Subscripts

c = cooling medium
f = feed
g = gas phase
i = gas-liquid interface
L = top of gas-liquid mixture in the column
l = liquid phase
lb = lower bound
ub = upper bound

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Diffusional Influences on Deactivation Rates

The interrelation between internal diffusion and concentration-independent deactivation is examined using a simple mathematical model. Analytical procedures are developed for evaluating the performance of single catalyst particles in the presence of diffusion and deactivation. By incorporating time-dependent effectiveness factors in design equations, reactor performance under the combined influence of diffusion and deactivation is predicted. By analogy to the effectiveness factor for non-deactivating systems, the concept of a deactivation effectiveness factor is introduced.

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SCOPE

The design and operation of catalytic reactors are complicated by the phenomenon of catalyst deactivation, whereby the catalyst activity decreases with time on-stream. Furthermore, for reactors utilizing solid catalysts, the presence of mass transfer limitations will have a significant effect on the time scale of decay of catalyst activity. Consequently, an analysis of deactivation data which ignores the masking effects of diffusional limitations will lead to erroneous measurements of deactivation rate constants. Levenspiel (1972) showed that for diffusion-free systems, simple analytical conversion-time relationships exist that predict the behavior of batch and continuous reactors experiencing concentration-independent decay.

However, the bulk of the existing literature on reactor design, under the combined influences of both diffusion and deactivation, deals with computer solutions of theoretical models that are so complex that ease of interpretation is lost. The purpose of the present work is to show that simple analytical conversion-time relationships, similar to those presented by Levenspiel for diffusion-free systems, can be developed for reactors operating under the combined influence of concentration-independent deactivation and diffusional limitations.

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CONCLUSIONS AND SIGNIFICANCE

The behavior of single catalyst particles can be described by means of an analytical expression that relates the catalytic effectiveness to the conventional Thiele modulus and time on-stream. More importantly, it is shown that this analytical relationship for the time-dependent catalytic effectiveness can be used to extend the diffusion-free analysis of Levenspiel (1972), for batch and flow reactors experiencing concentration-independent catalyst decay, to include the effects of internal diffusion. Resistances to internal diffusion can cause apparent deactivation rate constants, given by the slope of $\ln \ln(1/1 - x)$ vs. t Levenspiel plots to be significantly different from the intrinsic deactivation rate constant. For the extreme case of severe internal diffusion limitations, the apparent deactivation rate constant can be one-half the intrinsic value. This analysis has strong analogies to the classical kinetic analysis for non-deactivating systems.

INTRODUCTION

The importance of diffusional limitations on catalyst deactivation has been recognized for more than two decades. Wheeler (1951) developed the concept of selective pore mouth poisoning and derived analytical solutions for selective and nonselective (uniform) poisoning. Masamune and Smith (1966) solved the mass conservation equations numerically for reactant, impurity and product poisoning. For a single, isothermal, spherical catalyst pellet, with first-order reaction and deactivation, they concluded that maximum activity of catalyst is achieved for series (product) deactivation when intraparticle diffusional limitations are low. By contrast, for deactivation caused by reactant (parallel deactivation) or by an impurity in the feed, a catalyst with intermediate diffusion resistance is less easily deactivated. A similar treatment for non-isothermal pellets was carried out by Sagara et al. (1967).

The analysis of Masamune and Smith (1966) has been extended to Langmuir-Hinshelwood kinetics by Chu (1968), to account for relatively fast fouling by Murakami et al. (1968), and to include nonlinear reaction and poisoning kinetics by Hegedus and Petersen (1973). The general case of combined external and internal mass transfer resistances has been studied by Hegedus (1974). For parallel and impurity poisoning, he concludes that catalysts under the influence of internal and external mass transfer resistances have a longer life than those with only a kinetically controlled poisoning reaction, thereby corroborating the results of Masamune and Smith (1966).

Khang and Levenspiel (1973) tested the validity of using simple rate forms to describe complex pore diffusion-deactivation interactions. With first-order primary reaction, four mechanisms of deactivation were examined:

$$\frac{da}{dt} = -k_d C a^m \tag{1}$$

where C refers to the concentration of reactant, product or impurity for parallel, series or side by side deactivation mechanisms respectively. For independent deactivation, C is a constant. Except for one case (side by side deactivation with poisoning faster than reaction), a constant order of deactivation was found to satisfactorily represent deactivating catalysts over the whole range of diffusional limitations. For nonthermal, independent deactivation and some instances of series and product deactivation, $m = 1$ was found to be adequate.

