Local Effective Diffusivity in a Pellet Deactivated by Multilayer Coking

Hong H. Lee
Dept. of Chemical Engineering, Seoul National University, Seoul 151-742, Korea

A relationship is developed for the change in local effective diffusivity with coking using the models available for effective diffusivity. When this relationship is combined with the earlier multilayer kinetic model, the local effective diffusivity becomes dependent solely on the fraction of catalyst deactivated. Experimental procedures developed determine the relationship for the local effective diffusivity. These results provide a framework for a consistent and systematic treatment of the complex deactivation-diffusion problem caused by coking and coke growth. Unique aspects of coking are accounted for through the fraction of catalyst deactivated, which is the basic quantity for catalytic activity, rather than the coke content.

Introduction

There are two principal aspects of coking that differ from other types of catalyst deactivation. One is the manner in which the amount of coke deposits affects catalytic activity. As opposed to poisoning in which the catalytic activity decreases linearly with the amount of poison due to the monolayer nature of poisoning, the catalytic activity decreases nonlinearly with the amount of coke. This nonlinear relationship has been the subject of many studies (Froment and Bischoff, 1961; Weekman, 1968; Wojchiechowski, 1968; Dumez and Froment, 1976; Reiff and Kittrell, 1980) since the early work of Voorhies (1945). The fact that catalyst still retains its residual activity even when the amount of coke deposited is in far excess of that required for "monolayer" coverage is perhaps the most convincing example of the nonlinearity.

The other unique aspect of coking is its effect on the diffusion limitation. As the coke grows, the pores in the pellet get filled, and this filling process can eventually lead to complete pore blockage. The dual difficulties of dealing with the active sites coverage by coke deposits and the diffusion-limitation caused by coking are perhaps the reasons why the studies in coking have been empirical. The interrelated nature of the deactivation and the diffusion-limitation makes it very difficult to describe the deactivation-diffusion in a systematic and consistent way. Such a treatment of the deactivation-diffusion requires two basic ingredients: a relationship between catalytic activity and amount of coke deposits, and another between effective diffusivity and amount of coke deposits.

The intrinsic relationship between catalytic activity and the amount of coke deposits, which is applicable in the absence of diffusion limitation, has been developed (Klingman and Lee, 1986) based on a multilayer kinetic model. The kinetic model, which accounts for the multilayer nature of coke growth is applicable in its concept and approach to any type of coking, although the specific results are applicable to a class of coking in which an energetically uniform surface is involved in both the main and coking reactions.

In this article, we develop the other ingredient required to analyze the deactivation-diffusion problem, namely, the effect of coking on effective diffusivity. For this, we examine the use of effective diffusivity in the deactivation-diffusion problem as related to the measurement of the effective diffusivity and to the mass flux. This examination leads to the conclusion that position-dependent effective diffusivity is the proper one to use as opposed to the usual, overall effective diffusivity determined from a diffusion cell such as Wicke-Kallenbach chamber. The need for the position-dependent diffusivity has also been raised in biological problems (Kuhn et al., 1993). We then raise the central question in the deactivation-diffusion, namely, how the position-dependent effective diffusivity is affected by coking and how this should be related to the catalytic activity as affected by coking. In order to use the position-dependent effective diffusivity, however, there must be a way of determining the effective diffusivity experimentally. Therefore, we present a framework for experimental procedures for such a determination.

Coking and Effective Diffusivity

It is well known that effective diffusivity decreases with coking. Since the decrease is due to the coke accumulated on catalyst surface and this coke deposit occupies the pore volume which otherwise is available for the transport of reaction species, we may assume that the decrease in the pore volume due to coking is equal to the volume corresponding to the amount of deposited coke. Haldemann and Botty (1959) are perhaps the first who experimentally showed that the volume occupied by coke deposits was about the same as the observed reduction in pore volume. Thus, we may set the volume occupied by coke deposits equal to the reduction in pore volume:

