Greek Letters

Δp = pressure drop across a screen layer
Δp_o = pressure drop across a clean screen layer
ρ = density of gas
ρ_p = density of particle
η_o = initial single fiber efficiency
η_k = single fiber efficiency for the k-th layer screen
θ = time
μ = gas viscosity

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Heterogeneous Catalytic Reactors Undergoing Chemical Deactivation

Part I: Deactivation Kinetics and Pellet Effectiveness

A general expression for the time-dependence of the activity of a catalyst pellet affected by both chemical deactivation and diffusion is developed. Specific results are given for both uniform and pore-mouth poisoning, with parallel and series poisoning mechanisms. Comparisons show a satisfactory agreement between theoretical and experimental results. A pellet effectiveness representing the combined effect of deactivation and diffusion is also developed in a form suitable for direct inclusion in reactor conservation equations.

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SCOPE

The time dependence of loss of catalytic activity due to various mechanisms of deactivation is often described by empirical correlations based on time-on-stream. A few specific results of more theoretical nature are available and have been described by Carberry (1976), but these are very limited. An ultimate goal would be to describe the observable time dependence of the main and deactivation reactions in terms of pertinent physical and chemical parameters that can be determined in independent experimentation. In the present work we propose a formulation, so based, for description of the time dependence of loss of catalytic activity. The approach considers both deactivation and diffusion limitation in individual particles and yields a pellet effectiveness that can be incorporated directly into reactor design models.

CONCLUSIONS AND SIGNIFICANCE

A mechanistic representation of chemical deactivation by parallel and sequential schemes leads to a general form of deactivation kinetics that gives relatively simple expressions for pellet effectiveness for both uniform and pore-mouth poisoning. The agreement between theory and experimental data obtained for parallel pore-mouth poisoning is satisfactory, although it is shown that intraparticle diffusivity is a sensitive parameter. The quantities appearing in the theory are all accessible to determination in separate experimentation. Finally, the pellet effectiveness, expressed in terms of pellet surface conditions, is simple enough to be directly incorporated into reactor conservation equations, allowing some simplification of an inherently complicated design problem.

INTRODUCTION

Catalyst deactivation mechanisms have generally been classified as poisoning, coking or sintering, in which the first two are essentially chemical interactions and the latter physical. The present study is concerned with deactivation by poisoning in the classical sense of competitive chemisorption of poisoning species (parallel poisoning) on active sites. Also considered is the case of simple deposition of one of the main reaction products (sequential poisoning) on the surface, which is in principle one of the limiting cases of coke formation if we consider the product to be the coke precursor and coke formation from the precursor to be rapid.

The development below is restricted to energetically uniform catalytic surfaces and to the limitig cases of uniform and pore-mouth deactivation (Wheeler, 1955). In the derivation sequence, we first determine the fraction of activity remaining after deactivation (activity factor) for arbitrary deactivation kinetics, then develop specific cases for parallel poisoning and product deposition. The time progression of the activity factor resulting from the deactivation kinetics can then be determined and in turn incorporated into a pellet effectiveness factor representing the combined effect of diffusion and deactivation in terms of pellet surface conditions. This effectiveness factor is the basis for the reactor analysis offered in Part II.

It is convenient to define the activity factor, F, and the pellet effectiveness, ϵ_p, as follows:

$$F \equiv \frac{\text{rate of reaction for deactivated pellet}}{\text{rate of reaction for fresh pellet}} \tag{1}$$

$$\epsilon_p \equiv \frac{\text{observed rate}}{\text{intrinsic rate at pellet surface conditions}} \tag{2}$$

Thus:

$$\epsilon_p = \eta_f F \tag{3}$$

where η_f is the effectiveness factor for the fresh pellet in terms of surface conditions.

