore size distribution and a parallel fouling reaction. The model has been used to semiquantitatively describe catalyst deactivation in hydrotreatment of residual oils. Results showed that the use of smaller pellet size and/or larger pore size catalysts can significantly improve the catalyst life. This conclusion is a contradiction to that of Masamune and Smith; Murakami et al.; Lee and Butt; Polinski et al.; and Steigel et al.

In the study of solvent-refined coal (SRC) oil hydrotreatment using a Shell 324 NiMo-alumina catalyst, Chang et al. (1982) proposed a parallel fouling model that used catalyst coke content to account for the deactivation through active site coverage and pore size reduction. This model successfully represented the experimental observations including activity time profile, coke time profile, coke space profiles in reactor beds and catalyst pellets, and pore size-coke relationship. This paper extends their model to predict the effect of coke deposit, pore size, and pellet size on the catalyst activity and its decay.

EXPERIMENTAL

The oil feedstock used was a 30 wt. % SRC-I in 70 wt. % process solvent. Its properties are listed in Table 1. Table 2 shows the properties of Shell 324, NiMo/Al, the medium pore size catalyst used in this study.

A 0.5 × 0.13 m ID trickle-bed reactor equipped with automatic temperature, pressure, and flow controls and adequate safety monitoring systems was used in this study. The catalyst was calcined and presulfided before start-up. The nominal operational conditions were: temperature, 400°C; pressure, 13.9 MPa; liquid volume space time, 2.50 h; and hydrogen-to-oil ratio, 1,780 std m^3 H_2/m^3 oil. During shutdown, the reactor was cooled quickly with a high flow of hydrogen to prevent excess coking. The used catalysts were separated into five sections, 0.1 m each, extensively extracted with pyridine, and dried in a high vacuum oven. Thus, the coke content in this study is defined as pyridine insoluble carbonaceous material and was determined by oven combustion in air. Special care was taken to avoid moisture adsorption, which could badly mask the actual values of coke contents. The pore volumes and pore sizes were measured with a Micromeritics model 910 mercury porosimeter by assuming a contact angle of 130 degrees. Oil products were routinely analyzed for hydrogen and nitrogen contents with a Perkin-Elmer model 240B elemental analyzer. More details of this experimental work have been described by Chang (1982).

TABLE 1. PROPERTIES OF FEEDSTOCK

Feedstock	SRC*
Liquid density @ 20°C, kg/m^3	1,129
Normal boiling point**, °C	
IBP	242
5 vol %	258
10 vol %	273
20 vol %	288
30 vol %	303
40 vol %	322
50 vol %	344
60 vol %	382
70 vol %	439
Recovery, wt %	67
Residue, wt %	32
Loss, wt %	1
Elemental composition, wt %	
C	87.25
H	6.73
N	1.40
S	0.50
H/C atom	0.93
Ash	0.097

*A mixture of 30 wt % SRC-I in 70 wt % process solvent.
**Determined from ASTM D1160 at 2.67 kPa (20 mm Hg) vacuum.

TABLE 2. CATALYST PROPERTIES

Catalyst code	Shell 324
Chemical composition, wt %	
NiO	3.4 (3.4)*
MoO_3	19.3 (19.8)
Physical properties	
Geometry	1.6 mm (1/16 in) extrudate
Reactor density, kg/m³	0.790×10^3
Surface area, m²/kg	146×10^3 (150×10^3)
Pore volume, m³/kg	0.43×10^{-3} (0.48×10^{-3})
Most frequent pore dia., nm	11.8 (118 Å)
Pore size distribution, % pore vol. in pore	
Dia., nm	%
3.5–7.0	12
7.0–10.0	21
10.0–15.0	57
15.0–20.0	2
20.0–40.0	1
40.0–60.0	1
>60.0	6
Total	100

*Values in the parentheses are vendor's data.

MODEL DESCRIPTION

Assumptions, approaches, and derivations of the model are detailed in the Appendix; only a limited development is given in this paper. The major assumptions of this model are:

1. The main and coking reactions can be represented by two simple, pseudofirst-order, parallel reactions:

$$A \begin{cases} \xrightarrow{k_A} \text{products} \\ \xrightarrow{k_q} \text{coke} \end{cases} \qquad (1)$$

where k_A and k_q are rate constants for the main and the coking reactions, respectively.

2. Intrinsic rates of the main and the coking reactions decrease with increasing coke content on the catalyst. This assumption is to account for the active site coverage by the coke.