$$V(\epsilon_o-\epsilon)=\frac{C_c}{100\rho_c} \tag{1}$$

where ϵ_o and ϵ are the catalyst pellet porosities for fresh and coked catalyst respectively, V is the pellet volume per unit weight, C_c is the coke content in weight percent with respect to the pellet weight, and ρ_c is the coke density. Equation 1 can be rewritten as:

$$\frac{\epsilon}{\epsilon_o}=1-\alpha C_c; \quad \alpha=\frac{1}{100V\rho_c}\equiv\frac{1}{(C_c)_s} \tag{2}$$

where $(C_c)_s$ is the saturation coke content corresponding to the amount required to fill the initial pore volume per unit weight of fresh catalyst pellet. Although this relationship has been obtained for the whole pellet, it should also be applicable to any point in the pellet.

The change in the pellet porosity due to coking in turn can be related to the corresponding change in the diffusivity through the models already available for effective diffusivity. If we use a simplified version of the model due to Feng and Stewart (1973), the ratio of the diffusivity for coked catalyst D_e to that for fresh catalyst D_{e_o} is:

$$\frac{D_e}{D_{e_o}}=\frac{\epsilon/\kappa}{\epsilon_o/\kappa_o} \tag{3}$$

where κ is the tortuosity factor and the subscript o is for fresh, uncoked catalyst. The tortuosity factor represents correction for the diffusion path length along the pores which is greater than the measurable pellet thickness mainly due to their "zigzag" nature, although constrictions also play a role. Thus, the tortuosity factor may be assumed to be the same whether the pellet is coked or not since the same pellet is involved, for which the pore orientation is the same. In fact, for completely random pores, the model of Feng and Stewart leads to the tortuosity factor depending solely on the pore orientation. Under the assumption, Eqs. 2 and 3 give:

$$\frac{D_e(z)}{D_{e_o}}=1-\alpha C_c(z) \tag{4}$$

This result shows that the normalized effective diffusivity decreases linearly with the coke content. Here again, the relationship holds at any point z in the pellet. If we use the random pore model of Wakao and Smith (1964), on the other hand, the diffusivity ratio is given by:

$$\frac{D_e}{D_{e_o}}=\left[\frac{\epsilon}{\epsilon_o}\right]^2 \tag{5}$$

If we combine Eqs. 2 and 5, the local diffusivity is given by:

$$\frac{D_e(z)}{D_{e_o}}=[1-\alpha C_c(z)]^2 \tag{6}$$

We have seen that the exponent for the dependence of effective diffusivity on the coke content comes from the dependence of effective diffusivity on porosity. Although the simplified version of the model due to Feng and Stewart leads to the exponent of unity when the effect of coking on the tortuosity factor is neglected and the random pore model of Wakao and Smith leads to the exponent of two, a semi-empirical form applicable in general may be written as:

$$\frac{D_e(z)}{D_{e_o}}=\left[\frac{\epsilon}{\epsilon_o}\right]^\beta=[1-\alpha C_c(z)]^\beta \tag{7}$$

This form results in the model of Feng and Stewart if the tortuosity factor ratio is included in Eq. 3 as a power of (ϵ/ϵ_o). While the local effective diffusivity can be expressed in terms of the local coke content C_c, the average effective diffusivity cannot be expressed in terms of the total coke content of the pellet, as we shall soon see. According to the multilayer kinetic model (Klingman and Lee, 1986), the local coke content $C_c(z)$ normalized with respect to its "monolayer" coke content Q is related to the fraction of catalyst deactivated γ for the case of infinite number of layers allowed by:

$$\frac{C_c(z)}{Q}=\gamma(z)\left[1+\frac{\gamma}{\overline{K}_p(1-\gamma)}\right] \tag{8}$$

where

$$\overline{K}_p=\frac{k_{p_c}}{k_p}\frac{1}{[1+G(C)]^n} \tag{9}$$

Here k_{p_c} is the rate constant for the formation of monolayer coke, k_p is the rate constant for the formation of multilayer coke, C is the concentration of main reactant, and $(1+G)^n$ is the term for reactant/product inhibition. For the more rigorous case of finite number of layers N, we have:

$$\frac{C_c}{Q}=\gamma\left[\frac{1}{1-f}-\frac{Nf^N}{1-f^N}\right] \tag{10}$$

where:

$$f=\frac{1}{1+\overline{K}_p(1-\gamma)/\gamma} \tag{11}$$

The position-dependent, local effective diffusivity is thus given by Eqs. 7, and 8 or 10 with its position dependence determined by the fraction of catalyst deactivated γ and the product inhibition term.