An important use of the theory of time-dependent, single-particle effectiveness is the prediction of the effects of combined deactivation and diffusion on reactor performance. However, partly due to the complexity of the models investigated, incorporation of single-particle analyses presently available into macroscopic model for chemical reactor design can become unwieldy and tedious. For the model developed in the present study, simple analytical solutions exist, which in turn facilitate easy interpretation and analysis of deactivation data obtained from flow reactors.

SINGLE-PARTICLE ANALYSES

For an isothermal, spherical catalyst particle with constant properties, the mass conservation equation for a first-order reaction is given by:

$$D\left(\frac{d^2C_r}{dr^2} + \frac{2}{r}\frac{dC_r}{dr}\right) = k_i C_r a \tag{2}$$

where the deterioration of catalyst activity is assumed to be slow compared to the main reaction. For first-order concentration-independent deactivation, we have:

$$-\frac{da}{dt} = k_d a \tag{3}$$

Invoking the pseudo-steady state assumption and further assuming that catalyst activity is uniform within the spherical particles, Eq. 3 can be directly integrated to give:

$$a = a_o \exp(-k_d t) \tag{4}$$

where a_o is taken to be unity.

For negligible external diffusion resistance, Eqs. 2, 3 and 4 can now be solved simultaneously, with the following boundary conditions:

$$C_r = C_R;\ r = R$$
$$\frac{dC_r}{dr} = 0;\ r = 0 \tag{5}$$

This solution provides the concentration of reactant as a function of particle radius and time:

$$\frac{C_r}{C_R} = \frac{R}{r}\left\{\frac{\sinh[(\sqrt{k_i/D})\exp(-k_d t/2)r]}{\sinh[(\sqrt{k_i/D})\exp(-k_d t/2)R]}\right\} \tag{6}$$

In dimensionless form, this becomes:

$$\psi = \left(\frac{\sinh[3hA\xi]}{\sinh[3h A]}\right)\left(\frac{1}{\xi}\right) \tag{7}$$

where

$$\Psi = \frac{C_r}{C_R};\ A = \exp(-\theta/2);\ \theta = (k_d t);\ h = \frac{R}{3}\sqrt{k_i/D} \tag{8}$$

Pellet Effectiveness Factors

The combined effects of deactivation and diffusion on the main reaction can be depicted in the form of an initialized effectiveness factor for the catalyst particle. It can be defined as the overall rate for the particle at any time divided by the diffusion free rate at the surface of the catalyst, at zero time:

$$\eta_t = \frac{3}{h^2}\left(\frac{d\psi}{d\xi}\right);\xi = 1.0 \tag{9}$$

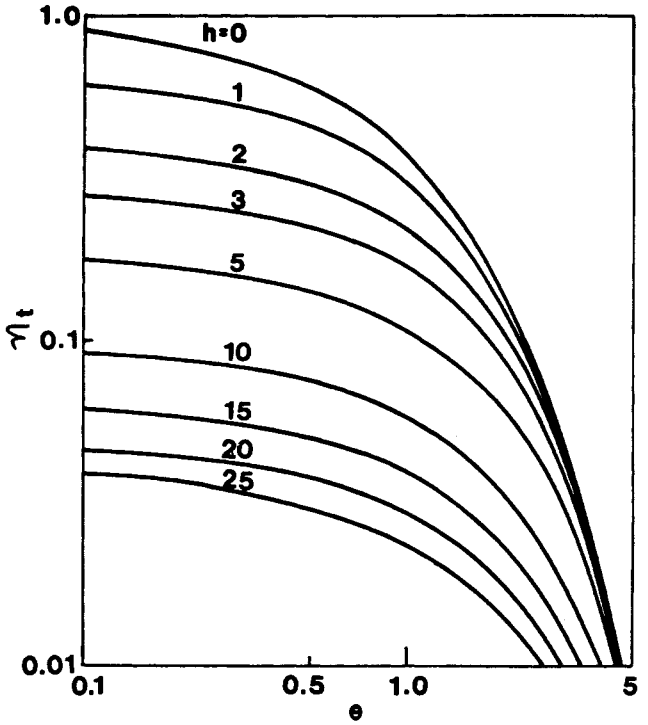

Figure 1. Initialized effectiveness factor vs. dimensionless time.

