Effect of Nonuniform Activity on Hydrodemetallation Catalyst

A model is developed to qualitatively predict the effect of a nonuniform activity distribution on the total quantity of metal deposited in hydrodemetallation catalysts. A fixed catalyst support system is assumed and no restrictions are placed on local or overall catalytic activity in seeking an optimal solution that maximizes the amount of contaminant metal deposition over the useful catalyst life. Results indicate that deposition capacity could be substantially increased by a nonuniform activity profile in which the activity at the catalyst center is higher than that at the outer edge. The shape of the optimum activity profile is presented along with practical design improvements.

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Introduction

Hydrotreating capacity and technology for the processing of heavy crude oils has increased over recent years, due in part to an increase in the availability of heavy crude oil. The processing of heavy crudes requires removal of various heteroatoms including metals. These heteroatoms are removed to prevent pollution and poisoning of downstream catalysts. Hydrodemetallation (HDM) catalysts are used to remove contaminant metals.

The bottom fraction or residuum of distilled crudes is typically processed in trickle bed reactors at temperatures of 350 to 450°C and pressures of 5,000 to 15,000 kPa (700 to 2,200 psig). Under these conditions metals deposit within the pores of and deactivate HDM catalyst. The optimum HDM catalyst design will result in the largest quantity of metal deposition over the useful catalyst life, which ends when some limiting observed metal removal rate is reached.

Metal deposits in the catalyst pores hinder reactant diffusion. The final stage of catalyst deactivation has been attributed to diffusion limitations in the pore mouth which limit reactant accessibility to the interior of the catalyst (Dautzenberg et al., 1978; Tamm et al., 1981; Hung et al., 1986). Deposition capacity could be increased if metals could be more uniformly deposited throughout the catalyst.

Past efforts to improve HDM catalysts include pore size optimization, which increases the rate of diffusion with respect to the rate of intrinsic reaction, and catalyst shape improvement, which decreases the effective size of catalysts. However, little consideration has been given to a third means of catalyst improvement: activity profile optimization. Catalyst life as well as deposition capacity could be increased by the implementation of a nonuniform activity profile. A center-loaded activity profile would allow the diffusion rate to increase relative to the intrinsic reaction rate in the pore mouth, while maintaining a high level of activity in the catalyst interior.

In the present study, we develop a model in which activity may be varied along the radius of a spherical catalyst. Changes in the local diffusion rate due to metal deposition are also included in the model. A finite-difference scheme is used to obtain numerical solutions that are in good agreement with those predicted through perturbation analysis. Optimal activity profiles are approximated and are presented along with practical catalyst design improvements.

For the class of catalytic deposition reactions considered here, the optimum catalyst performance is obtained by a center-loaded activity profile. When the limiting observed rate of reaction R_{min} is arbitrarily small, the optimum profile would be curved, having a second derivative d^2k/dr^2 that is positive. As diffusion limitations increase, the amount of curvature in the optimum activity profile will also increase.

Industrial catalysts are replaced when R_{min} reaches some finite value. In this case, the optimum activity profile, although similar in other respects to the arbitrarily small R_{min} case, decreases sharply as it approaches the outer edge of the catalyst. Results indicate that existing HDM catalysts might be markedly improved by simply lowering the activity near the catalyst edge. Specifically, a 25% increase in deposition capacity over the optimum uniform activity case was predicted for HDM catalysts when the uniform activity profile was reduced by 60% at the catalyst edge.

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Comparison with literature data shows that uniform activity model results are in good agreement with experimental results for unimodal pore size HDM catalysts. Spherical catalysts with a unimodal pore size distribution were modeled. Industrial HDM catalysts, however, have various shapes and pore size distributions. Nevertheless, the deposition capacity of any practical uniform activity catalyst can be increased by the introduction of a nonuniform activity profile. In cases where strong diffusion limitations exist, deposition capacity might be substantially increased.

Experimental determination of the effect of deposition on the activity profile is needed before the design improvement of nonuniform activity can be analyzed on a case-specific basis.

Background

Hydrometallation catalysts remove metals from resid oil. This type of catalyst may be used upstream of a more easily deactivated hydrodesulfurization (HDS) catalyst to improve the overall performance and catalyst life.

Neilsen et al. (1981) demonstrated experimentally that the use of an HDM catalyst guard bed could improve overall performance when heavy residual feedstocks are processed. Reactor system performance was compared on the basis of equal sulfur conversion. A substantially longer catalyst life was observed when an HDM catalyst was used in combination with HDS catalyst.

HDM catalysts are designed to withstand a high level of metal deposition while maintaining a reasonable level of metal removal activity. Efforts to improve catalyst performance have traditionally fallen into three categories: catalyst shape improvement, pore size optimization, and catalyst activity optimization.

Catalyst shapes that reduce diffusion limitations while maintaining a reasonably low reactor pressure drop include Unocal's clover leaf, AKZO Chemie/Ketjen's asymmetric quadrolobe, Chevron's bumpy oval, and W. R. Grace's minilith or spoked extrudate (Quann et al., "Catalytic Hydrodemetallation of Petroleum," unpublished).