Direct measurements of gas-effective diffusivities have been made as a function of coke content by several investigators (Ozawa and Bischoff, 1968; Suga et al., 1967; Butt et al., 1975). The measurement of effective diffusivity often involves the use of a diffusion cell such as the Wicke-Kallenbach chamber, which gives an overall effective diffusivity for a catalyst pellet. Consider the relationship between this overall effective diffusivity and the local effective diffusivity. Determination of the overall effective diffusivity $(D_e)_p$ from a diffusion cell (Wicke-Kallenbach cell) involves the following relationship:

$$-(D_e)_p\left[\frac{C_e-C_i}{H}\right]=N \tag{12}$$

where H is the pellet length in the direction of diffusion, N is the measured flux, and C_e and C_i are the concentration of diffusing species at the top and bottom of the pellet, respectively. For the constant diffusivity assumed, the concentration profile is linear and Eq. 12 holds. If we let the diffusivity be dependent on the position z, we have in place of Eq. 12:

$$-D_e(z)\frac{dC}{dz}=N \tag{13}$$

Since the measured flux N is the same in both cases, Eqs. 12 and 13 can be combined and then integrated with respect to z to give:

$$\frac{1}{(D_e)_p}=\frac{1}{H}\int_0^H\frac{1}{D_e(z)}dz \tag{14}$$

This relationship between the experimentally determined overall effective diffusivity $(D_e)_p$, which is not even an average diffusivity, and the local diffusivity clearly shows that the experimental overall effective diffusivity does not reveal any information on the nature of the local diffusivity unless coking is uniform. For instance, the fact that the overall effective diffusivity changes linearly with the total coke content of the pellet does not necessarily mean that the local diffusivity also changes linearly with the local coke content. In fact, one would expect that the overall effective diffusivity $(D_e)_p$ would change nonlinearly with the total pellet coke content if the local diffusivity changes linearly with the local coke content, as can be seen by substituting Eq. 4 into 14, since the total pellet coke content is the local coke content integrated over z. Only when the coking occurs uniformly throughout the pellet would the overall diffusivity reveal the nature of the local effective diffusivity.

Diffusion-Reaction in Pellets Deactivated by Multilayer Coke

Consider deactivation-diffusion taking place in a slab-like pellet for the following reaction:

$$A \xrightarrow{k} B \quad \text{main reaction}$$

In general, the intrinsic rate of a structure-insensitive main reaction can be written as follows:

$$r_c=k(1-\gamma)g_1[C,K] \tag{15}$$

where g_1 represents the dependence of the rate on the main reactant concentration C and equilibrium constant K. The rate at which the fraction of catalyst deactivated γ changes with time is given by:

$$r_p=k_{p_c}(1-\gamma)g_2[C,K] \tag{16}$$

where g_2 represents the dependence of the rate on C and K. Then the conservation equations are:

$$\frac{d}{dz}\left[D_e(z)\frac{dC}{dz}\right]=k(1-\gamma)g_1[C,K] \tag{17}$$

$$\frac{d\gamma}{dt}=k_{p_c}(1-\gamma)g_2[C,K] \tag{18}$$

where the effective diffusivity is given by:

$$D_e(z)=D_{e_o}\left\{1-\alpha Q\gamma\left[1+\frac{\gamma}{\overline{\overline{K}}_p(1-\gamma)}\right]\right\}^{\beta} \tag{19}$$