Differentiating Eq. 7 and substituting in Eq. 9 yields:

$$\eta_t = \frac{A}{h}\left(\coth \phi' - \frac{1}{\phi'}\right) \tag{10}$$

where $\phi' = (3\ hA)$

Figure 1 shows plots of η_t vs. dimensionless time, with Thiele modulus h as parameter. The shapes of these curves are similar to those obtained by Masamune and Smith (1966) for concentration-dependent fouling and for fouling caused by impurity in the feed stream (which they refer to as independent fouling). A cross-plot of η_t vs. h, with θ as parameter, is shown in Figure 2, illustrating the influence of diffusion on the effectiveness factor. The dotted line represents the zero-time relationship, for which Eq. 10 becomes the conventional isothermal effectiveness factor solution for non-deactivating systems, with $\phi = 3h$.

The initialized effectiveness factor given by Eq. 9 is defined on the basis of a zero-time surface rate; it is convenient to use since all of the time-dependent terms are in the numerator. An alternate definition, which is intuitively more pleasing, compares the ratio of the overall rate for the particle at any time, to the rate at surface conditions at the same instant of time. This definition leads to the instantaneous effectiveness factor:

$$\bar{\eta}_t = \left(\frac{3}{\phi'}\right)\left[\coth \phi' - \frac{1}{\phi'}\right] \tag{11}$$

As shown in Figure 3, the instantaneous effectiveness factor increases with time, approaching unity as $t \rightarrow \infty$, corresponding to a completely deactivated particle. Since an independent deactivation scheme has been assumed (Eq. 3), the activity vs. time relationship will be identical for diffusion-free and diffusion-limited particles. However, as the catalyst deactivates and the reaction rate decreases with time, the diffusional restrictions will, by comparison, become less important. For the diffusion-limited particle, this results in a slower rate of decline in conversion as compared to the diffusion-free particle. This behavior is reflected by the plots of Figure 3. Note that Eq. 11 is of the same form as the conventional effectiveness factor for a non-deactivating catalyst, with the deactivation modulus (hA) replacing the Thiele modulus h. The effectiveness factors of Eqs. 10 and 11 are, of course, related by:

$$\bar{\eta}_t = (\eta_t/A^2) \tag{12}$$

CONVERSION IN FLOW REACTORS

Since a simple analytical expression for the time-dependent effectiveness factor is now available, the solution of the reactor design equation, incorporating diffusion-deactivation effects, becomes straightforward.

For an isothermal plug flow reactor, the definition of catalytic effectiveness given by Eq. 10 can be incorporated into the mass balance for the integral reactor. Subsequent integration of the mass balance leads to the following relationship:

$$ln\ ln(1/1 - x) = ln(k\tau) + ln(\eta_t) \tag{13}$$

where η_t is a function of time as given by Eq. 10.

Conversion vs. time data created for various particle sizes were plotted as $ln\ ln\ (1/1 - x)$ vs time with Thiele modulus as parameter, Figure 4. It is apparent that the plots for $h = 0$ and for large values of $h (h > 10)$ are linear. In the absence of diffusional limitations, i.e., when $h \rightarrow 0$, the effectiveness factor as described by Eq. 10 reduces to:

$$\eta_t = A^2 = \exp(-k_d t) \tag{10a}$$

and Eq. 13 becomes:

$$ln\ ln\left(\frac{1}{1 - x}\right) = ln(k\tau) - k_d t \tag{13a}$$

Eq. 13a is the diffusion-free conversion-time relationship for a plug flow reactor, as given by Levenspiel (1972). Hence, experimental data plotted as $ln\ ln\ 1/1 - x$ vs. t for diffusion-free systems gives a valid estimate of k_d, the intrinsic deactivation rate constant.

At the other extreme, in the presence of severe diffusional limitations, Eq. 10 can be approximated as:

$$\eta_t \simeq \frac{A}{h};\ (hA) \geq 5.0 \tag{10b}$$

and Eq. 13 for this case becomes:

$$ln\ ln\left(\frac{1}{1 - x}\right) = ln(k\tau\eta) - \left(\frac{k_d}{2}\right)t;\ (hA) \geq 5.0 \tag{13b}$$

where η refers to the conventional effectiveness factor for non-deactivating systems, approximated as $1/h$ for large values of h. Hence, for the case when severe diffusional limitations are present, a plot of $ln\ ln(l/l - x)$ vs. t will again result in a straight line for $(hA) \geq 5.0$, with the intercept equal to $ln\ k\eta\tau$. The measured slope, however, would be one-half the true value. (This apparent reduction in the magnitude of the rate constant has been reported by Ollis (1972) in connection with enzyme