3. Coke can form in multilayers on the catalyst pore surfaces and thus reduce the pore size and restrict the diffusion rates inside the pore. Furthermore, the effective diffusivity of the reactants in the porous catalyst, D_{Ae}, can be represented by the following expression (Satterfield et al., 1973):

$$D_{Ae} = \frac{D_A \varepsilon_p}{\tau} e^{-4.6\lambda} \qquad (2)$$

This imperial expression is valid for the solute-to-pore diameter ratios, λ's, in the range of $0.1 \sim 0.5$.

Mass balance equations over the catalyst pellet, Eqs. A16 and A17, and the reactor bed, Eqs. A33 and A34, for both the main and the coking reactions were solved simultaneously to obtain the activity and coke profiles as functions of time on stream. The model predictions were compared to experimental observations resulting from the hydrotreatment of the SRC oil over the Shell 324 catalyst. The constants used in the calculations are listed in Table 3. The parameters resulting from data fitting are shown in Table 4. These parameters fall in reasonable ranges. The main and coking activities have different order-dependencies on coke content, one-half and two, respectively. Figure 1 shows decreasing coke profiles along the reactor beds, a condition necessary if coke formation was via a parallel route, which is an assumption in the model development. Figure 2 shows that the pore diameter decreases with the increase of the coke content on catalyst. The data in Figure 2 were obtained with the same fresh catalyst, but with various amounts of coke deposit at various stages of deactivation. Figure 3 shows that the hydrogenation and hydrodenitrogenation activities can be correlated to the coke on catalyst, a valid deactivation parameter. Other experimental data including hydrotreatment activity time on stream relationship and coke profiles in catalyst pellets also support the current model (Chang, 1982). With confidence established in the model by detailed matching of predicted and experimental values, the model was next used for predictive purposes beyond those covered by experiments.

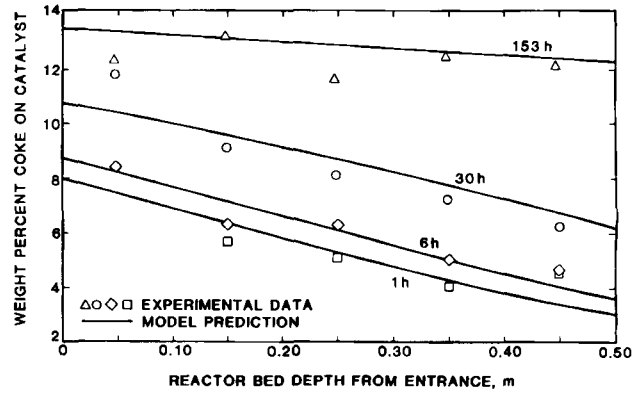

Figure 1. Coke profiles in the trickle-bed reactor for four experimental runs.

TABLE 3. CONSTANTS* USED IN MODEL CALCULATIONS

Feedstock density	$\rho_A = 1.13 \times 10^3$ kg/m^3
Catalyst bulk density	$\rho_p = 1.42 \times 10^3$ kg/m^3
Catalyst packed density	$\rho_b = 0.78 \times 10^3$ kg/m^3
Coke density	$\rho_q = 0.80 \times 10^3$ kg/m^3
Catalyst pellet porosity	$\varepsilon_p = 0.60$
Catalyst bed porosity	$\varepsilon_b = 0.78$
Feedstock hydrogen content	$C_{Ao,\,H} = 6.73$ wt %
Feedstock nitrogen content	$C_{Ao,\,N} = 1.40$ wt %
Maximum coke content	$Q_M = 0.34$ kg coke/kg catalyst
Equivalent radius of catalyst pellet	$r_e = 1.0 \times 10^{-3}$ m
Initial pore dia.	$PD_o = 11.0$ nm
Reactor length	$L = 0.5$ m
Critical solute, dia.**	$SD = 3.3$ nm
Bulk diffusivity**	$D_A = 0.19 \times 10^{-9}$ m^2/s

* Experimentally determined.
**Estimated.

TABLE 4. MODEL PARAMETERS FROM DATA FITTING

Variable	Description	Value
	Intrinsic kinetic rate constants, m^3/s · kg catalyst	
k_A	Main reaction	1.13×10^{-6}
$k_{q,\,H}$	Coking reaction in terms of Hydrogen content	0.95×10^{-9}
$k_{q,\,N}$	Nitrogen content	3.70×10^{-9}
	Order of catalytic site dependency	
m	Main reaction	1/2
n	Coking reaction	2
h_A	Thiele modulus for the main reaction at clean catalyst conditions	11.4
n_A	Effectiveness factor for the main reaction at clean catalyst conditions	0.25

MODEL PREDICTIONS

In addition to interpreting experimental data, the model was used to predict the effect of diffusional resistance, i.e., pore size and pellet size, on catalyst activity and its life. For quantitative comparison purposes, all parameters except catalyst pore size and pellet size are fixed at the values shown in Tables 3 and 4. Physically this means that the predictions are for the hydrotreatment of the SRC oil over Shell 324 catalysts in a trickle-bed reactor at a condition of 400°C and 13.9 MPa, but assumes that catalyst pore size and pellet size can be changed without changing the intrinsic activities.