This relationship results from Eqs. 7 and 8 for the case of infinite number of layers allowed. The global rate is simply:

$$R_G=-\frac{1}{L}\overline{D}_e\frac{d\overline{C}}{dz} \tag{20}$$

where the overbar denotes the quantities evaluated at the pellet surface and L is the characteristic pellet length. For structure-insensitive reactions and those structure-sensitive reactions in which coking is random, which are being considered, the activity factor A defined as the ratio of the rate of reaction of coked catalyst to that for fresh catalyst is simply:

$$A=1-\gamma \tag{21}$$

in the absence of diffusional effect. Otherwise, the activity factor is given by:

$$A=R_G/(R_G)_f \tag{22}$$

where $(R_G)_f$ is R_G for the fresh catalyst.

The equations are rendered dimensionless to give:

$$\frac{d}{dy}\left(D(y)\frac{du}{dy}\right)=\phi^2(1-\gamma)G_1[u,K] \tag{23}$$

$$\frac{d\gamma}{d\tau}=\mu(1-\gamma)G_2[u,K] \tag{24}$$

$$D(y)=\left\{1-\lambda_\gamma\left[1+\frac{\gamma}{\overline{\overline{K}}_p(1-\gamma)}\right]\right\}^{\beta} \tag{25}$$

$$r_G=-\overline{D}\frac{d\overline{u}}{dy} \tag{26}$$

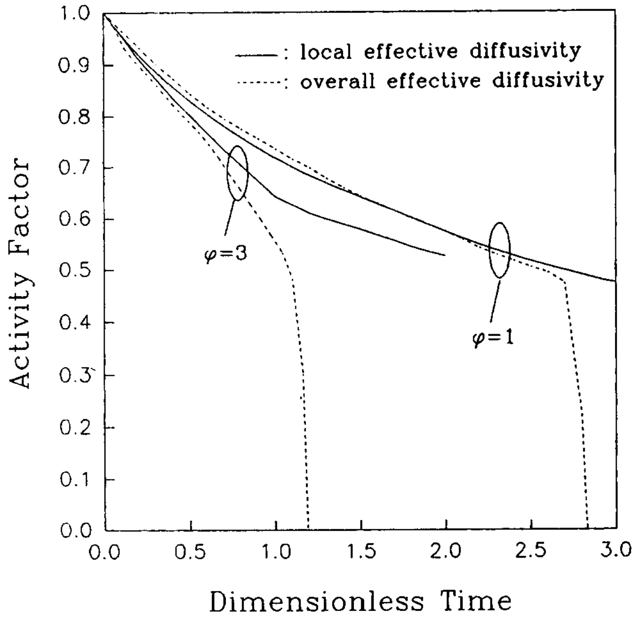

Figure 1. Catalytic activity based on: local effective diffusivity (——) vs. overall effective diffusivity (·····) for pore blockage at pore core.

$\phi = 1$ or 3, $\mu = 2$, and $\lambda = 0.02$. See Table 1 for β and $\overline{K}_p$.

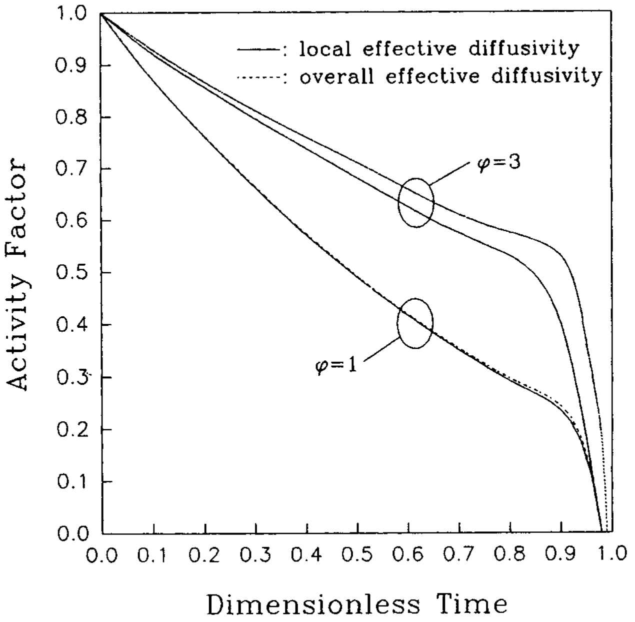

Figure 2. Catalytic activity based on: local effective diffusivity (——) vs. overall effective diffusivity (·····) for pore blockage at pore mouth.