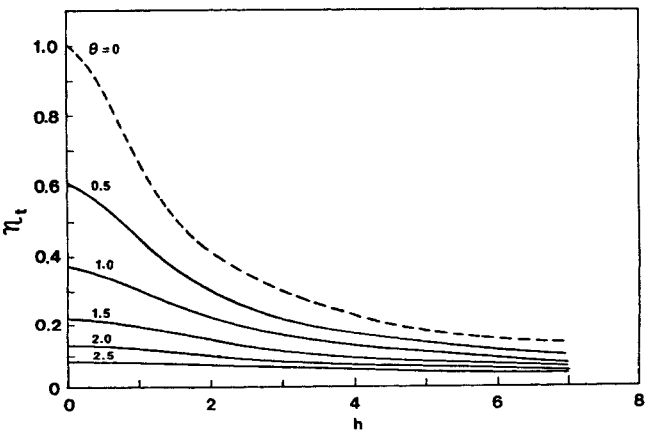

Figure 2. Initialized effectiveness factor vs. Thiele modulus.

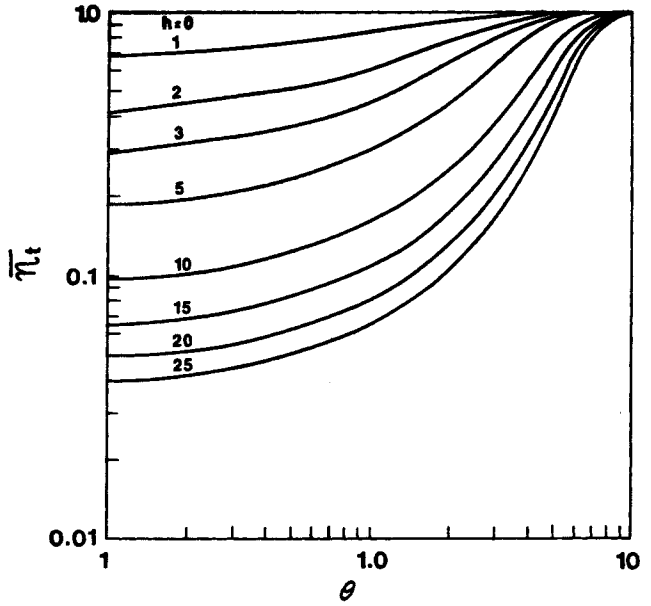

Figure 3. Instantaneous effectiveness factor vs. dimensionless time.

deactivation). This result is illustrated by the plots of Figure 4. The slope of the lines changes from k_d for $h = 0$ and approaches $k_d/2$ as internal diffusion limitations become severe. The intercept is given by $ln\ (k\tau\eta)$, where η varies from unity to $1/h$ as h increases from 0 to values greater than 5.

It is important to note that the Levenspiel plots will be linear, with a slope of $k_d/2$, only if the deactivation modulus (hA) is $\geq$ 5.0, (i.e., if the approximation used to derive Eq. 10b is valid). Eventually, as time $t \to \infty$, $a \to 0$, $\overline{\eta}_t \to 1$ and the slope of the plots will change from $k_d/2$ to k_d even when strong internal diffusion resistances are present. Setting $(hA) = 5.0$, the fractional conversion x_s, corresponding to time t_s when the Levenspiel plot will begin to exhibit nonlinearity under extreme diffusional limitations, is given by:

$$x_s = 1 - (1 - x_o)^{5/h};\ h > 5 \tag{14}$$

where x_o is conversion at zero time. For the example of Figure 4, $x_o = 0.25$ for $h = 10$ and x_s, from Eq. 14, is 0.134. As fractional conversion decreases below 0.134, the slope of the lines will gradually increase from 0.025 to 0.05 h^{-1} as t approaches infinity.