ACTIVITY FACTOR

We will consider a reaction of the general rate form:

$$r_c = kg(\underline{C}) = kg(C,\underline{K}) \tag{4}$$

in a pellet of slag geometry. In Eq. 4 $g(\underline{C})$ is the concentration dependence of the rate of formation for the key species C on all species involved, $\underline{C}$. This can be written in terms of C and the equilibrium constants $\underline{K}$, with the aid of reaction stoichiometry, as shown. Now the fraction of catalyst deactivated, γ, can be defined as:

$$\gamma = \frac{\text{number of active sites after deactivation}}{\text{number of initial active sites}} \tag{5}$$

and the corresponding global rate $\mathcal{R}$ in the case of uniform deactivation is:

$$\mathcal{R} = \eta_d k(1-\gamma)g(\underline{C}) \tag{6}$$

where η_d is the generalized efffectiveness factor (Aris, 1965; Bischoff, 1965; Petersen, 1965) for the deactivated pellet and is given by:

$$\eta_d = \frac{[2Dk_s(1-\gamma)]^{1/2}}{Lk_s(1-\gamma)g(C_s)}\left[\int_{C_L}^{C_s} g(\alpha)d\alpha\right]^{1/2} \tag{7}$$

Quantities subscripted s refer to peller surface conditions and L pellet center conditions at a distance L from the surface. The effective diffusivity D is assumed constant, independent of the extent of the deactivation. The effective rate constant, $k(1-\gamma)$, varies with the extent of deactivation, deactivation is uniform, and the pellet is taken to be isothermal (Carberry, 1975; Butt et al., 1977). From the definition of ϵ_p it follows that:

$$F = \frac{\eta_d}{\eta_f}(1-\gamma) \tag{8}$$

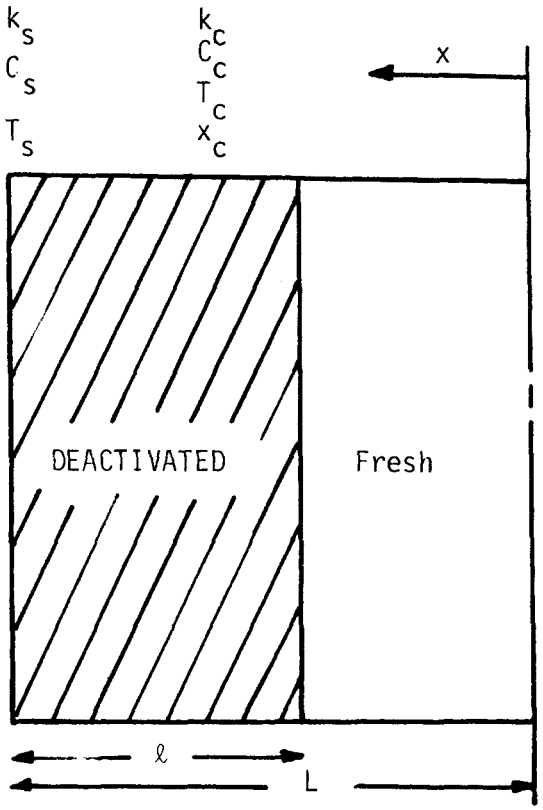

Figure 1. Quantities for pore-mouth poisoned pellet.

where η_f for the fresh catalyst is obtained from Eq. 7 for $\gamma = 0$. Since the effectiveness factors appear in ratio in Eq. 8, evaluation of F from Eqs. 7 and 8 for limiting cases is simple:

$$F = \begin{cases} & \text{diffusion-free main reaction} \\ (1-\gamma) & \text{(uniform deactivation)} \\ (1-\gamma)^{1/2} & \text{diffusion-limited main reaction} \end{cases} \tag{9}$$

Wheeler's analysis (1955) for pore-mouth deactivation and slab geometry leads to:

$$C_s - C_c = \left(\frac{L^2k_c}{D}\right)\gamma(1-\gamma)(\eta_{in})_d g(C_c) \tag{10}$$

where the effectiveness factor for the undeactivated inner core is given by:

$$(\eta_{in})_d = \frac{[2Dk_cI(C_c)]^{1/2}}{(L-l)k_cg(C_c)} \tag{11}$$

with:

$$I(C_c) \equiv \int_{C_L}^{C_c} g(\alpha)d\alpha$$

The quantities used in Eqs. 10 and 11 are described in Figure 1. Application of the definition of the activity factor yields, for the pore mouth case:

$$F = \frac{(\eta_{in})_d(1-\gamma)}{\eta_f}\frac{g(C_c)}{g(C_s)} \tag{12}$$

Now, the activity factors of Eqs. 9 and 12 contain γ, which must be calculated. This requires some specific form of deactivation kinetics for evaluation.

DEACTIVATION KINETICS

For irreversible parallel poisoning the rate at which active sites disappear is equivalent to the rate of chemisorption of poison.