Pore size optimization has been considered from both experimental (Hardin et al., 1978; Nielsen et al., 1981; Plumail et al., 1983; Shimura et al., 1986) and theoretical points of view. Many investigators have modeled the deactivation of hydrotreating catalysts. Early efforts include those of Newson (1975), who modeled deposition as uniform and extending to a calculated pore depth, and Dautzenberg et al. (1978), who correlated the reduction of pore mouth cross-sectional area to catalyst activity. Rajagopalan and Luss (1979) developed a model to predict the optimum unimodal pore size for maximum initial and lifetime HDM activity. Nitta et al. (1979) developed a model that includes both coke and metal deposition. Agrawal (1980) modeled the HDM of porphyrins in unimodal and bimodal pore catalysts. Results indicated that bimodal catalysts may have a higher initial activity and longer life than unimodal catalysts. More recent modeling efforts include the work of Smith (1983), which emphasized the importance of metal compound exclusion from small pores; Leung and Haynes (1983), which demonstrated the importance of macroporosity; Ahn and Smith (1984), which contrasted the effects of surface poisoning and pore mouth plugging on HDS activity; and Shimura et al. (1986), in which the influence of pore mouth plugging on HDM activity was considered. None of the above studies considered catalysts with an initial nonuniform distribution of activity.

The nonuniform distribution of catalytic activity has been reviewed by Lee and Aris (1985) and Komiyama (1985), and by Dougherty and Verykios (1987). Little consideration, however, has been given to the case of hydrometallation catalysts.

The activity of hydrotreating catalysts to metal removal may be varied by the use of dopants. Ware and Wei (1985) found halogen dopants to increase the rate of demetallation and alkali dopants to decrease the rate of demetallation of nickel porphyrins.

Hung et al. (1986) have compared catalysts of differing uniform initial surface activity and found metal deposition to be more uniform in catalysts with lower activity. These authors also note that a noniuniform activity could be obtained by varying the amount, type, or distribution of catalytically active materials or other chemical modifiers on the catalyst surface.

Catalyst Performance

In deposition processes where changes in catalyst pore geometry are slow in comparison to the rate of reaction and diffusion, the concentration profile within the catalyst may be described as pseudosteady state. In this analysis of first-order deposition kinetics, the species conservation balance for a spherical pellet

$$SkC = \frac{\rho_O}{\rho_C}\frac{d}{r^2 dr}\left(r^2 De\frac{dC}{dr}\right) \tag{1}$$

with boundary conditions

$$\frac{dC}{dr} = 0 \qquad r = 0 \tag{2}$$

$$C = C_R \qquad r = R \tag{3}$$

is assumed valid at any instant in time.

The local rate of deposition is

$$\left(\frac{\partial M}{\partial t}\right)_r = SkC \tag{4}$$

Intrinsic kinetics are assumed to be unaffected by deposition, and diffusion is assumed to be a strictly decreasing function of deposition quantity.

The observed rate of reaction averaged over a spherical pellet,

$$R_{obs} = \frac{\int_o^R SkCr^2\,dr}{\int_o^R r^2\,dr} \tag{5}$$

decreases with time as the quantity of deposition increases and the diffusion rate decreases. HDM catalysts, among others, are usually replaced when their observed rate of reduction reaches some limiting value R_{min}, at which time t_u, the useful catalyst life, is defined to end. The limiting observed rate is typically reached before total deactivation occurs.

We compare theoretically aged catalysts on the basis of total deposition M_{tot}. We deviate from the traditional basis of constant total activity since the economic objective in HDM catalyst design is to increase deposition capacity, rather than to decrease the amount of catalytic material required to achieve a given conversion.

For a spherical pellet,

$$M_{tot} = \frac{\int_0^R Mr^2\,dr}{\int_0^R r^2\,dr} \tag{6}$$

Combining Eqs. 4, 5, and 6 yields the total deposition over the useful catalyst life:

$$M_{tot}(t_u) = \int_0^{t_u} R_{obs}\,dt \tag{7}$$

Optimum catalyst performance is defined as that which yields the maximum total deposition over the useful catalyst life.

Another useful variable to describe aged catalyst is the ratio of total deposition to the maximum local deposition. Tamm et al. (1981) compared catalysts on the basis of this ratio, which they designated the distribution factor θ:

$$\theta = \frac{M_{tot}}{M_{max}} \tag{8}$$

The distribution factor will be small when the deposition profile is skewed toward the pore mouth and may reach a maximum of one when deposition is uniform. A qualitative estimate of θ may be obtained from the modified Thiele modulus

$$\phi = R\sqrt{\frac{\rho_c k_o S_f}{\rho_o D_f}} \tag{9}$$

Large values of ϕ will result in small values of θ, while very small values of ϕ will result in a θ closer to unity.

Uniform activity

We will consider the case of a uniform-activity profile first. In accordance with Eq. 1, when diffusion limitations exist the maximum reactant concentration will be at the outer edge of the catalyst. Therefore, the point of maximum deposition, or pinch point, will be located at the outer edge of the catalyst in the pore mouth. The deposition thickness in the pore mouth, δ, may be calculated from

$$\delta = \frac{kC_R t}{\rho_D} \tag{10}$$

As shown in Figure 1, when the pore mouth is constricted to the size of the reactant molecule,

$$\delta = r_p - r_m \tag{11}$$

When pore mouth plugging occurs, diffusion through the pore mouth ceases and the catalyst becomes inactive. Combining Eqs. 10 and 11 yields the time to completely deactivate the catalyst:

$$t_p = \frac{\rho_D(r_p - r_m)}{kC_R} \tag{12}$$

Catalysts that are overly active or have small pores will die quickly and therefore perform poorly. Low-activity catalysts may be too inactive to perform well, Figure 2.

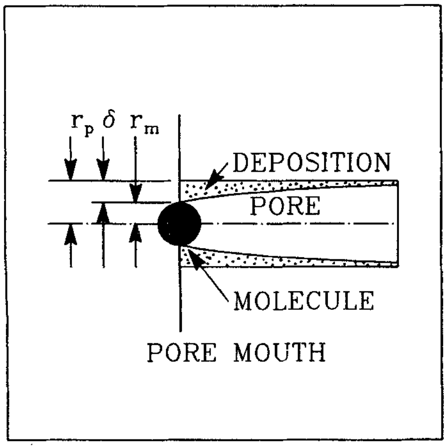

Figure 1. Pore mouth plugging.