Analogies to Classical Kinetic Analysis

Strong analogies exist between diffusional characteristics in non-deactivating and deactivating systems. In kinetic analysis, conversion vs. temperature relationship for a first-order reaction in a plug flow reactor is given by:

$$ln\ ln\left(\frac{1}{1-x}\right) = ln(K_o\tau) - \frac{E}{R_G}\left(\frac{1}{T}\right) \tag{15a}$$

where K_o is the pre-exponential factor; E, the activation energy; T, the reaction temperature; and R_G, the gas constant. The slope of this "Arrhenius plot" gives a valid estimate of the true activation energy. When diffusional resistances to internal transport are high, the apparent activation energy is one-half the true value:

$$ln\ ln\left(\frac{1}{1-x}\right) = ln(K'_o\tau) - \frac{E}{2R_G}\left(\frac{1}{T}\right) \tag{15b}$$

where $K'_o = f(K_o, D, r)$

Note that Eqs. 15a and 15b are analogous to Eqs. 13a and 13b which represent Levenspiel plots for deactivating catalysts. Eq. 13b is applicable when $(hA) > 5.0$, i.e., for large h and small t. Similarly, Eq. 15b is applicable for large h and small values of $(1/T)$.

Furthermore, the apparent rate constant in reaction kinetics is given by:

$$k_p = k\eta \tag{16}$$

where the effectiveness factor η is inversely proportional to the radius of the catalyst particle. By analogy, the apparent deactivation rate constant can be defined as:

$$k_{dp} = k_d\eta_d \tag{17}$$

where η_d is termed the "deactivation effectiveness factor" and also exhibits a reciprocal dependence on particle size. Table 1 summarizes the characteristics of this diffusional analogy.

The nature of η_d for intermediate diffusion regimes $(0 < hA < 5)$ and the estimation of intrinsic deactivation rate constants from deactivation data will be discussed in a forthcoming paper on experimental confirmation of this theoretical analysis. The results for extremes of negligible and severe internal diffusion limitations are presented in Table 2.

Extensions to General Cases

Retaining the assumption of concentration-independent deactivation, the analysis presented for first-order reaction and deactivation in a plug flow reactor can be extended to other reaction and deactivation orders and to other reactor configurations. The expected conversion-time behavior for these cases is discussed below.

The assumption of a first-order main reaction permits an analytical solution of the mass conservation equation for the spherical catalyst particle (Eq. 2), thereby resulting in analytical expressions relating the effects of diffusion and deactivation on the rate of the primary reaction. Extension to the general case of n-th order primary reaction is conceptually straightforward, but analytical solutions are no longer possible. However, even for

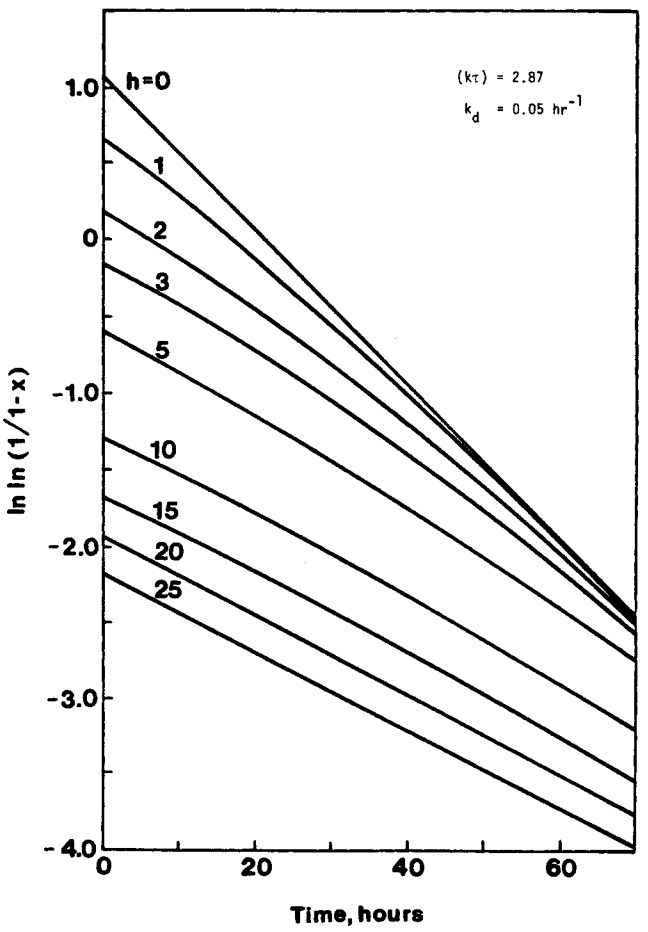

Figure 4. Conversion function vs time (Levenspiel plot).