A Thiele modulus, a measure of the diffusional rate relative to the reaction rate, is defined as:

$$h = r_e (\rho_p k_A / D_{Ae})^{1/2} \tag{3}$$

In this equation, both the pellet size, r_e, and the effective diffusivity, D_{Ae} are incorporated. But since the effective dif-

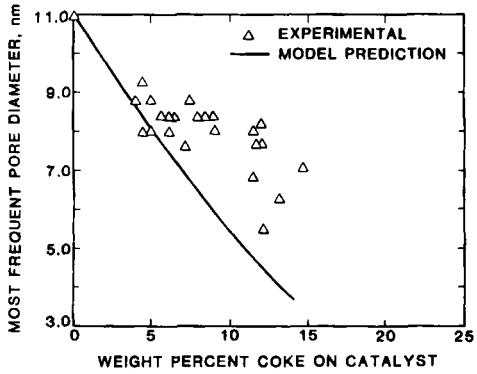

Figure 2. Most frequent pore dia. vs. catalyst coke content.

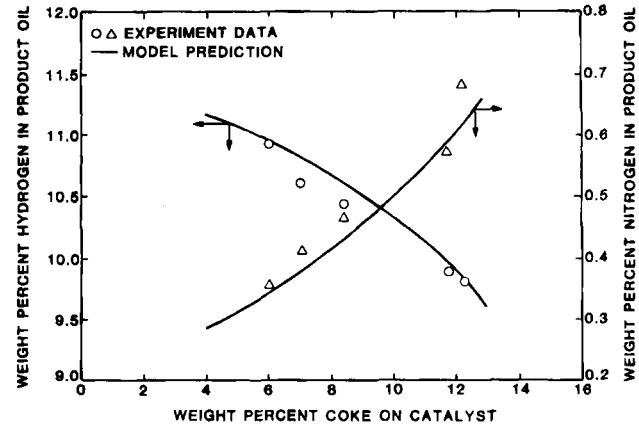

Figure 3. Catalyst activity vs. average coke content over the reactor.

fusivity is a function of pore diameter, as shown in Eq. 2, diffusivity changes with coke content and thus with time on stream. Consequently, the effect of changing pore size, PD, on the catalyst deactivation can not be exactly the same as that of changing pellet size, r_e, even though the initial Thiele modulus is kept the same in both cases. In this section, the effects of both pore size and pellet size are presented separately.

Pore Size Effects

Figures 4–7 present the effects of pore diameter on the performance of the hydrotreating catalyst. The reference pellet diameter is 2.0 mm, which is equivalent to the size of a 1/16 in cylindrical extrudate used in the experimental study, Shell 324 catalyst. Dimensionless units (Appendix) are used in both the ordinate and abscissa of each graph. There are four pore diameters illustrated in each figure, 33.0, 16.5, 11.0, and 8.25 nm, which are values used in the calculations. These median pore catalysts are often used in hydrotreatment operations, and correspond to initial Thiele moduli of 7.4, 9.1, 11.4, and 14.3, respectively. Figure 4 shows that the effectiveness factor, a measure of the catalyst activity defined as the ratio of the actual reaction rate to the maximum reaction rate on clean catalyst basis (see Eq. A24), increases with increasing pore diameter. The effectiveness factors parallel each other for different pore size catalysts. Because of the higher activity for the larger pore diameter catalysts, coke accumulation is also higher, as shown in Figure 5. However, since the larger pores provide less resistance to diffusion, large pores can accommodate more coke deposit and still maintain higher activity. The influence of coke deposition on effectiveness factor is further depicted in Figure 6. The smaller pore catalyst is more severely deactivated by the coke. When these effects are incorporated in trickle-bed reactors, the pore size effect is more significant. Figure 7 shows that larger pore catalysts give much better initial activity and significantly slower activity decay in terms of conversion at the reactor exit.