Thus:

$$r_p = k_p N s \tag{13}$$

where s is the fraction of vacant sites per unit volume of pellet and N the concentration of poison. A balance on the total number of sites gives:

$$C_t = C_p + C_v[1 + \sum_i (K_i C_i)^{m_i}]^n \tag{14}$$

where m_i is 0, $\frac{1}{2}$ or 1 (Froment and Bischoff, 1979) depending upon whether there is no adsorption, respectively. C_t represents total sites, C_p those occupied by poison, C_v those vacant, and C_i the concentration of any species involved in the reaction elementary steps other than the poison. The value of n ranges from 1 to 3 depending upon the mechanism and rate controlling steps of the main reaction. From Eq. 14 we can obtain the following:

$$s = \frac{C_v}{C_t} = \frac{1 - \gamma}{\left[1 + \sum_i (K_i C_i)^{m_i}\right]^n} \tag{15}$$

since $C_t - C_p = C_t(1 - \gamma)$. Combining Eqs. 13 and 15 gives:

$$r_p = \frac{k_p N(1 - \gamma)}{\left[1 + \sum_i (K_i C_i)^{m_i}\right]^n} = \frac{k_p N(1 - \gamma)}{[1 + G(C,\underline{K})]^n} \tag{16}$$

where the term $G(C,\underline{K})$ represents a normal adsorption inhibition term, for example, in a Langmuir-Hinshelwood correlation and can be written, as shown, in terms of the concentration of the key species C and corresponding equilibrium constants.

For an example of application of this development, let us consider the academic isomerization reaction $A \rightleftarrows B$. The elementary steps are:

$$A + S \rightleftarrows AS \ (K_A)$$

$$AS \rightarrow BS \ (k_s, \text{slow})$$

$$BS \rightleftarrows B + S \ (K_B)$$

with:

$$N + S \rightarrow N \cdot S \ (\text{poisoning})$$

In this case the rate of poisoning is given by:

$$r_p = \frac{k_p N(1 - \gamma)}{1 + K_A C_A + K_B C_B}$$

and $G(C,\underline{K})$ for this example is:

$$G(C,\underline{K}) = K_A C_A + K_B C_B = (K_A - K_B)C_A + K_B C_{B_0}$$

where A has been taken as the key species.

If we follow a similar development for the case of the sequential product deposition, the deactivation kinetics turn out also to be given by Eq. 16. However, now the concentration of poisoning species N depends upon the kinetics of the main reaction. The rate at which these species is formed is all that is required for pellet effectiveness, as shown later.

FRACTION DEACTIVATED

Uniform Poisoning-Parallel Mechanism

Let Q be the maximum uptake of poisoning species by the catalyst in mols per unit apparent pellet volume. Then one has for the rate of poisoning:

$$\frac{d}{dt}(Q\gamma) = r_p = \frac{(k_p)N_s(1 - \gamma)}{[1 + G(C_s)]^n} \tag{17}$$

The rate of poisoning generally is much slower than the rate at which the concentration reaches the steady state within the pellet. Under these pseudo steady state conditions, Eq. 17 can be integrated into:

$$\gamma = 1 - e^{-B(t)}; \quad B(t) = \int_0^t \frac{(k_p)_s N_s}{Q[1 + G(C_s)]^n} dt \tag{18}$$

where it has been taken that there is no diffusional limitation of the main reaction. When this is not the case, $G(C,\underline{K})$ is dependent upon the pellet coordinate x. However, the uniform poisoning γ is by definition independent of x, yet from Eq. 17 this cannot be so if $G(C_s) = f(x)$. We are left with the conclusion that, for this model of deactivation kinetics, uniform poisoning will occur only when $G(C_s) \ll 1$. Thus, for a diffusion-limited main reaction and uniform deactivation:

$$\frac{d}{dt}(Q\gamma) = r_p = (k_p)_s N_s(1 - \gamma) \tag{19}$$

and:

$$\gamma = 1 - e^{-B'(t)}; \quad B'(t) = \int_0^t \frac{(k_p)_s N_s}{Q} dt \tag{20}$$

The concentration between γ and $G(C,\underline{K})$ here arises from the fact that γ depends upon the chemisorption kinetics which in turn depend upon the fraction of vacant sites, given by $(1 - \gamma)/(1 + G)^n$. Thus, G is a measure of available vacant sites for which both main and poisoning reactions compete.