TABLE 1. ANALOGOUS CHARACTERISTICS OF DIFFUSION FOR DEACTIVATING AND NONDEACTIVATING SYSTEMS

Condition	Kinetic Analysis	Deactivation Analysis
Slope with Diffusion	E	k_d
Slope with Severe Internal Diffusion	$E/2$	$k_d/2$ $(hA \geq 5.0)$
Dependence on Particle Size	Reciprocal	Reciprocal

TABLE 2. CATALYST DEACTIVATION IN A PLUG FLOW REACTOR

$$\ln\ln(1/1-x) = \ln k\tau + \ln\eta_t = \ln k_p\tau - k_{dp}t$$

k_p = pseudo-reaction rate constant = $k\eta$

k_{d_p} = pseudo-deactivation rate constant = $k_d\eta_d$

Limiting Cases of Levenspiel Plots with Internal Diffusion

Modulus Term	Effectiveness Factors: Kinetic	Deactivation
$h = o$	$\eta = 1$	$\eta_d = 1$
$hA \geq 5$	$\eta \simeq 1/h$	$\eta_d \simeq 1/2$

n-th order primary reaction kinetics, the effectiveness factor under severe diffusional limitations is approximated by:

$$\bar{\eta}_{tn} = \frac{3}{R}\sqrt{\frac{D}{k_i a C_o^{n-1}}} = \frac{1}{(h_n A)}; \left.\begin{matrix} n = 1 \\ (h_n A) \geq 5.0 \end{matrix}\right\} \quad (18)$$

The conversion-time relationship for n-th order reaction in a plug flow reactor, analogous to Eq. 13a for the diffusion-free case is:

$$\ln[(1-x)^{1-n} - 1] = \ln[k\tau(n-1)C_o^{n-1}] - k_d t;\ n \neq 1 \quad (19a)$$

If the effectiveness factor relationship of Eq. 18 is used, the corresponding equation for the severely diffusion-limited case becomes:

$$\ln\left[(1-x)^{\frac{1-n}{2}} - 1\right] = \ln\left[\bar{k}\tau\left(\frac{n-1}{2}\right)C_o^{\frac{n-1}{2}}\right] - k_d t/2; \left.\begin{matrix} n = 1 \\ (h_n A) \geq 5.0 \end{matrix}\right\} \quad (19b)$$

where $\bar{k} = f(\sqrt{k}, D \text{ and } R)$. Therefore, the deactivation rate constant would be one half the true value when $(h_n A)$ is ≥ 5.0, even for a general n-th order reaction. However, since the kinetics of the primary reaction are altered by the presence of diffusional limitations, the logarithmic conversion function is different for the two extremes of diffusional limitations.

For any general order of concentration-independent deactivation m, Eq. 3 becomes:

$$\frac{da}{dt} = -k_d a^m \quad (20)$$

With first-order primary reaction, the effectiveness factor definitions of Eqs. 10 and 11, and the corresponding plug flow reactor conversion-time relationship of Eq. 13 still apply with A_m replacing A, where:

$$A_m = [1 + (m-1)k_d t]^{\frac{1}{2(1-m)}};\ m \neq 1 \quad (21)$$

The diffusion-free and diffusion-limited forms of Eq. 13, for this case, are:

$$\ln\ln\left(\frac{1}{1-x}\right) = \ln(k\tau) - \frac{1}{(m-1)}\ln[1 + (m-1)k_d t];\ m \neq 1 \quad (22a)$$

and

$$\ln\ln\left(\frac{1}{1-x}\right) = \ln(k\tau/h) - \frac{1}{2(m-1)}\ln[1 + (m-1)k_d t];\ m \neq 1 \quad (22b)$$

If $[(m-1)\,k_d \cdot t]$ is $<< 1.0$, Eqs. 22a and 22b will be identical to Eqs. 13a and 13b and m-th order deactivation will be indistinguishable from first-order deactivation.

Extensions to other types of reactors such as batch and stirred-tank configurations are also straightforward. For the case of batch solids and mixed flow of fluids, for example, Eq. 13 is applicable with $\ln(x/1-x)$ replacing $\ln\ln(1/1-x)$.

IN CONCLUSION

For first-order reaction and deactivation, the analysis of Levenspiel for diffusion-free deactivation has been extended to include the effects of intraparticle diffusion. Extensions to higher orders of reaction and deactivation have been discussed.