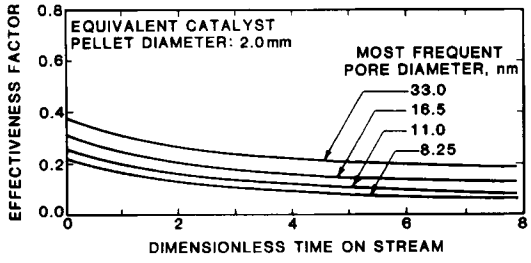

Figure 4. Effect of catalyst pore dia. on catalyst activity decay; effectiveness factor vs. time.

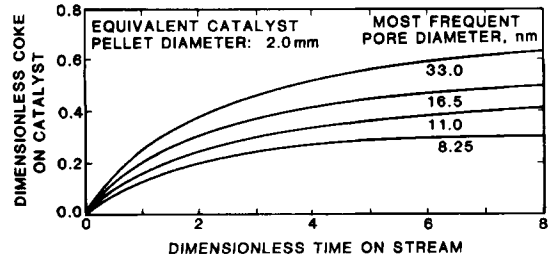

Figure 5. Effect of catalyst pore dia. on catalyst activity decay; coke content vs. time.

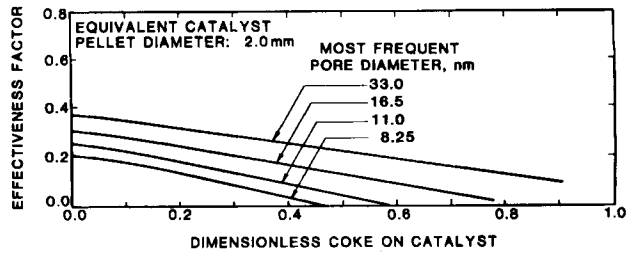

Figure 6. Effect of catalyst pore dia. on catalyst activity decay; effectiveness factor vs. coke content.

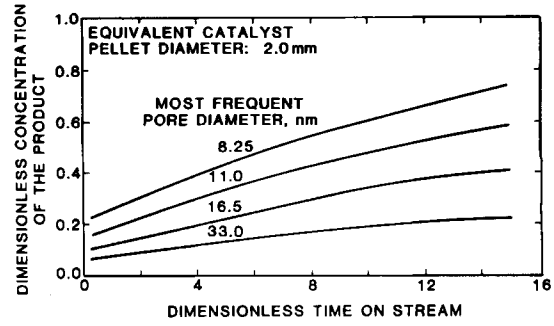

Figure 7. Effect of pore dia. on trickle-bed reactor performance; concentration vs. time.

Pellet Size Effects

The effects of catalyst pellet diameter on catalyst deactivation at a fixed pore size are shown in Figures 8–11. There are four pellet sizes in each figure: 0.6, 1.0, 2.0, and 3.4 mm dia. These pellet sizes are equivalent to cylindrical extrudates of 1/64, 1/32, 1/16, and 1/8 in, and give initial Thiele moduli of 3.4, 5.7, 11.4, and 19.4, respectively. These figures show that decreasing pellet size has an effect similar to increasing pore size, although not quantitatively the same. This is expected since both result in decreasing intraparticle diffusional restrictions, and thus yield better catalyst activity and longer catalyst life. One difference noted, however, is that the effectiveness factor appears to be approaching an asymptotic value for all particle sizes.

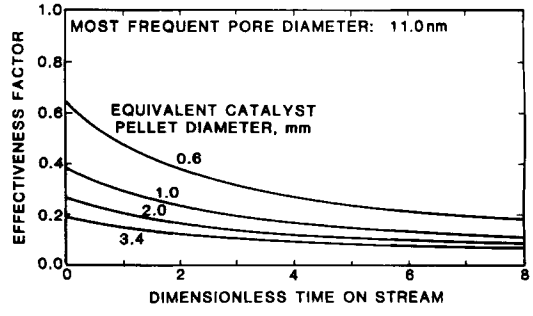

Figure 8. Effect of catalyst pellet size on catalyst activity decay; effectiveness factor vs. time.

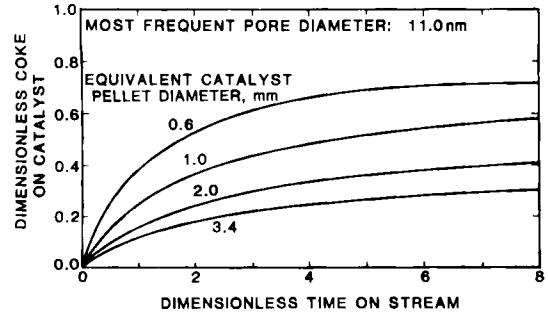

Figure 9. Effect of catalyst pellet size on catalyst activity decay; coke content vs. time.