Nonuniform activity

The case of nonuniform-activity profiles and arbitrarily small R_{min} will be considered here. In the uniform activity case, the pinch point is located at the outer edge of the catalyst. Increasing the activity above that of the optimum uniform activity case at the catalyst edge would accelerate catalyst failure and decrease $M_{tot}(t_u)$. In contrast, the introduction of a center-loaded activity profile could compensate for low reactant concentration at the catalyst center and increase the amount of deposition.

Increasing the level of activity in the catalyst interior can shift

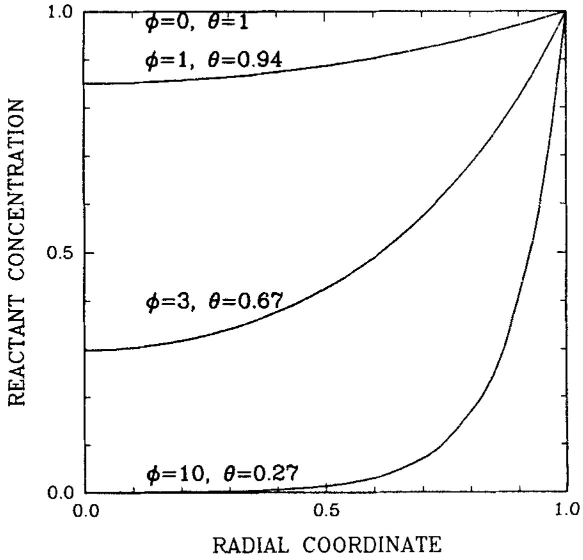

Figure 2. Effect of ϕ on initial concentration and initial distribution factor θ in a spherical catalyst pellet.

the pinch point from the catalyst edge toward the center. Diffusion through the pinch point is limited, yielding catalyst to the inside of this point relatively inaccessible. It follows from Eqs. 5 and 7 that the catalyst must fill with deposition from the center outward to maximize R_{obs} and consequently M_{tot} over the useful catalyst life. The optimum activity profile will therefore result in an initial pinch point at the center of the catalyst.

The reactant concentration profile monotonically decreases toward the catalyst center, and the second derivative of concentration with respect to the radial coordinate, d^2C/dr^2, is positive. The optimum activity profile must therefore monotonically increase toward the catalyst center and have a second derivative, d^2k/dr^2, that is positive. Otherwise, the catalyst will develop a noncentral pinch point. In addition, since the curvature of the concentration profile will increase with diffusion limitations, the curvature of the optimum activity profile should also increase with diffusion limitations.

A nonuniform activity profile is especially desirable when strong diffusion limitations exist, since the potential gain in M_{tot} is large.

To illustrate the effects of a nonuniform activity distribution in a more quantitative manner, and provide an analytical comparison for our numerical results, we will consider a catalyst with a linear k profile. Since R_{min} is arbitrarily small, the useful catalyst life may be described by Eq. 12. A uniform surface activity of k_o will be compared to the surface activity distribution

$$k = k_o[1 + \epsilon(1 - 2\hat{r})] \tag{13}$$

where the perturbation parameter, ϵ, is small. Figure 3 describes several activity distributions resulting from Eq. 13. Large ϵ profiles are not relative to our perturbation analysis and will be discussed later.

For convenience, we introduce

$$\hat{C} = C/C_R \tag{14}$$

$$\hat{r} = r/R \tag{15}$$

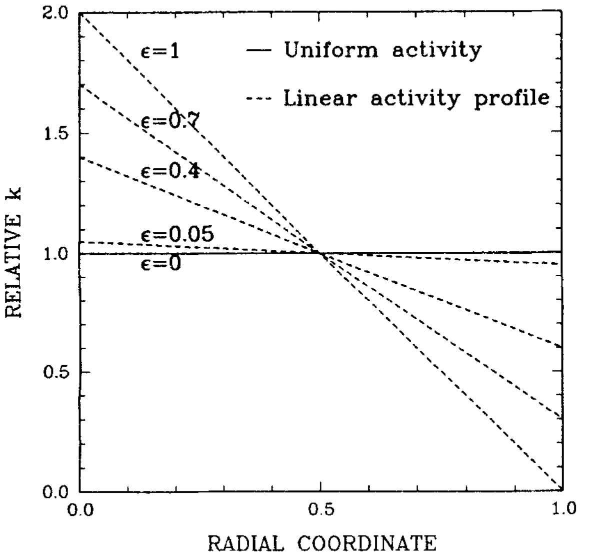

Figure 3. Effect of perturbation parameter ϵ on activity profile.