$\phi = 1$ or 3, $\mu = 2$, and $\lambda = 0.02$. See Table 1 for β and $\overline{K}_p$.

where

$$D(y) = D_e(y)/D_{e_0}, \quad y = \frac{z}{L}, \quad u = \frac{C}{C_s}, \quad \tau = \frac{t}{t_r}$$

$$\phi^2 = \frac{L^2 k g_1[C_s, K]}{D_{e_0} C_s}, \quad \mu = t_r k_{p_c} g_2[C_s, K], \quad \lambda = \alpha Q$$

$$G_1 = \frac{g_1[C, K]}{g_1[C_s, K]}, \quad G_2 = \frac{g_2[C, K]}{g_2[C_s, K]}, \quad r_G = \frac{R_G}{(D_{e_0} C_s / L^2)} \qquad (27)$$

Here, t_r is a reference time, ϕ is the usual Thiele modulus for fresh catalyst, and C_s is the surface concentration.

To evaluate the sensitivity of the results to the usual treatment of the diffusion-reaction problem, we consider a simple case in which $g_1 = g_2 = C$ which corresponds to pore-mouth closure since the main reactant is the coke precursor. Another case considered is for $g_1 = C$ and $g_2 = C_p$ where C_p is the concentration of a product formed from a parallel side reaction, which is the coke precursor. This leads to pore-core blockage. Simulation results for pore blockage at the mouth and the core are shown in Figures 1 and 2. Dimensionless parameters used in the simulation are given in Table 1. For both cases, simulation was carried out using first the position-dependent effective diffusivity and then the effective diffusivity integrated according to Eq. 14 to obtain the overall effective diffusivity $(D_e)_p$, which would be the value determined from a diffusion cell, for use in the simulation for the case of constant effective diffusivity.

The inadequacy of using the overall effective diffusivity is most dramatic when the pore blockage is localized at the core, as shown in Figure 1 in which the rate of reaction for deactivated catalyst normalized with respect to the rate for fresh catalyst (activity factor) is given as a function of time on-stream. When the pore blockage occurs at the core, the overall effective diffusivity as determined by a diffusion cell is zero, and the rate for the deactivated catalyst is also zero if we use the overall effective diffusivity in writing the pellet mass balance. This is shown in Figure 1 as the dotted line. It is seen that the rate becomes zero as the normalized time exceeds 1.2 if we use the overall effective diffusivity. As pointed out earlier, much of the catalyst in the pores is still accessible to reactants even when the blockage occurs at the core, and thus the rate is far from zero, as shown by the solid line in Figure 1 for the position-dependent effective diffusivity. The same holds regardless of the initial Thiele modulus and the dimensionless parameters, μ and λ. A larger value of either λ or μ results in a shorter time at which the core blockage occurs.

Although Figure 1 does not show the asymptotic value of the activity for the local diffusivity model, the activity declines gradually with time and then reaches zero activity as the pore core blockage progresses toward the pore mouth and the pore mouth closes. The same trend holds regardless of Thiele modulus value.

Table 1. Parameters Used in the Simulation

Symbol	Value
ϕ	varied
β	1
$\overline{K}_p$	0.1
λ	varied
μ	varied

The contrast is not dramatic when the pore blockage is localized at the mouth, as shown in Figure 2. In general, the rate calculated on the basis of overall effective diffusivity is larger than that calculated on the basis of position-dependent effective diffusivity. As shown in the figure, the difference between the two cases, that is, local and overall effective diffusivity, gets larger with larger initial Thiele modulus, the difference being almost negligible for $\phi = 1$.