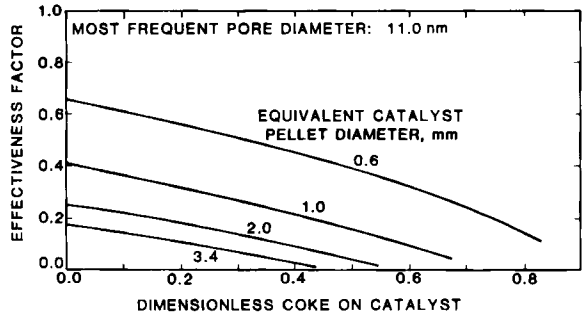

Figure 10. Effect of catalyst pellet size on catalyst activity decay; effectiveness factor vs. coke content.

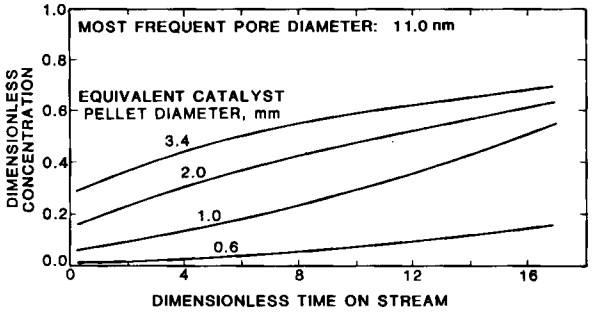

Figure 11. Effect of catalyst pellet size on trickle-bed reactor performance, concentration vs. time.

DISCUSSION

From the above results for hydrotreating the SRC coal oil used in this study, decreasing internal diffusional resistance is beneficial to both initial activity and life of the catalyst. This prediction is consistent with the theoretical treatment by Haynes and Leung (1983), and is supported by the results from fuel oil hydrotreatment (Newson, 1975). On the other hand, this conclusion disagrees with that of Masamune and Smith (1966), Murakami et al. (1968), Lee and Butt (1973), Polinski et al. (1981), and Stiegel et al. (1982). They concluded that for parallel fouling, some internal diffusional resistance can give the catalysts better stability and longer life. This difference results from assumptions made and systems investigated. The latter authors did not account for the effect of coke deposits on effective diffusivity. Therefore, their results can only be applied to those cases where coke deposits do not severely reduce the pore size, and where reactant molecular sizes are relatively small compared to the pore sizes. In this SRC oil hydrotreatment study, the average molecular size of the coal liquid was 3.3 nm (Table 3), which approaches the diameter of the catalyst pores, 11.0 nm; moveover, coke deposits can reduce the pore size by as much as 50%, as Figure 2 shows. Based on these and other observations (Chang, 1982), this model was proposed to account for pore diffusion reduction as well as active site coverage by heavy coke deposition. The model predicts the trends reported by Newson (1975), and could be applied to petroleum or other heavy oils hydrotreatment where coke deposition can reduce the pore sizes and even completely destroy the catalyst although much of its internal surface is still active.

Finally, in the prediction of pore and pellet size effects the current model has predicted an important and common phenomenon in heavy oil hydrotreatment. Coke buildup is primarily responsible for the initial rapid activity decay, but it levels off after a certain period (Dautzenberg et al., 1978). As shown in Figures 5 and 9, the catalyst coke content quickly builds up and levels off regardless of pore and particle sizes. Since coke is a true deactivation parameter, the effectiveness factor and this the catalyst activity approach an asymptotic value as Figures 4 and 8 show.

ACKNOWLEDGMENT

We appreciate the support for this work from the U.S. Department of Energy, Grant No. D-AC22-79-ET-14876, and Oklahoma State University.

NOTATION

C = concentration of reactant in liquid, kg/m^3
D = dimensionless effective diffusivity, D_{Ae}/D_{Aeo}
D_A, D_{Ae} = bulk and effective diffusivity, m^2/s
E, G = dimensionless groups, $E = Q_M/C_{Af}k_qT$, $G = k_A\rho_bQ_M/C_{Af}k_q$
F = volumetric oil feed rate, m^3/s
h = Thiele modulus, $h_A = r_e(\rho_pk_A/D_{Aeo})^{1/2}$