NOTATION

A = $\exp(-k_d t/2)$
a = fractional catalyst activity
C_r = concentration of reactant inside spherical particle, g mol/cc
C_R = concentration of reactant at the surface of spherical particle, g mol/cc
C = bulk stream concentration of reactant, g mol/cc
D = effective diffusivity of reactant within spherical particle, cm^2/s
E = activation energy for reaction
h = Thiele modulus, $(R/3)\sqrt{k_i/D}$
(hA) = deactivation modulus, $= (R/3)\sqrt{k_i a/D}$
k_i = intrinsic reactant rate constant, s^{-1}
k = reaction rate constant, (cc)/(s) (g cat)
k_d = deactivation rate constant, h^{-1}
k_{dp} = pseudo-deactivation rate constant, h^{-1}
K_o = pre-exponential factor
n = order of main reaction
m = order of deactivation
R = radius of spherical particle, cm
r = radial position, cm
t = process time, h
T = reaction temperature
x = fractional conversion of reactant

Greek Letters

$\underline{\eta_t}$ = initialized effectiveness factor given by Eq. 10
η_t = instantaneous effectiveness factor given by Eq. 11
η_d = deactivation effectiveness factor
θ = dimensionless time, $= (k_d t)$
ξ = dimensionless radial position $= r/R$
τ = space time, (s) (g cat)/(cc)
ϕ = dimensionless group, $= (3h)$
ϕ' = dimensionless group $= (3hA) = (\phi A)$
ψ = dimensionless concentration $= C_r/C_R$

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Effect of External Diffusion on Deactivation Rates

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Alteration in concentration-independent catalyst decay rates due to the presence of finite external and internal mass transfer resistances is examined. Analytical expressions for external and overall time-dependent catalytic effectiveness are developed. Analysis of diffusion-limited catalyst deactivation in flow reactors is discussed.

SCOPE

The presence of internal and external mass transfer resistances can alter the time scale of decay of solid catalysts. In another paper (Krishnaswamy and Kittrell, 1981), the interaction between internal diffusion and deactivation was examined. Analysis of the performance of reactors operating under these combined influences was discussed. In addition, the rate of diffusion-limited decay of catalysts was shown to be very different from that for diffusion-free systems. In many instances of industrial use, catalysts often operate under the combined influence of internal and external mass transport resistances. Further alternation of decay rates is likely to occur when resistances to internal as well as external transport exist.

The purpose of this paper is to extend the analysis of diffusion-limited deactivation to include the effects of external transport resistances. For illustrative purposes, the first-order reaction and deactivation model is retained.

CONCLUSIONS AND SIGNIFICANCE

A simple analytical solution can be derived for the time-dependent external catalytic effectiveness of a deactivating, nonporous particle, as well as the overall effectiveness of a deactivating porous catalyst. Extensions of this analysis to particles of nonspherical geometry and to the general case of a n-th order deactivation process are both straight-forward.

The expressions for time-dependent catalytic effectiveness can be incorporated in plug flow reactor design equations leading to analytical conversion-time relationships. Theoretical results indicate that the effect of a finite external mass transfer resistance is to further decrease the magnitude of the apparent deactivation rate constant, thereby increasing catalyst lifetime. While the lower limit on this magnitude for severe internal diffusion is $k_d/2$ for deactivation modulus $(hA) \geq 5.0$, that for a particle with severe internal and external diffusional limitations is zero. Certain analogies exist between non-deactivating and deactivating systems subject to internal and external transport resistances.

The impact of overall catalytic effectiveness on the yields of products in non-deactivating complex reaction networks has been considered by Carberry (1976). The results of this paper indicate that the concept of a time-dependent overall effectiveness will have a profound effect on such product yields, depending on the relative rates and characteristics of the diffusion and deactivation processes associated with the various reactions in any complex network.

The influence of intraparticle resistance alone on catalyst poisoning has been investigated by Masamune and Smith (1966), Chu (1968), Murakami et al. (1968), Ollis (1972), Hegedus and Petersen (1973), and Krishnaswamy and Kittrell (1981).

Hegedus (1974) studied the effects of both external and internal mass transfer resistance on porous catalysts being poisoned either by the reactant or an impurity in the feed stream. Due to the complexity of the equations, an analytical solution was not possible. His numerical results indicated that both external and internal mass transfer resistances tend to increase the lifetime of the catalyst, for impurity and reactant poisoning. Lin (1975) solved the problem of a non-isothermal deactivating enzyme catalyst, with finite mass transfer resistances, for Michaelis-

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