calculated for the three systems are shown in Figures 1, 2 and 4, where they can be compared with the experimental results.

Variation in the value of T with the volume fraction dispersed for the system toluene-water, with toluene dispersed, is plotted in Figure 5, using agitator speed as parameter. The line for "$T = 1.0$" is also shown, and the abscissa for the intersection of this line with each curve gives the inversion point. Corresponding plots for the other systems studied here have been prepared by Arashmid (1979). The points obtained from this type of curve were then transferred to the normal phase inversion curve as shown in Figures 1, 2 and 4. In all cases, the agreement between the predicted phase inversion curve and the experimental curve is exceptionally good. The difference between the experimental and predicted inversion concentration was generally less than 2.0% volume fraction. The greatest difference was observed with the system carbon tetrachloride-water with water dispersed. In that case, differences of the order of 4% were observed. Generally better agreement was obtained when the organic liquid was dispersed, and improved agreement can be seen for each system as the agitator speed increases.

NOTATION

g = gravity acceleration constant
k_1 = proportionality constant characteristic of the agitator
k_3 = combined constant in drop size equation
m = gradient of drop size vs. hold-up relationship
m_1 = parameter correlated by Equation (11)
n = number of drops per unit volume
N = agitator speed in rpm
N_c = coalescence frequency
N_T = collision frequency
p = drop size
p_0 = drop size at zero hold-up
P_0 = power transmitted by agitator
T = ratio of N_c/N_T

Greek Symbols

ζ = energy of turbulence
ν_c = kinematic viscosity of continuous phase
ρ_c = density of continuous phase
ρ_d = density of dispersed phase
θ = time
μ_c = viscosity of continuous phase
μ_d = viscosity of dispersed phase
ϕ = fractional hold-up of dispersed phase

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Effectiveness and Deactivation of a Diluted Catalyst Pellet

In this article, we analyze the performance of a diluted catalyst pellet consisting of inert and active particles, under diffusion influenced conditions and pore-mouth poisoning. First, we establish the requirements for validity of the analytical solutions of the diluted pellet equations. Secondly, we show that, under pore-mouth poisoning conditions, a diluted pellet can display considerably longer lifetimes than a uniformly impregnated catalyst. Conversely, for the same lifetime, use of a diluted pellet can result in savings of the catalytic agent. These advantages are not offset by difficulties in catalyst manufacture, as is the case for previous designs.

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SCOPE

Many catalytic processes of industrial importance operate in the temperature region where the reaction is essentially diffusion controlled, and only a small fraction of total catalyst volume is effective in the reaction. In situations where shell-progressive or pore-mouth type poisoning describes the deactivation process, the catalyst may suffer a precipitous decline in activity by virtue of the fact that

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it is these very outer layers of active material that are poisoned first. However, proper design of the diffusion characteristics of a catalyst shows promise for more efficient utilization of active material and of mitigating the effects of poisoning processes.

These goals have been actively pursued in relation to the important area of catalysts for automotive exhaust pollution control. Previous proposed designs that, in theory showed promise for improvement, consisted of catalysts with non-uniform distribution of active materials, and composite catalysts made of layers of different diffusive properties. Ruckenstein (1970) analyzed the effectiveness of a diluted catalyst pellet consisting of microspheres imbedded in an inert porous media. With this configuration, pellet effectiveness can be modified by selecting the proper diffusivity of the inert media. The objective here is to analyze the performance of such diluted catalysts under conditions of pore-mouth poisoning, a question which has not been investigated before. First, we analyze the effectiveness of the diluted pellet using more realistic assumptions regarding its effective diffusivity, to represent pellet behavior over the entire possible range of dilution more correctly than in previous models. Results indicate that for a given value of the diffusivities of the porous inert media and active particles, there is an optimal dilution which gives maximum effectiveness. Secondly, these results are combined with pore-mouth poisoning equations to predict the reaction rate versus time-on-stream behavior of the diluted catalysts, relative to that of undiluted catalysts of the same dimensions.

CONCLUSIONS AND SIGNIFICANCE

The analysis of the diffusion-reaction equations used to describe a diluted catalyst pellet showed that a valid analytical solution is possible with the use of a consistent expression for the effective diffusivity. This is true only when the active porous particles within the diluted pellet are themselves not diffusion limited. Our results validate the assumptions made in the model depicting the diluted pellet. The analysis of pore-mouth poisoning in the diluted catalyst showed that increasing the diffusivity of the inert media and its "poison-getter" capacity can increase catalyst lifetime and savings in active material required.

A diluted catalyst pellet should not present significant manufacturing difficulties: diffusivity and poison-getter capacity can be enhanced by selecting an appropriate pore structure for the inert media and/or a modifying of its chemical nature. Results suggest that there are significant advantages to using diluted catalysts where diffusion limitations and pore-mouth poisoning conditions exist.