$$h_q = r_e(k_qC_{Ab}\varepsilon_{Po}/D_{Aeo}Q_M)^{1/2}$$

k = intrinsic rate constant, m^3/s · kg catalyst
L = total length of reactor bed, m
M,N = exponents of the main and the coking reactions
PD = most frequent pore diameter, nm
q = dimensionless coke constant, Q/Q_M
Q = coke content, kg coke/kg catalyst, Q_M maximum coke content
R = intrinsic reaction rate, kg/s · kg catalyst
$R_{A,obs}$ = observed reaction rate of A, kg/s · kg catalyst
r = radial position from the center of the catalyst pellet, m
r_e = equivalent radius of the catalyst pellets, m
S = reactor cross-sectional area, m^2
SD = critical solute diameter, nm
T = liquid volume space time, s
t = time on stream, s
x = dimensionless position, $x_b = z/L$, $x_p = r/r_e$
y = dimensionless concentration, $y_b = C_{Ab}/C_{Af}$, $y_p = C_{Ap}/C_{Ab}$
z = longitudinal position in reactor bed from entrance, m

Greek Letters

β, γ = dimensionless group, $\beta = \varepsilon_{po} D_A / D_{Aeo} \tau$, $\gamma = Q_M \rho_p / \varepsilon_{po} \rho_q$
τ = tortuosity
θ = dimensionless time, $\theta_b = C_{Af} k_q t / Q_M$, $\theta_p = C_{Ab} k_q t / Q_M$
η = effectiveness factor
λ = ratio of critical solute diameter to pore diameter, SD/PD
ρ = density, kg/m^3
ε = porosity ratio, $\varepsilon_p / \varepsilon_{po}$
$\varepsilon_p, \varepsilon_{po}$ = porosities, volume fraction of void space of a catalyst pellet

Subscripts

A = main reactant
b = reactor bed
f = feedstock
o = initial conditions
p = catalyst pellet
q = coke

APPENDIX: MODEL DEVELOPMENT

Assumptions and Methods

1. The catalyst pellet is surrounded by a liquid film.
2. A large excess of hydrogen is available for reactions in the liquid phase. This implies that the hydrogen solubility is high enough for the reactions and no mass transfer limitation exists between gas and liquid phase. This assumption has been verified by Soni (1974) and Sooter (1974) in their coal oil hydrotreatment experiments.
3. Catalyst pores are filled with coal-derived liquid. Under reaction conditions of 13.9 MPa (2,000 psig) and 400°C (750°F) coal liquid can encounter lesser resistances due to lower viscous and surface tension forces, and hence can be assumed to completely fill the pores.
4. Only those reactions catalyzed by catalyst surfaces are significant. Most of the surface area lies within the internal porous structure, as in the case for the high surface area catalyst as used in this study. The reactants must diffuse into the pores to utilize the internal surface area.
5. The reactor is in ideal plug flow with negligible radial gradients and axial dispersion.
6. The reactor is isothermal throughout.
7. The main and coking reactions can be represented by two simple, pseudofirst-order, parallel reactions.

$$A \xrightarrow{k_A} \text{products}, \quad A \xrightarrow{k_q} \text{coke} \tag{A1}$$

8. The coking rate is much slower than the main reaction rate, that is $k_q << k_A$.
9. The intrinsic reaction rates decrease with increasing coke content on the catalyst. For first-order reactions, these can be expressed as:

$$R_A = -k_A (1 - q_p)^M C_{Ap} \tag{A2}$$

$$R_q = k_q (1 - q_p)^N C_{Ap} \tag{A3}$$

q_p represents the fraction of the available space occupied by the coke deposit. The last two equations show that instead of relating to time directly, the activity decay is related to the coke content, which is the true catalyst deactivation parameter in this study.

10. The catalyst porosity is reduced by the coke according to the equation:

$$\varepsilon_p = \varepsilon_{po} - Q_p (\rho_p / \rho_q) \tag{A4}$$

11. The catalyst pellet consists of cylindrical pores that are parallel to each other. The diameters of these pores are uniform initially and are uniform at the same cross face at any time. Thus the local pore diameter can be expressed as:

$$PD = PD_o (\varepsilon_p / \varepsilon_{po})^{1/2} \tag{A5}$$

12. Effective diffusivity of the reactant in the porous catalyst, D_{Ae}, follows the correlation (Satterfield et al., 1973):

$$D_{Ae} = \frac{D_A \varepsilon_p}{\tau} e^{-4.6\lambda} \tag{A6}$$

Equation A6 is valid for the λ values in the range of 0.1 – 0.5, which encompasses the values of this study.