The simulation results given in Figure 1 sufficiently demonstrate the inadequacy of using the overall effective diffusivity when the pore blockage occurs at the core. Thus, any correlation relating the experimentally determined overall effective diffusivity to total coke content would not serve a useful purpose in describing the deactivation-diffusion in this case. In order to use the local effective diffusivity $D_e(z)$, however, there has to be an independent experimental method of determining $D_e(z)$. This independent determination is extremely difficult to make and this difficulty perhaps explains why there are no published results for the local effective diffusivity, verified by an independent experimental method. We develop in the following section experimental procedures for determining the local effective diffusivity $D_e(z)$.

Determination of Local Effective Diffusivity, $D_e(z)$

Determination of the local effective diffusivity involves the parameters α and β in Eq. 7. Experimental determination of the local effective diffusivity and the local coke content as a function of the pellet position z is very difficult, if not impractical, and thus the parameters of α and β cannot be identified readily. Given this fact, an alternative is to determine experimentally the local effective diffusivity at one point in the pellet and then use the result to identify the parameters.

The local effective diffusivity is rewritten in a more suitable form than Eq. 7 as follows with the aid of Eqs. 7 and 8:

$$D_e(z) = D_{e_o}\left\{1 - \alpha Q\gamma\left[1 + \frac{\gamma}{\overline{K}_p(1-\gamma)}\right]\right\}^{\beta} \tag{28}$$

Since the parameters Q and $\overline{K}_p$ are known from the data of activity vs. total coke content obtained under diffusion-free conditions, which are detailed elsewhere (Klingman and Lee, 1986), the problem is again that of determining α and β. The definition of α, which is the inverse of the total coke content required to fill the pores, enables one to determine α from the measurements of porosity and total coke content. Thus the problem is simply that of determining β. Suppose that the local effective diffusivity at the pellet surface $\overline{D}_e$ and the local value of γ at the pellet surface $\overline{\gamma}$ are known. Then, we have from Eq. 19:

$$\ln \overline{D}_e = \ln D_{e_o} + \beta \ln\left\{1 - \alpha Q\overline{\gamma}\left[1 + \frac{\overline{\gamma}}{\overline{K}_p(1-\overline{\gamma})}\right]\right\} \tag{29}$$

A ln-ln plot of Eq. 29 should yield β as its slope.

Consider the usual Wicke-Kallenbach cell for the determination of $\overline{D}_e$. Equation 13 still applies for the diffusion experiment; if we integrate this equation by parts, we get:

$$-\overline{D}_e(\overline{C}_i - C_e) + \int_0^H C\frac{dD_e}{dz}dz = NH \tag{30}$$

since the coke profile is symmetric such that $\overline{D}_e$ is the same at both ends of the pellet. Suppose that we carry out the experiments for two different gases A and B with a common gas for the binary diffusion of A or B in the common gas. If we let the *square root* of the molecular weight ratio of A to B be M, Graham's law for binary diffusion gives:

$$M = \frac{\overline{D}_{eB}}{\overline{D}_{eA}} = \frac{D_{eB}}{D_{eA}} \tag{31}$$

An inherent assumption here is that the effective diffusivities of A and B are the same function of z. If we write Eq. 30 for A and B, we have:

$$-\overline{D}_{eA}(C_{Ai} - C_{Ae}) + \int_0^H C_A\frac{dD_{eA}}{dz}dz = N_A H \tag{32}$$

$$-M\overline{D}_{eA}(C_{Bi} - C_{Be}) + M\int_0^H C_A\frac{dD_{eA}}{dz}dz = N_B H \tag{33}$$

where $d(D_{eB})/dz = Md(D_{eA})/dz$ according to Eq. 31. Equation 13 can also be rewritten as $dC/dz = -N/D_e$ and, upon integration, yields:

$$C_A - C_{Ae} = -N_A\int_0^z \frac{dz}{D_{eA}} \tag{34}$$

$$C_B - C_{Be} = -N_B\int_0^z \frac{dz}{D_{eB}} \tag{35}$$

Equations 34 and 35 can be combined to give:

$$\frac{M}{N_B}(C_B - C_{Be}) = \frac{1}{N_A}(C_A - C_{Ae}) \tag{36}$$

This relationship can be used in Eq. 33 so that Eqs. 32 and 33 can be solved for $\overline{D}_{eA}$, yielding:

$$\overline{D}_{eA} = \frac{(N_A - N_B)H}{(C_{Ai} - C_{Ae}) - M(C_{Bi} - C_{Be})} \tag{37}$$