The initial concentration profile may be calculated from the species conservation balance

$$[1 + \epsilon(1 - 2\hat{r})]\hat{C} = \frac{1}{\phi^2\hat{r}^2}\frac{d}{d\hat{r}}\left(\hat{r}^2\frac{d\hat{C}}{d\hat{r}}\right) \tag{16}$$

$$\frac{d\hat{C}}{d\hat{r}} = 0 \qquad \hat{r} = 0 \tag{17}$$

$$\hat{C} = 1 \qquad \hat{r} = 1 \tag{18}$$

We assume the solution to be a regular perturbation expansion of the form

$$\hat{C} = C_o + \epsilon C_1 + O(\epsilon^2) \tag{19}$$

subject to the boundary conditions

$$\frac{dC_o}{d\hat{r}} = 0, \frac{dC_1}{d\hat{r}} = 0 \qquad \hat{r} = 0 \tag{20}$$

$$C_o = 1, C_1 = 0 \qquad \hat{r} = 1 \tag{21}$$

Substitution of Eqs. 19, 20, and 21 into Eq. 16 yields

$$C_o = \frac{\sinh(\phi\hat{r})}{\hat{r}\sinh(\phi)} \tag{22}$$

$$C_1 = \left[\frac{1}{2\sinh(\phi)}\right] \cdot \left[\sinh(\phi\hat{r}) - \frac{\sinh(\phi\hat{r})}{\hat{r}} + (1 - \hat{r})\phi\cosh(\phi\hat{r})\right] \tag{23}$$

Figure 4 compares the first perturbation concentration C_1 and the unperturbed concentration C_0. At small ϕ, C_1 is negligible in

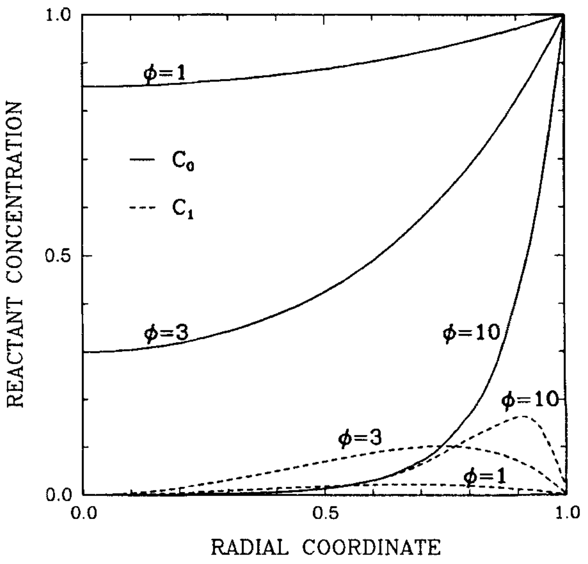

Figure 4. Effect of ϕ on unperturbed concentration C_o and first perturbation concentration C_1.

$\epsilon = 0.05$

comparison to C_0; therefore, the impact on $\hat{C}$ of an $O(\epsilon)$ nonuniformity in activity will be substantially less than $O(\epsilon)$. The local rate of deposition

$$\left(\frac{\partial M}{\partial t}\right)_r = k_o[1 + \epsilon(1 - 2\hat{r})]SC \qquad (24)$$

will, therefore, undergo a fractional change of $O(\epsilon)$. As ϕ increases, C_1 increases with respect to C_0. Introduction of an $O(\epsilon)$ nonuniformity in the activity still results in some shift in the deposition rate, however. As shown in Figure 5, the rate of deposition will decrease in the pore mouth by $O(\epsilon)$ and increase at the catalyst center.

The result of this shift in deposition will be a fractional increase in θ and $M_{tot}(t_u)$ of $O(\epsilon)$, provided ϕ is at some intermediate value.

Deactivation Model

A model describing demetallation in a spherical, nonuniform-activity HDM catalyst was developed. Several investigators have observed the rate of metal removal to be first order with respect to metal concentration (Larson and Beuther, 1966; Chang and Silvestri, 1974; Spry and Sawyer, 1975; Dautzenberg et al., 1978; Riley, 1978; Pazos et al., 1981; Galiasso and Morales, 1983; Higashi et al., 1985). More complex reaction mechanisms have also been observed which may cause a local deposition maximum just inside the pore mouth. A first-order isothermal reaction was assumed. A unimodal pore size catalyst was modeled, and the pseudosteady state approximation was made. This approximation is justified by the slow rate of pore size change with respect to the rates of diffusion and reaction.

The species conservation balance given in Eq. 1 was solved by a finite-difference method with the boundary conditions given in Eqs. 2 and 3. In cases where deposition blocked reactant transport within the catalyst, the zero concentration gradient boundary condition was applied at the point of blockage.

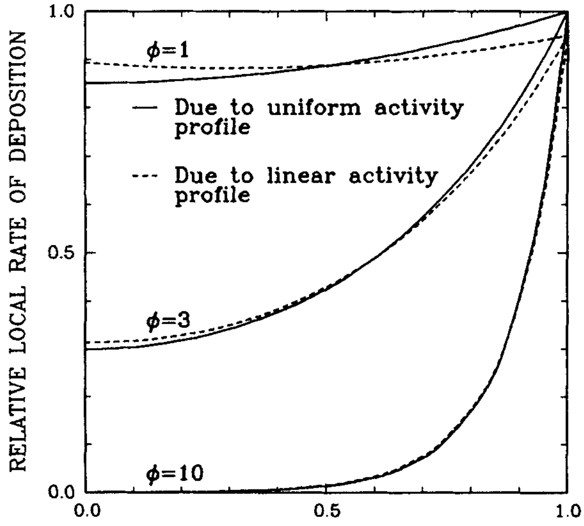

Figure 5. Local rate of deposition for uniform and linear activity profiles.

$\epsilon = 0.05$

Metal deposition has been shown to be catalytically active to hydrodemetallation (Dautzenberg et al., 1978; Takeuchi et al., 1985; Higashi et al., 1985). Little information is available, however, to quantify the effect of deposition on activity. For simplicity, we assume the intrinsic activity per unit surface area to be unaffected by deposition. The intrinsic reaction rate was adjusted only for the loss of surface area due to deposition.

At high hydrogen partial pressure, coke deposition may reach a steady state relatively early in the life of the catalyst (Dautzenberg et al., 1978; Nielsen et al., 1981). The deposition of coke was assumed to be steady state in the model.