Mass Balance Over the Catalyst Pellet

For the unsteady states reaction-diffusion problem, a mass balance for species A on a spherical shell of thickness Δr within a single catalyst particle can be written as:

$$N_{Ar}|_r \cdot 4\pi r^2 - N_{Ar}|_{r+\Delta r} \cdot 4\pi (r + \Delta r)^2 + R_A \cdot 4\pi r^2 \Delta r \rho_p = \varepsilon_p \frac{\partial C_{Ap}}{\partial t} \cdot 4\pi r^2 \Delta r \tag{A7}$$

Here $N_{Ar}|_r$ is the mass of A passing in the r direction through an imaginary spherical surface at a distance r from the center of the sphere. The source term $R_A \cdot 4\pi r^2 \Delta r \rho_p$ gives the mass of A being produced by chemical reaction, and the accumulation term $\varepsilon_p \cdot \partial C_{Ap}/\partial t \cdot 4\pi r^2 \Delta r$ gives the mass change in the shell of thickness Δr. Applying the usual limiting process gives:

$$\lim_{r \to 0} \frac{(r^2 N_{Ar})|_r - (r^2 N_{Ar})|_{r+\Delta r}}{\Delta r} + r^2 \rho_p R_A = r^2 \varepsilon_p \frac{\partial C_{Ap}}{\partial t} \tag{A8}$$

or

$$-\frac{\partial}{\partial r}(r^2 N_{Ar}) + r^2 \rho_p R_A = r^2 \varepsilon_p \frac{\partial C_{Ap}}{\partial t} \tag{A9}$$

The effective diffusivity, D_{Ae}, in the porous medium can be defined by the equation:

$$N_{Ar} = -D_{Ae} \frac{\partial C_{Ap}}{\partial r} \tag{A10}$$

Substituting Eqs. A2 and A10 into Eq. A9 yields:

$$\frac{\partial}{\partial r}\left(r^2 D_{Ae} \frac{\partial C_{Ap}}{\partial r}\right) - \rho_p r^2 k_A (1 - q_p)^M C_{Ap} = \varepsilon_p r^2 \frac{\partial C_{Ap}}{\partial t} \tag{A11}$$

Since no diffusion is possible for deposited coke, the mass balance for coke, Q_p, can be written directly from Eq. A3:

$$\frac{\partial Q_p}{\partial t} = k_q (1 - q_p)^N C_{Ap} \tag{A12}$$

D_{Ae} in Eq. A11 cannot be taken as a constant, since it is a function of coke content, which in turn is a function of time and position.

Since the reactor was started by filling it with gas and liquid at lower than the normal reaction temperature, the void spaces

in the catalyst pellet and in the reactor bed can be assumed to be filled with liquid initially. Thus the initial and boundary conditions can be written as follows:

Initial conditions:

$$\text{at } t = 0 \quad \text{and} \quad 0 \leq r \leq r_e, \qquad C_{Ap} = C_{Ab} \quad \text{and} \quad Q_p = 0 \tag{A13}$$

Boundary conditions:

$$\text{at } r = 0 \quad \text{and} \quad t > 0, \qquad \frac{\partial C_{Ap}}{\partial r} = 0 \tag{A14}$$

$$\text{at } r = r_e \quad \text{and} \quad t > 0, \qquad C_{Ap} = C_{Ab} \tag{A15}$$

The last boundary condition, Eq. A15, is derived from the assumption that diffusional resistances external to the pellet are negligible.

For convenience and broader application, the above equations are expressed in terms of dimensionless parameters as follows:

1. For the main and coking reactions (from Eqs. A11 and A12):

$$\frac{1}{x_p^2}\frac{\partial}{\partial x_p} D x_p^2 \frac{\partial y_p}{\partial x_p} - h_A^2 (1 - q_p)^M y_p - h_q^2 \varepsilon \frac{\partial y_p}{\partial \theta_p} = 0 \tag{A16}$$

$$\frac{\partial q_p}{\partial \theta_p} = (1 - q_p)^N y_p \tag{A17}$$

2. For catalyst porosity and effective diffusivity (from Eqs. A4–A6):

$$\varepsilon = 1 - \gamma q_p \tag{A18}$$

$$\lambda = \lambda_0/\varepsilon^{1/2} \tag{A19}$$

$$D = \beta \varepsilon e^{-4.6\lambda} \tag{A20}$$

3. For initial and boundary conditions (from Eqs. A13–A15):

$$\text{at } \theta_p = 0 \quad \text{and} \quad 0 \leq x_p \leq 1, \qquad y_p = 1,\ q_p = 0,\ \varepsilon = 1, \quad \text{and} \quad D = 1 \tag{A21}$$

$$\text{at } x_p = 0 \quad \text{and} \quad \theta_p > 0, \qquad \frac{\partial y_p}{\partial x_p} = 0 \tag{A22}$$

$$\text{at } x_p = 1 \quad \text{and} \quad \theta_p > 0, \qquad y_p = 1 \tag{A23}$$