It is seen that the measurements of concentrations and fluxes in two experiments involving two gases of differing molecular weight yield the effective diffusivity at the pellet surface. This diffusivity can be converted to $\overline{D}_e$ with the aid of Eq. 31 applied to the species of interest and the gas A.

The value of $\overline{\gamma}$ corresponding to $\overline{D}$ (or $\overline{D}_e$) can be obtained using the data in the initial stage of coking under diffusion-limited reaction conditions. According to the result by Lee (1981), the flux at the pellet surface is given by:

$$\begin{aligned}\overline{D}_e\frac{dC}{dz} &= \left[2\overline{D}_e(1-\overline{\gamma})\int_0^{C_s} r(C)dC\right]^{1/2}\\ &= \left[2\overline{D}_e(1-\overline{\gamma})\int_0^{C_s} kg_1[C, K]dC\right]^{1/2}\end{aligned} \tag{38}$$

Thus, the observed rate (which is equivalent to the flux in Eq.

38) as a function of time yields $\overline{D}_e(1-\overline{\gamma})$ as a function of time. This result along with the effective diffusivity given by Eq. 37 at various times on-stream in turn provides $\overline{\gamma}$ for the determination of local effective diffusivity.

Conclusions

Coking is unique in that the catalyst still retains its activity even when the amount of coke deposits is in excess of the amount that is needed for complete coverage of active sites. Further, coking induces diffusion limitation as the coke deposits build up in the pores of catalyst pellet, eventually leading to complete pore blockage. These two unique features make it very difficult to analyze the deactivation-diffusion caused by coking in a systematic and consistent way based on physically meaningful models. Therefore, empirical relationships have been used, which are not always consistent with respect to the two unique aspects of coking in dealing with the deactivation-diffusion problem.

A model for the local effective diffusivity, which is based on the models due to Feng and Stewart (1973) and Wakao and Smith (1964), has been obtained to represent the change of the local diffusivity with local coke content. When this is combined with the multilayer kinetic model developed earlier, the local effective diffusivity is given in terms of the fraction of catalyst deactivated, which is the basic quantity representing the local catalytic activity. The overall effective diffusivity for coked catalyst, which is usually determined in a diffusion cell, has been shown to be inadequate in dealing with the deactivation-diffusion problem. Further, a correlation between the overall effective diffusivity and total pellet coke content would not serve any useful purpose in analyzing the deactivation-diffusion. Thus, there is a need to develop a relationship for the local effective diffusivity. Determination of such a relationship in an independent experiment is extremely difficult since it involves the measurements of the local effective diffusivity and coke content as a function of pellet position. Experimental procedures have been devised for such a determination.

The framework developed here for the deactivation-diffusion caused by coking allows one to deal with the deactivation problem in a systematic and consistent way and opens the way to an *a priori* modeling, which has not been possible due to the complexity caused by coke growth. The simplification made possible by the multilayer kinetic model and the model for the local effective diffusivity allows one to describe the coking effects solely in terms of the fraction of catalyst deactivated.