A restricted diffusion mechanism has been observed for the diffusion of large molecules, such as metal-containing compounds, in hydrotreating catalyst and support (Spry and Sawyer, 1975; Prasher et al., 1977; Chantong 1982). Restricted diffusion occurs when diffusing molecules are of the same order of magnitude size as catalyst pores. Spry and Sawyer correlated initial activity data for nine hydrotreating catalysts and obtained

$$D_e = \frac{D_b}{\tau}\mu[1 - \lambda]^4 \qquad (25)$$

Effective diffusivities were calculated according to Eq. 25, and the pore radius was adjusted locally within the catalyst to account for metal deposition. Metal deposition was assumed to be impervious and to coat the pore walls. Coke deposition was assumed to be of a constant total volume and pore diameters used in the model are the effective diameters after coke deposition.

The amount of metal deposition was determined at equally spaced radial coordinates after each time interval from the reaction rate equation

$$\Delta M = SkC\Delta t \qquad (26)$$

Surface activity for demetallation was varied as a function of the dimensionless catalyst radius $\hat{r}$, and held constant over the life of the catalyst.

Parameter Estimation

A spherical catalyst of 1.27×10^{-3} m (1/20 in.) dia. was modeled. The catalyst was assumed to have a unimodal pore size distribution. The average pore diameter after coke deposition was varied from 1×10^{-8} to 2×10^{-8} m (100 to 200 Å).

The fresh catalyst surface area was estimated from hydrotreating catalyst data in order to combine the effects of pore volume and pore diameter changes. Surface area was calculated

Table 1. Physical Properties of Fresh Hydrotreating Catalyst*

Catalyst	Surface Area m^2/g	Pore Volume cm^3/g	Avg. Pore Diam.** Å
E	219	0.57	104
A	194	0.60	124
F	125	0.54	173

*From Johnson (1985)

**Calculated from surface area and pore volume data from the correlation

$$S_f = d_p(-1.37 \times 10^{13}) + 3.626 \times 10^5 \qquad (27)$$

Equation 27 was developed from data for fresh Haldor Topsoe hydrotreating catalyst taken from the thesis of Johnson (1985) and listed in Table 1. Equation 27 has a correlation coefficient of -0.997.

A heavy residue feed stock was modeled. An average molecule diameter of 6.0×10^{-9} m was estimated for metal-containing species from the work of Hall and Herron (1981). Metal deposition was assumed to have a density of 2,420 kg metal/m^3.

The effective diffusivity was modeled according to the correlation of Spry and Sawyer (1975), given by Eq. 25, who estimated the value of $D_b\mu/\tau$ to be 3×10^{-12} m^2/s. Other researchers, such as Newson (1970), have estimated the effective diffusivity to be faster. The value of $D_b\mu/\tau$ was varied from 1×10^{-12} to 1×10^{-10} m^2/s for comparison.

Catalyst life was defined to end when the instantaneously observed overall rate of demetallation fell below a limiting value R_{min} of 10 wt. % metal/yr.

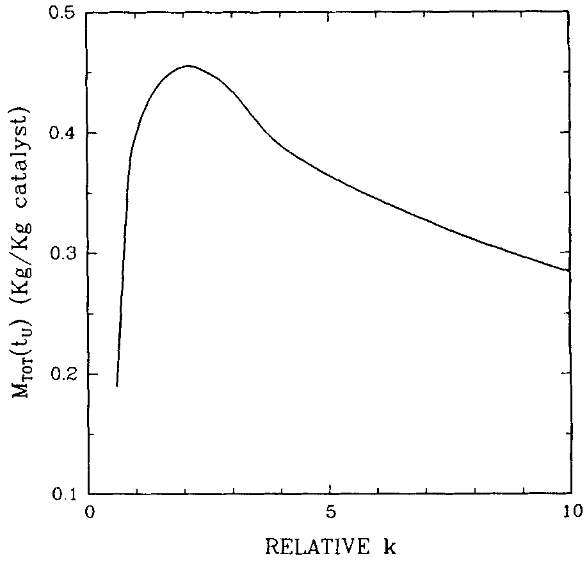

Figure 6. Total quantity of metal deposition $M_{tot}(t_u)$ vs. uniform intrinsic rate constant k.

All k are compared at their respective optimum pore diameters $D = 1$, $R_{min} = 10$ wt. % metal/yr

Model Results

The deposition capacity of HDM catalysts with various activity distributions was examined. Optimal catalyst performance was defined as that which yielded a maximum quantity of metal deposition over the useful catalyst life. Results are reported in terms of ϕ, relative k, and relative diffusivity D, since any multiple of a given k, D_e, R_{min} set will yield identical model results. The relative diffusivity D was taken as $D_b\mu/\tau \times 10^{-11}$ m^2/s, and the relative k was taken as $k/2.78 \times 10^{-8}$ kg oil/m^2 s.

Uniform activity

Uniform-activity catalysts were first optimized in order to have an equitable comparison with nonuniform-activity catalysts. Model results were also compared with experimental data in the literature.

Intrinsic rate constants k were compared at their respective optimum pore diameters to determine the optimum combination of k and pore diameter for a given D. R_{min} was held constant throughout the analysis of uniform-activity catalysts.

Figure 6 illustrates how the optimum k was determined at a D of 1. When k is too large, pore mouth plugging reduces θ and catalyst life. When k is too small the observed rate falls quickly below R_{min} as the catalyst ages.

Figure 7 describes the relation of $M_{tot}(t_u)$, θ, and the optimum pore diameter to ϕ in optimized uniform-activity catalysts. At each D, ϕ was calculated from the optimum k and d_p. The modified Thiele modulus, ϕ, increases with diffusion limitations; therefore, $M_{tot}(t_u)$ and θ decrease and the optimum pore diameter increases.