Pore-Mouth Poisoning-Parallel Mechanism

In this case we may envision there to be a very thin band of a deactivation reaction zone at the moving interface separating the outer deactivated zone from the still active inner zone. In this band the rate of deactivation or chemisorption of poisoning species dominates and chemisorption of main reaction species is negligible. Thus, deactivation kinetics are approximated by:

$$r_p = k_p N s \approx k_p N \tag{21}$$

Then:

$$\frac{d}{dt}(Q\gamma) = (k_p)_c N_c \tag{22}$$

Setting the rate of diffusion or poison through the deactivated zone equal to the rate of deactivation yields:

$$N_s = \left[1 + \frac{(k_p)_c L}{D_p}(L - x_c)\right] N_c \tag{23}$$

where subscript c refers to the interface position. Eqs. 22 and 23 are combined to give:

$$\frac{d\gamma}{dt} = \left[\frac{(k_p)_c}{Q}\right]\left[\frac{N_s}{1 + (\phi_p)_c^2 \gamma}\right] \tag{24}$$

with

$$(\phi_p)_c = L[(k_p)_c/D_p]^{1/2} \tag{25}$$

For isothermal conditions the solution to Eq. 24 can be written as:

$$\gamma = -\frac{1}{(\phi_p)_c^2} + \left[\frac{1}{(\phi_p)_c^4} + \frac{2D_p}{QL^2}\int_0^t N_s dt\right]^{1/2} \tag{26}$$

Uniform Poisoning-Sequential Mechanism

As indicated previously, an additional conservation equation is required in this case for the rate of formation of poisoning species. For example, the following must be solved simultaneously for uniform poisoning:

$$\frac{d\gamma}{dt} = \frac{k_p N(1 - \gamma)}{Q(1 + G)^n}$$

$$\frac{dN}{dt} = k_1(1 - \gamma)g_1(\underline{C})$$

where $k_1 g_1(\underline{C})$ is the rate of formation of the poisoning species. This must be specified. If one lets G' be this rate and Q' be the mols of deposited species per unit pellet volume sufficient to completely deactivate the catalyst, then γ can be obtained from:

$$\frac{d}{dt} Q'\gamma = G'[\underline{C}_s, \underline{k}_s(1-\gamma)]$$

Pore-Mouth Poisoning-Sequential Mechanism

Here the rate of deposition is given by:

$$\frac{d}{dt} Q'\gamma = G'[\underline{C}_c, \underline{k}_c(1-\gamma)]$$

and the diffusion-reaction balance is, for species i:

$$D_i \frac{C_{s_i} - C_{c_i}}{L\gamma} = L(1-\gamma)[k_c(\eta_{in})_d g(C_c)]_i$$

In either of these cases all that is required for γ is the specification of all reaction paths and the corresponding kinetics.

PELLET EFFECTIVENESS

The pellet effectiveness defined by Eq. 2 can now be derived from the activity factor and the γ expressions. We shall limit our attention here to parallel poisoning, which admits of general treatment, recognizing that similar procedures obtain for the sequential model upon specification of the detailed kinetics.

The pellet effectiveness for uniform poisoning is given by:

$$\epsilon_p = e^{-B(t)};\ B(t) = \int_0^t \frac{(k_p)_s N_s}{Q[1 + G(C_s)]^n}\, dt \tag{27}$$

for a diffusion-free main reaction, and by:

$$\epsilon_p = (e^{-B'(t)}/2)\left[\frac{\sqrt{2Dk_s}}{Lk_s g(C_s)}\right]\left[\int_{C_L}^{C_s} g(\alpha)d\alpha\right] \tag{28}$$

$$B'(t) = \int_0^t \frac{(k_p)_s N_s}{Q}\, dt$$

for a diffusion-limited main reaction. Equation 27 is obtained from combination of Eqs. 3, 9 and 18, while Eq. 28 derives from Eqs. 3, 10 and 20.

For pore-mouth poisoning, pellet effectiveness is given by:

$$\epsilon_p = \left(\frac{D}{L^2 k_c \gamma}\right)\left(\frac{C_s - C_c}{g(C_s)}\right) \tag{29}$$

where C_c is the solution of:

$$C_s - C_c = \left(\frac{L\gamma}{D}\right)\sqrt{2Dk_c}\left[\int_{C_L}^{C_c} g(\alpha)d\alpha\right]^{1/2} \tag{30}$$

and γ is given by Eq. 26. Equation 29 is the combination of Eqs. 3, 10 and 12, and Eq. 30 that of Eqs. 10 and 11.