Effectiveness factors for the main and coking reactions, η_A and η_q, defined as the ratios of the actual reaction rates at time θ_p to the maximum reaction rates on a clean catalyst without diffusional limitations can be calculated from the following equations:

$$\eta_A = \frac{\int_0^{r_e} k_A (1 - q_p)^M C_{Ap} (4\pi r^2) dr}{\frac{4}{3}\pi r_e^3 k_A C_{Ab}} = 3\int_0^1 (1 - q_p)^M y_p x_p^2 dx_p \tag{A24}$$

$$\eta_q = \frac{\int_0^{r_e} k_q (1 - q_p)^N C_{Ap} (4\pi r^2) dr}{\frac{4}{3}\pi r_e^3 k_q C_{Ab}} = 3\int_0^1 (1 - q_p)^N y_p x_p^2 dx_p \tag{A25}$$

These effectiveness factors are indications of the catalyst pellet performance under a coking environment. In the absence of deactivation, the effectiveness factor can be expressed as a function of Thiele modulus. In the presence of deactivation, the catalyst effectiveness factor can be expressed as a function of coke content and Thiele modulus when the coke is the only deactivation parameter. Alternatively, the effectiveness factor can be expressed as a function of Thiele modulus and time on stream since coke content is in turn a function of time on stream.

Mass Balance Over the Reactor Bed

The mass balance for the main reactant, A, over the fixed-bed reactor can be written as:

$$FC_{Ab}|_z - FC_{Ab}|_{z+\Delta z} + S\Delta z\, \rho_b R_{A,\text{obs}} = S\, \Delta z\, \varepsilon_b \frac{\partial C_{Ab}}{\partial t} \tag{A26}$$

where FC_{Ab} is the mass rate of A passing in the z direction through a cross face at z position. The term $S\, \Delta z\, \rho_b R_{A,\text{obs}}$ and the term $S\, \Delta z\, \varepsilon_b\, \partial C_{Ab}/\partial t$ are the rates of reaction and accumulation, respectively, of A in a disk of thickness Δz. Division by $S\Delta z$ and letting $\Delta z \to 0$ gives:

$$-\frac{F}{S}\frac{\partial C_{Ab}}{\partial z} + \rho_b R_{A,\text{obs}} = \varepsilon_b \frac{\partial C_{Ab}}{\partial t} \tag{A27}$$

For pseudofirst-order reaction, the observed reaction rate can be written as:

$$R_{A,\text{obs}} = -k_A \eta_A C_{Ab} \tag{A28}$$

Substituting Eq. A28 into A27, yields:

$$-\frac{F}{S}\frac{\partial C_{Ab}}{\partial z} - \rho_b k_A \eta_A C_{Ab} = \varepsilon_b \frac{\partial C_{Ab}}{\partial t} \tag{A29}$$

Since the coke is assumed to deposit on the catalysts, no flow of coke is possible. The mass balance for the first-order, coking reaction in a fixed-bed reactor can thus be written directly as:

$$\frac{\partial Q_b}{\partial t} = k_{q,\text{obs}} C_{Ab} = k_q \eta_q C_{Ab} \tag{A30}$$

with initial conditions

$$\text{at } t = 0 \quad \text{and} \quad 0 \leq z \leq L, \qquad C_{Ab} = C_{Af}, \quad \text{and} \quad Q_b = 0 \tag{A31}$$

and boundary conditions

$$\text{at } z = 0 \text{ and } t > 0, \qquad C_{Ab} = C_{Af} \tag{A32}$$

In terms of dimensionless form, Eqs. A29–A32 can be written as:

$$\frac{\partial y_b}{\partial \theta_b} + E\frac{\partial y_b}{\partial x_b} + G\eta_A y_b = 0 \tag{A33}$$

$$\frac{\partial q_b}{\partial \theta_b} = \eta_q y_b \tag{A34}$$

$$\text{at } \theta_b = 0 \quad \text{and} \quad 0 \leq x_b \leq 1,$$
$$y_b = 1 \quad \text{and} \quad q_b = 0 \tag{A35}$$
$$\text{at } x_b = 0 \quad \text{and} \quad \theta_b > 0,$$
$$y_b = 1 \tag{A36}$$

Equations A16 through A25 and A33 through A36 were solved simultaneously using a numerical method to obtain activity profiles and concentration profiles, both within catalyst pellets and reactor beds as functions of time on stream, as shown in the main text.

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