Model-generated values of θ and initial activity of the catalyst, calculated at a ϕ of 4, agree well with those reported in the literature. In comparing model results to those in the literature, all model parameters except pore diameter were set equal to those for an optimized ϕ of 4. Total metal deposition $M_{tot}(t_u)$ was also in good agreement with reported values.

Hung et al. (1986) observed that vanadium distribution factors for unimodal pore size cylindrical catalysts increased from roughly 0.2 to 0.6 when the relative pore diameter was doubled. Model results predict an increase in θ from 0.2 to 0.6 when the pore size is increased from 1.05×10^{-8} to 1.97×10^{-8} m (105 to 197 Å). A direct comparison at specific operating conditions is not possible, however, since operating conditions and catalyst age were not reported.

Several researchers have compared the initial vanadium removal activity of hydrotreating catalysts according to their average pore diameter. An average pore diameter in the range of 1.4×10^{-8} to 1.8×10^{-8} m was found to have the highest initial activity by Plumail et al. (1983). Similar results were observed

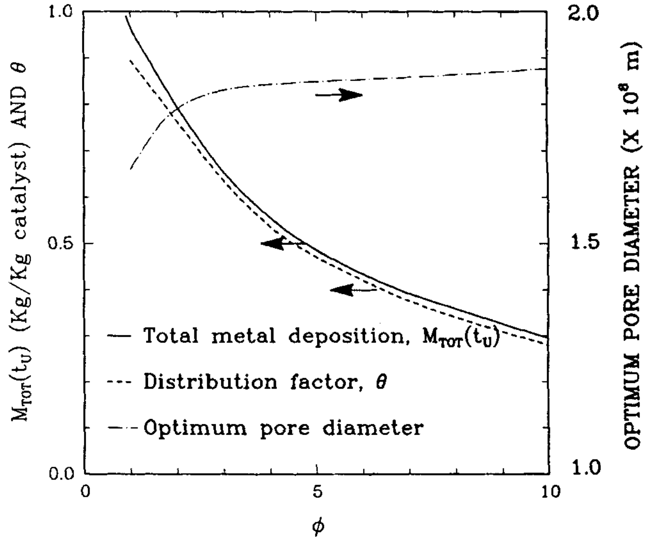

Figure 7. Total quantity of metal deposition, distribution factor, and optimum pore diameter dependence on ϕ in optimized uniform-activity catalysts.

$R_{min} = 10$ wt. % metal/yr

by Hardin et al. (1978) and Shimura et al. (1986) in catalysts with a less narrow pore size distribution. The model predicted the maximum initial activity to occur at 1.6×10^{-8} m.

Total metal deposition calculated by the model agrees well with that reported by Higashi et al. (1985), which was over 100 wt. % metal deposition for a relatively uniform deposition profile. The model predicts metal deposition in excess of 100 wt. % for a θ of roughly 0.9 to 1, depending on the pore diameter.

Nonuniform activity

Catalysts with linear and optimum activity profiles were compared to uniform-activity catalysts. As predicted, $M_{tot}(t_u)$ and θ were increased by the use of a nonuniform-activity profile. Small deviations from uniform activity were first considered for comparison with our perturbation analysis.

A linear activity profile, described by Eq. 13, was numerically perturbed. In accordance with our perturbation analysis, an $O(\epsilon)$ deviation in the linear activity profile resulted in an $O(\epsilon)$ change in $M_{tot}(t_u)$ at intermediate values of ϕ, and smaller changes in $M_{tot}(t_u)$ at very large or very small values of ϕ.

Although the perturbation analysis does not apply at large ϵ, some of the conclusions drawn from that analysis do. As ϵ is increased, the rate of deposition relative to the uniform case will increase at the catalyst center and decrease by $O(\epsilon)$ at the outer edge.

Figures 3 and 8 describe the shift in activity and corresponding shift in the metal deposition profile as a function of ϵ. In Figure 8, curves calculated at an ϵ of 0.7 and 1 are similar in that both have a characteristic S shape. Deposition profiles have a discontinuous derivative at the catalyst center because modeled activity profiles have a discontinuous derivative there. The decrease in deposition between the catalyst center and pinch point could be eliminated by the use of a curved activity profile in which d^2k/dr^2 is positive.

Optimum activity profiles were approximated through a numerical variation technique. Activity was varied on a ten-point grid along the catalyst radius. The activity profile was defined as optimum when a 1 to 500% variation in activity at any single point did not increase $M_{tot}(t_u)$ by more than 0.1%. Single-point optimum profiles were determined since the ten-point optimal solution is intractable. Catalyst activity was optimized at several reactant diffusion rates. Catalyst performance was then compared to the optimum uniform-activity case at each diffusion rate. The optimum profile will depend on how catalyst activity changes with deposition, as well as the catalyst pore structure, catalyst shape and size, catalyst location in the reactor, reactor operating conditions, and feed stock composition. With the

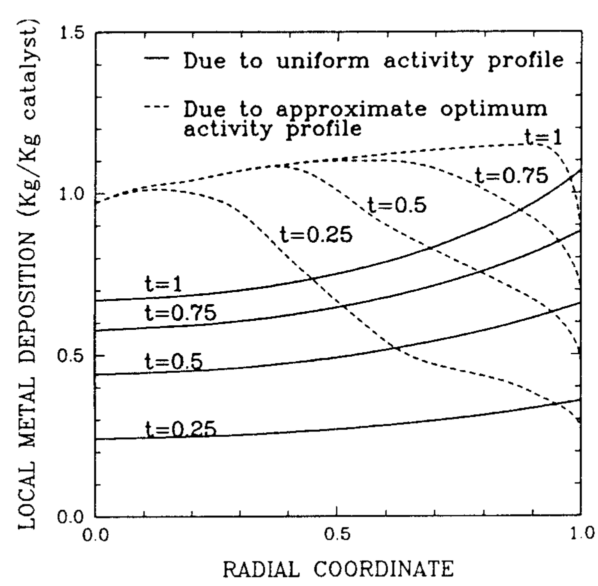

Figure 9. Metal deposition profiles resulting from optimum uniform and approximate optimum activity profile.