COMPARISON WITH EXPERIMENT

The intraparticle deactivation of Ni/kieselguhr by thiophene in benzene hydrogenation has been reported by Lee et al. (1978). Under the general conditions of experimentation—low benzene concentrations and temperatures in the range of 100°C—the reaction is pseudo first order in benzene and highly diffusion-limited. It was also demonstrated experimentally that poisoning occurred via a shell-progressive or pore-mouth mechanism, hence the theoretical development presented here in Eqs. 26, 29 and 30 should apply.

Our major concern here is the poisoning data for Run 2U presented in Figure 1 of Lee et al. This was a pellet deactivation experiment conducted at 110°C with benzene and thiophene mol fractions of 0.16 and 0.01, respectively. The kinetic parameters for benzene hydrogenation on this catalyst have previously been reported by Kehoe and Butt (1972), and under these experimental conditions $k_c = 0.15\ s^{-1}$ with an apparent activation energy of 4 kcal/mol. The corresponding $g(\alpha)d\alpha$ is thus simply CdC, where C is the intraparticle benzene concentration. The effective diffusivity, D, of benzene within the particle was measured to be 0.052 cm^2/s via a helium-argon counterdiffusion experiment (Foster et al., 1964) with molecular weight correction. Lee et al. also report an estimate of D from random pore theory of 3×10^{-2} cm^2/s. There is no reason to expect the effective diffusivity of thiophene, D_p, to differ greatly from this value, so $D = D_p$ has been assumed in the calculations to follow. The poison capacity parameter, Q, has also been measured in separate experiments. It is, unfortunately, a somewhat elusive number that seems to vary somewhat for pellets of differing composition as investigated by Lee et al. and subsequently by Downing et al. (1979). However the value of Q for all pellets involved in these investigations was bounded by the range of 1×10^{-4} to 6×10^{-4} mol/cm^3, and we have used a representative value of $Q = 4 \times 10^{-4}$ mol/cm^3 here.

Table 1. Parameter Values; Pore-Mouth Poisoning in the Hydrogenation of Benzene on Ni/Kieselguhr by Thiophene (Run 2U, Lee et al.)

$D = D_p = 0.052$ cm^2/s (counterdiffusion) or 0.03 cm^2/s (random pore)	
$L = 0.65$ cm	
$Q = 4 \times 10^{-4}$ mol/cm^3	$k_c = 0.15\ s^{-1}$
$(k_p)_c = 28\ s^{-1}$	$C_s = 5.7 \times 10^{-6}$ mol/cm^3
$(\phi_p)_c = L\sqrt{(k_p)_c/D} = 15.1$ (for $D = 0.052$)	$N = 3.6 \times 10^{-7}$ mol/cm^3

We may estimate a value for the poisoning rate constant $(k_p)_c$ from the initial rate of deactivation in the experiment. Under initial conditions, $\gamma = 1$, and $(d\gamma/dt)_0$ estimated from the data is ca. $2.5 \times 10^{-2}\ s^{-1}$. Hence:

$$(4 \times 10^{-4})\left(\frac{d\gamma}{dt}\right)_0 = (k_p)_c N \tag{31}$$

For experimental conditions, $N = 3.6 \times 10^{-7}$ mol/cm^3. Inserting this value and that for $(d\gamma/dt)_0$ into Eq. 31 yields:

$$(k_p)_c \approx 28\ s^{-1}$$

Finally, a value of the characteristic dimension, L, is required for the calculation. Although the experiments were carried out with cylindrical particles, the diameter was very large compared to poison penetration and thus the reaction-poisoning system "saw" something more akin to slab geometry. In this case we use the radius of the pellet as an appropriate dimension, whence $L = 0.65$ cm as given in Table 2 of Lee et al. A summary of parameter values is given in Table 1.