Notation

C_A = concentration of species A in the pellet placed in diffusion cell
C_{A_e} = C_e for species A
C_{A_i} = C_i for species A
C_b = bulk fluid value of C
C_B = concentration of species B in the pellet placed in diffusion cell
D = dimensionless effective diffusivity defined in Eq. 27
D_e = local effective diffusivity; pellet effective diffusivity in the absence of diffusion-limitation
$\overline{D}_e$ = D_e at the pellet surface
D_{e_A} = D_e for species A
D_{e_B} = D_e for species B
f = quantity defined by Eq. 11
G_1, G_2 = dimensionless form of G defined in Eq. 27
k = rate constant for main reaction
n = constant in Eq. 9
N_A = flux for species A
N_B = flux for species B
r_c = rate of main reaction
r_G = dimensionless global rate defined in Eq. 27
r_p = rate given by Eq. 16
R_G = global rate for r_c
u = dimensionless concentration of the main reactant defined in Eq. 27
y = dimensionless coordinate defined in Eq. 27
z = pellet coordinate

Greek letters

α = $1/(C_c)_s$
β = constant exponent in Eq. 7
γ = fraction of catalyst deactivated
$\overline{\gamma}$ = γ at pellet surface
γ_o = γ for fresh catalyst
κ_o = κ for fresh catalyst
τ = dimensionless time defined in Eq. 27

Superscript

$-$ = evaluated at pellet surface

Literature Cited

Butt, J. B., S. Delgado-Diaz, and W. E. Muno, "Effects of Coking on the Transport Properties of H-Mordenite," *J. Catal.*, **37**, 158 (1975).

Dumez, F. Z., and G. F. Froment, "Dehydrogenation of 1-Butene into Butadiene: Kinetics, Catalyst Coking, and Reactor Design," *Ind. Eng. Chem. Proc. Des. Dev.*, **15**, 291 (1976).

Feng, C. F., and W. E. Stewart, "Practical Models for Isothermal Diffusion and Flow of Gases in Porous Solids," *Ind. Eng. Chem. Fund.*, 12, 143 (1973).

Froment, G. F., and K. B. Bischoff, "Nonsteady-State Behavior of Fixed Bed Catalytic Reactors due to Catalyst Fouling," *Chem. Eng. Sci.*, **16**, 189 (1961).

Haldemann, R. G., and M. C. Botty, "On the Nature of Carbon Deposit of Cracking Catalysts," *J. Phys. Chem.*, **63**, 489 (1959).

Klingman, K. J., and H. H. Lee, "Catalyst Deactivation by Multilayer Coking: A Kinetic Model," *AIChE J.*, **32**, 309 (1986).

Kuhn, R., S. Peretti, and D. Ollis, "Acid Inhibition of Immobilized Cells—Quantitative Comparison of Model and Experiment," *Appl. Biochem. Biotech.*, **39**, 401 (1993).

Lee, H. H., "Generalized Effectiveness Factor for Pellets with Nonuniform Activity Distribution," *Chem. Eng. Sci.*, **36**, 192 (1981).

Mesamune, S., and J. M. Smith, "Performance of Fouled Catalyst Pellets," *AIChE J.*, **12**, 384 (1966).

Ozawa, Y., and K. B. Bischoff, "Coke Formation Kinetics on Silica-Alumina Catalyst," *Ind. Eng. Chem. Proc. Des. Dev.*, **7**, 67 (1968).

Reiff, E. K., Jr., and J. R. Kittrell, "Use of Active Site Balance for Catalyst Deactivation Models," *Ind. Eng. Chem. Fund.*, **19**, 128 (1980).

Suga, K., Y. Morita, E. Kunigita, and T. Odake, "Deterioration of Catalysts for the Dehydrogenation of *n*-Butane due to Diffusion in Particles," *Int. Chem. Eng.*, **7**, 742 (1967).

Szepe, S., and O. Levenspiel, *Proc. Eur. Fed., Chem. Reaction Eng.*, Pergamon, London (1970).

Voorhies, A., "Carbon Formation in Catalytic Cracking," *Ind. Eng. Chem.*, **37**, 318 (1945).

Wakao, N., and J. M. Smith, "Diffusion and Reaction in Porous Catalysts," *Ind. Eng. Chem. Fund.*, **3**, 123 (1964).

Weekman, V. W., Jr., "Optimum Operation-Regeneration Cycles for Fixed-Bed Catalytic Cracking," *Ind. Eng. Chem. Proc. Des. Dev.*, **17**, 252 (1968).

Manuscript received July 19, 1993, and revision received Jan. 4, 1994.