$D = 10$; $R_{min} = 10$ wt. % metal/yr

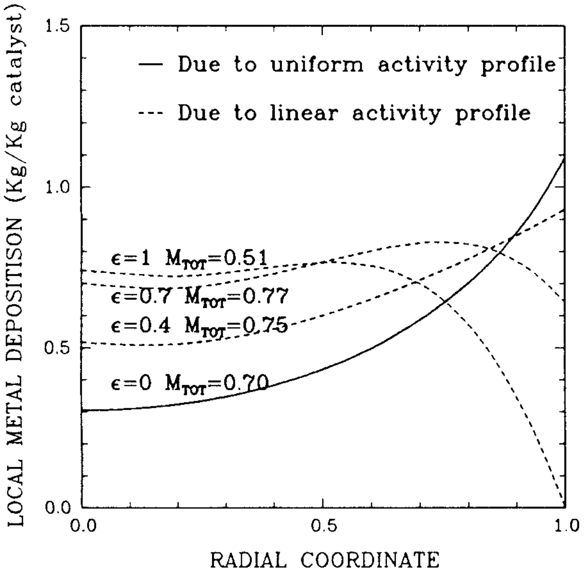

Figure 8. Effect of ϵ on local quantity of deposition at end of useful catalyst life.

$\phi = 3$; $d_p = 1.80 \times 10^{-8}$ m; $R_{min} = 10$ wt. % metal/yr

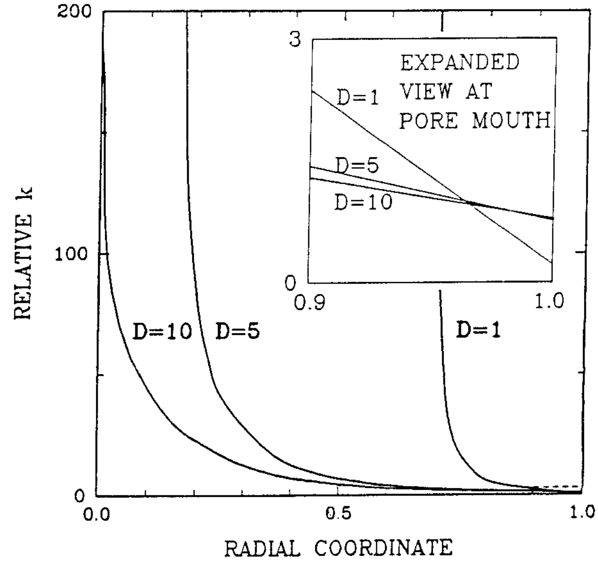

Figure 10. Comparison of approximate optimum-activity profiles.

$R_{min} = 10$ wt. % metal/yr

exception of activity, all model parameters were set equal to those of the corresponding uniform-activity case.

Metal deposition capacity was dramatically increased by activity profile optimization. Figure 9 describes the metal deposition profiles for the approximate optimum-activity and uniform-activity cases calculated at a relative diffusivity D of 10. Time is normalized with respect to the useful catalyst life. In the optimum-activity case, the maximum amount of deposition initially occurred at the catalyst center. The catalyst filled with deposition from the center outward. In the uniform-activity case pore mouth plugging occurred. Some discrepancy between the true optimum and our approximation of the optimum-activity profile is evident from the deposition profile. Our approximation resulted in a slight decrease of deposition in the center region of the catalyst. The true optimum-activity profile would result in a deposition profile that is flat near the catalyst center.

Figure 10 describes optimum-activity profiles approximated at a D of 10, 5, and 1. The optimum activity at a D of 1 is extremely high near the catalyst center and exceeded our computational ability. As predicted, the optimum-activity profiles increased monotonically toward the catalyst center. The ratio of activity at the catalyst center to activity at the outer edge increased with diffusion limitations, as did the curvature of the optimum profile. In contrast to our earlier analysis at an arbitrarily small R_{min}, a sharp decline in the optimum activity near the outer edge of the catalyst was predicted for a finite R_{min} of 10 wt. % metal/yr. The second derivative of the optimum profile, d^2k/dr^2, was positive except in the small region near the outer edge of the catalyst where activity decreased sharply.

Implementation of optimum-activity profiles may not be practical since it requires high activity at the catalyst center. In contrast, simply reducing the activity at the catalyst edge may be implemented easily and would also increase $M_{tot}(t_u)$. Uniform-activity profiles were reduced at the catalyst edge for a D of 10, 5, and 1.5, resulting in 9, 13, and 25% increases in $M_{tot}(t_u)$ over the optimum uniform-activity cases, respectively. The case of D equal to 1.5 is of particular interest since the optimum uniform activity at a D of 1.5 corresponds to a ϕ of 4. As described earlier, industrial HDM catalysts were best modeled at a ϕ of 4.