Carrying out the integration indicated in Eq. 30 and solving for C_c yields:

$$C_c = \frac{C_s}{1 + \dfrac{L\gamma k_c^{1/2}}{D^{1/2}}} \tag{32}$$

Equation 29 becomes

$$\epsilon_p \frac{D}{L^2 k_c \gamma}\left(\frac{C_s - C_c}{C_s}\right) \tag{33}$$

For the very large value of $(\phi_p)_c$ pertaining to these experiments, the reciprocal terms in Eq. 26 are small and γ is well approximated by:

$$\gamma \cong (2D_p N t/QL^2)^{1/2} \tag{34}$$

In Figure 2 are presented the results of calculations for the parameter set of Run 2U in comparison with measured values. One can see that the effectiveness is overestimated for $D = 0.052$ cm^2/s; unfortunately, this parameter is a very sensitive one in the calculation since it appears essentially as a final multiplier in Eq. 33 for

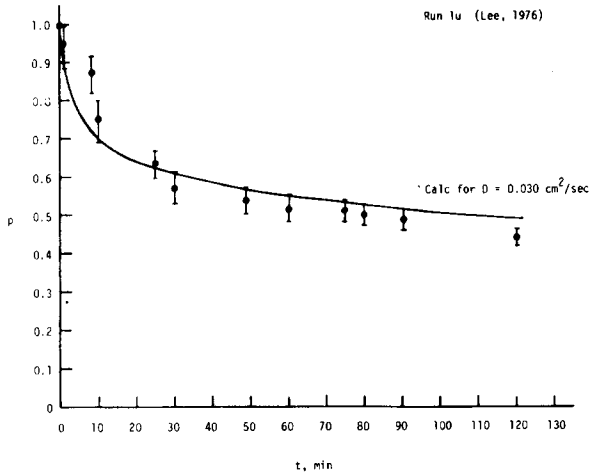

Figure 2. Comparison of theoretical results with experimental values: 110°C, 1% thiophene.

ϵ_p. If we use the estimate $D = 0.03$ cm^2/s obtained from random pore theory, the agreement is much better, as shown.

As a further test of the pore-mouth poisoning theory, we have selected a second run, not reported in the paper of Lee et al., but given in the dissertation of Lee (1976). This run, 1U, was carried out under similar conditions save that the temperature was 85°C and the thiophene concentration was 0.375%. The intrinsic poisoning constant, $(k_p)_c$ is little affected by the temperature in this range, as is Q (just a reflection of the very rapid and irreversible interaction of thiophene with nickel). However for an activation energy of 4 kcal the value of k_c becomes 0.10 s^{-1}. The approximation of Eq. 34 for γ is again valid, and the results of calculation ($D = 0.03$ cm^3/s) vs. experiment are shown in Figure 3. The agreement is satisfactory, although sensitivity to D of course remains.

It could be remarked that some inconsistencies of the calculation as compared to experimental data appear to show up in the initial term of poisoning (small times). It is difficult to make a quantitative judgment on the matter, since rather large experimetnal uncertainties are involved in the determination of activity at short times when the poisoning process is very rapid.

CONCLUDING REMARKS

Deactivation kinetics and pellet effectiveness factors have been developed for parallel and sequential poisoning mechanisms, in the limiting cases of uniform and pore-mouth deactivation. The agreement with the theory and experimental results obtained for parallel pore-mouth poisoning is satisfactory, although the intraparticle diffusivity is a sensitive parameter in the analysis. Parameters appearing in the theoretical development are in general quantities that can be measured in independent experimentation, allowing us to move one step closer to true a priori design of heterogeneous catalytic reactors affected both by chemical deactivation and diffusion limitation.

It is seen that the activity factor and the pellet effectiveness are not simple functions of time but rather depend on the kinetics of the main reaction, even for the case of parallel (independent) poisoning.

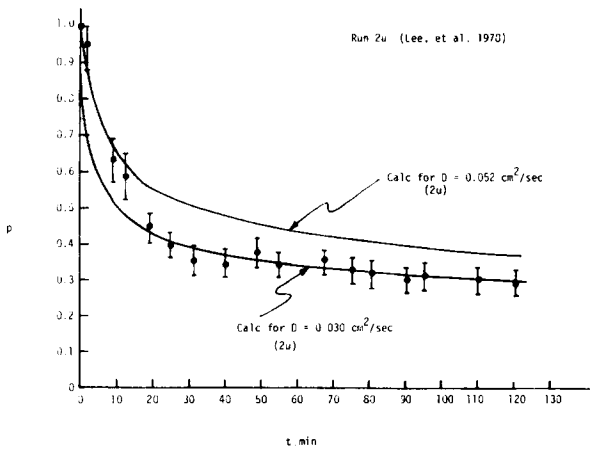

Figure 3. Comparison of theoretical results with experimental values: 85°C, 0.375% thiophene.