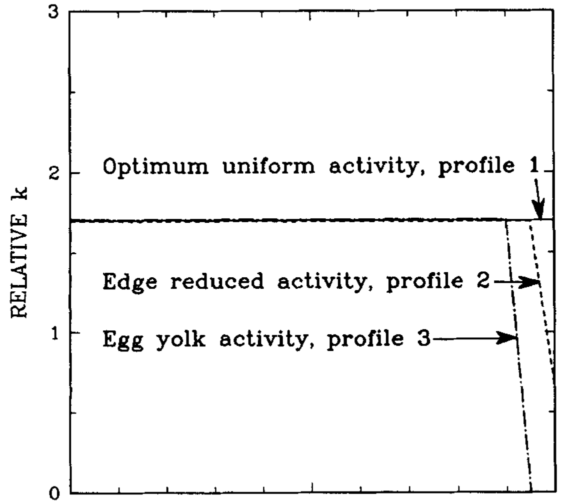

Figure 11. Uniform, edge-reduced, and egg yolk activity profiles.

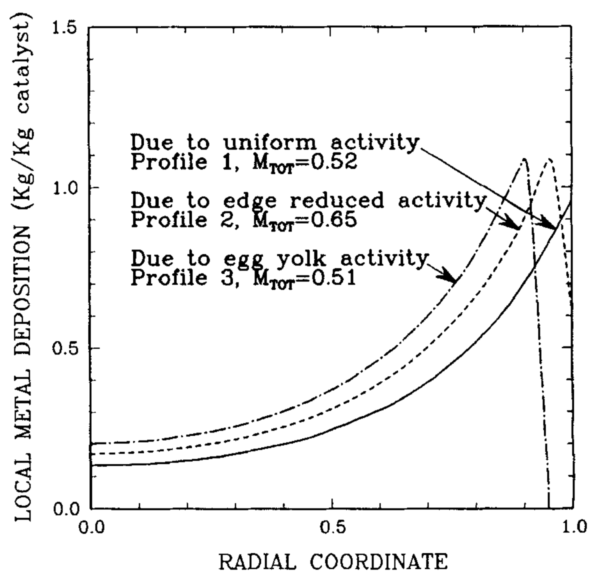

Figure 12. Metal deposition profiles resulting from uniform, edge-reduced, and egg yolk activity profiles shown in Figure 11.

$D = 1.5$; $d_p = 1.86 \times 10^{-8}$ m; $R_{min} = 10$ wt. % metal/yr.

To further explore the effect of edge-reduced activity on HDM catalyst performance, we examine the case of D equal to 1.5 in more detail. Activity profiles described in Figure 11 were modeled. Numerical calculations were made on a 20-node grid.

Profile 2 in Figure 11 is an edge-reduced profile, meaning that the activity is reduced only at the outer edge of the catalyst. Profile 3 will be referred to as an egg yolk profile since the catalyst is active in the center, or egg yolk, portion and not active in the outer, or egg white, region. Egg yolk profiles have been made with nickel, as well as other metals, in alumina pellets through competitive adsorption techniques (Komiyama, 1985). Edge-reduced activity profiles might be made in a similar manner.

Figure 12 describes the local metal deposition profiles that resulted from the uniform, edge-reduced, and egg yolk activity profiles described in Figure 11. Profile 2, an edge-reduced case, resulted in an interior pinch point and increased $M_{tot}(t_u)$ by 25% over profile 1, the optimum uniform-activity case. Egg yolk profiles also move the pinch point to the catalyst interior; however, these profiles underutilize the egg white portion of the catalyst. Profile 3 reduced $M_{tot}(t_u)$ by 2%.

A final consideration in the optimization of the activity profile is the effect of deposition on activity. Since the uniform-activity case must result in pore mouth plugging, the optimum activity profile will be nonuniform whether the activity is increased, decreased, or unchanged by deposition. Optimum performance will be obtained in catalysts that are more active at the center than at the outer edge.

Notation

C = concentration of reactant, kg/kg oil
C_R = concentration of reactant at $r = R$, kg/kg oil
C_o = unperturbed concentration
C_1 = first perturbation concentration
$\hat{C}$ = dimensionless concentration

D = relative diffusivity
D_b = bulk diffusivity of reactant, m^2/s
D_e = effective diffusivity of reactant, m^2/s
D_f = effective diffusivity in fresh catalyst, m^2/s
d_p = pore diameter, m
k = intrinsic rate constant of demetallation, kg oil/$m^2 \cdot s$
k_o = average intrinsic rate constant, Eq. 13, kg oil/$m^2 \cdot s$
M = mass of local metal deposition, kg metal/kg cat
ΔM = mass of local metal deposition per unit time, kg metal/kg cat
M_{max} = maximum mass of local metal deposition, kg metal/kg cat
M_{tot} = total mass of metal deposition as averaged over entire catalyst, kg metal/kg cat
r = radial coordinate, m
$\hat{r}$ = dimensionless radial coordinate
r_m = molecule radius, m
r_p = pore radius, m
R = catalyst radius, m
R_{min} = limiting observed rate of reaction, kg metal/kg cat $\cdot$ s
R_{obs} = observed rate of reaction, kg metal/kg cat $\cdot$ s
S = surface area of catalyst, m^2/kg cat
S_f = fresh catalyst surface area, m^2/kg cat
t = time, s
Δt = unit time interval, s
t_p = potential catalyst life, s
t_u = useful catalyst life, s
V_p = pore volume, m^3/kg cat

Greek letters

δ = deposition thickness in pore mouth, m
ϵ = perturbation parameter, or deviation in linear activity distribution at $r = R$
θ = distribution factor
λ = ratio of molecular to pore radius
μ = catalyst porosity
ρ_c = catalyst density, kg/m^3
ρ_D = deposit density, kg/m^3
ρ_o = oil density, kg/m^3
τ = catalyst tortuosity
ϕ = modified Thiele modulus

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