NOTATION

B = function defined by Eq. 18
B' = function defined by Eq. 20
C = concentration of key species
$\underline{C}$ = concentrations of all species, a vector of C_i
C_L = concentration of key species at pellet center
C_p = number of active sites occupied by poisoning species per unit pellet volume
C_t = total number of active sites per unit pellet volume
C_v = number of vacant sites per unit pellet volume
D, D_i = effective diffusivity of key species, ith species
D_p = effective diffusivity of poisoning species
F = activity factor defined by Eq. 1
g = functional dependence of rate of formation on C
$G(C,\underline{K})$ = adsorption inhibition terms in Eq. 16
$G(C_s)$ = $G(C,K)$ evaluated at surface conditions
I = quantity defined by Eq. 11
k = rate constant for main reaction
k_p' = rate constant for poisoning reaction
$\underline{k}_p$ = $k_p' C_t$
$\bar{k}_p$ = $k_p C_t (\Delta L/L)$
K = $K_A K_B K_C$
K_i = equilibrium constant for ith species
L = volume/external surface area of pellet, half-thickness of slab
ΔL = length of small band for deactivation reaction at the forefront of deactivated outer shell (Figure 1)
m_i = constant exponent in Eq. 16
n = constant exponent in Eq. 16
N = concentration of poisoning species
Q = maximum uptake of poisoning species by catalyst in moles per unit apparent volume of pellet
r_c = rate of formation of key species
r_p = rate of chemisorption of poisoning species or rate of deactivation
$\mathcal{R}$ = global rate or observed rate
t = time

Greek Letters

γ = fraction of catalyst deactivated defined by Eq. 5
ϵ_p = pellet effectiveness defined by Eq. 2
η_f = $\dfrac{\sqrt{2Dk_s}}{Lk_s g(C_s)}[I(C_s)]^{1/2}$, effectiveness factor for fresh pellet
η_d = effectiveness factor for deactivated pellet given by Eq. 7
$(\eta_{in})_d$ = effectiveness factor for fresh inner core of deactivated pellet given by Eq. 11
ϕ_c = $L(k_c/D)^{1/2}$
$(\phi_p)_c$ = Thiele modulus given by Eq. 25

Subscripts

s = pellet surface
c = at the forefront of deactivated outer shell (Figure 1)

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Part II. Design and Analysis: Approach of Reactor Point Effectiveness

A design method is presented that takes into account the effects of both diffusion and deactivation on heterogeneous catalytic reactors. Improvements that can be made by the method are demonstrated and an efficient methodology is developed by which the design problem as well as associated optimization problems can be solved in a routine manner. The approach is based on the reactor point effectiveness for global rate of reaction in terms of bulk fluid conditions. Some important features emerge from the examples presented.

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SCOPE

Heterogeneous catalytic reactors are usually designed on the basis of initial catalyst activity, even when deactivation is known to occur, and compensation made via subsequent operating conditions. An exception is the work of Weekman (1968) on catalytic cracking of gas oil affected by coking. In the present paper a design practice including the effect of catalyst deactivation is presented to demonstrate the improvements possible by such methods. While the problem including both deactivation and diffusion limitation is difficult (particularly so for complex kinetics), it is possible to develop an efficient methodology for solution based on the reactor point effectiveness factor for global rate of reaction in terms of bulk conditions.

CONCLUSIONS AND SIGNIFICANCE

If the effect of catalyst deactivation on reactor operation is included in the design phase, improvements in performance can be obtained that are not possible with the usual design practice based on the activity of fresh catalyst. In fact, decisions based on the latter method can lead to incorrect conclusions regarding reactor performance. The proposed methodology here allows routine solution for heterogeneous catalytic reactors affected by diffusion and either uniform or pore-mouth deactivation. The procedure can also be used for the optimization of an operating reactor.

INTRODUCTION

Very little attention has been directed to the design and analysis problem of heterogeneous catalytic reactors subject to the double jeopardy of diffusion limitation and catalyst deactivation. The work of Dumez and Froment (1976) is among the very few in which both deactivation and diffusion are treated within the context of a heterogeneous reactor model. Studies employing pseudo homogeneous models have been reported by Froment and Bischoff (1961) for coking, and by Butt and coworkers (1975, 1977) for independent poisoning. These later workers have also studied the behavior of individual catalyst pellets affected by both diffusion and deactivation (1975, 1979).

Usual design practices for heterogeneous reactors are normally

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