Remedies to diffusional intrusions in catalyst pellets and mitigation of their poisoning have been the preoccupation of many investigators, particularly in connection with catalysts for the control of automobile emissions. Two approaches, namely that of nonuniform distribution of active material on supports, and that of composite catalysts having layers of different diffusive properties, have been proposed. Becker and Wei (1977) examined the effects of 'egg yolk,' 'egg white' and 'egg shell' modes of active material deposition within a uniform support on their activity in reactions of bimolecular Langmuir kinetics, and on their resistance to poisoning in first order reactions. Wolf (1977) proposed the use of a composite catalyst having a protective outer layer of higher reactant diffusivity and analyzed its performance under pore-mouth poisoning conditions, such as those described by Wheeler (1951). Polomski and Wolf (1978) extended the analysis to include the bimolecular Langmuir type kinetics. The above analyses indicate that the deposition of active material in the interior of the catalyst pellet can lead to higher activity in the high reactant concentration region for bimolecular Langmuir kinetics and improve substantially the deactivation characteristics for both first order and bimolecular Langmuir kinetics under pore-mouth poisoning conditions. These advantages were more pronounced for the composite catalysts where the opportunity of minimizing the diffusion resistance of the protective layer of inert material existed. It may be noted that poison precursors in automotive exhausts (P, Pb and S compounds) typically result in pore-mouth type poisoning by strong adsorption on supports, as well as on active components (Hegedus and Cavendish, 1977; McArthur, 1975).

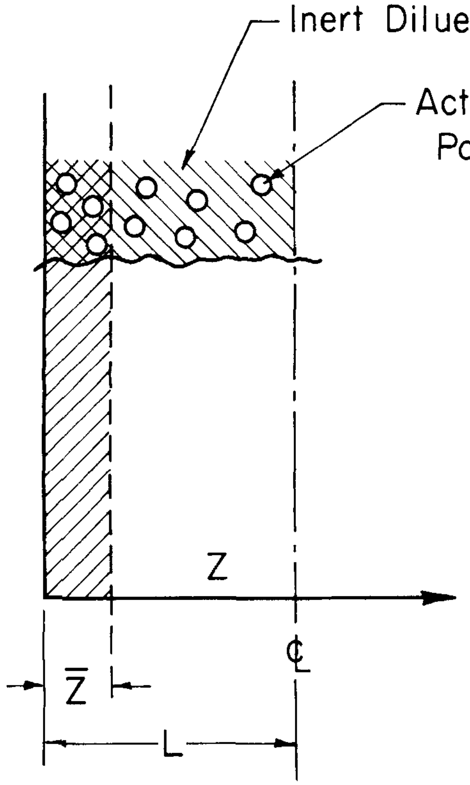

Figure 1. Schematic diagram of the diluted pellet showing the coordinate system and the poison front.

Ruckenstein (1970) proposed the use of a diluted catalyst pellet, composed of microspheres of active catalyst imbedded in an inert porous medium of advantageous diffusion characteristics, to permit more efficient utilization of the active material. Such a catalyst allows the use of a high area support, such as is necessary to obtain high dispersion of valuable active metals, in the active particles. It is also more easily manufactured than the composite or nonuniform catalysts, by pelleting mixtures of active and inert particles. Hegedus and Summers (1977) demonstrated that by modifying pore volumes and macro-micropore distribution within a support, the net rate of a poisoning reaction may be selectively manipulated with respect to the rate of the main reaction to produce catalysts of improved poison resistance. This suggests that in diluted catalysts, the degree of freedom represented by the choice of the inert porous medium may be exploited to design a catalyst of significantly improved poison resistance.

In this paper, we first analyze the validity of the assumptions necessary to describe correctly a dilute catalyst pellet; next, we develop the analytical solutions describing the dilute pellet under pore-mouth poisoning conditions and use them to compare such catalysts with conventional ones.

CATALYST ACTIVITY

The following development applies to an isothermal first order reaction in a catalyst of slab geometry, consisting of a uniform distribution of small porous catalytically active spheres imbedded in a catalytically inert porous medium as shown schematically in Figure 1. It may be noted that the internally isothermal model of the catalyst pellet is a satisfactory representation of solid catalyzed gas phase reactions (Carberry 1976), and that first order kinetics are approximately valid for the low concentration region of bimolecular Langmuir kinetics. Also, extension of the following results to other catalyst geometries is easily achieved by the use of well-known similarity relations (Aris, 1957).

Properties of the inert porous medium are designated by subscript 1 and that of the active particles by subscript 2. For the microspheres of active catalyst having radius a and effective diffusivity D_2:

$$D_2 \frac{d}{dr}\left(4\pi r^2 \frac{du}{dr}\right) = 4\pi r^2 k u \tag{1}$$

$$u = u_o \quad \text{at} \quad r = a; \quad \frac{du}{dr} = 0 \quad \text{at} \quad r = 0$$

The concentration profile inside the particle is thus given by

$$u = \frac{a u_o}{r} \frac{\sinh(r\sqrt{k/D_2})}{\sinh(a\sqrt{k/D_2})} \tag{2}$$

where u_o is the concentration at the surface of the particle.

For the diluted catalyst slab of half-thickness L and overall effective diffusivity D_e:

$$D_e \frac{d^2C}{dz^2} = m D_2 \left(\frac{du}{dr}\right)_{r=a} 4\pi a^2 \tag{3}$$

$$C = C_o \quad \text{at} \quad z = L; \quad \frac{dC}{dz} = 0 \quad \text{at} \quad z = 0$$

where m is the number of active particles per unit volume of the catalyst. When $u_o = C$ at the surface of each microsphere Equation 3 becomes

$$\frac{d^2C}{dz^2} = AC \tag{4}$$

such that

$$A = m 4\pi a \frac{D_2}{D_e} \left[a\sqrt{k/D_2} \coth\left(a\sqrt{k/D_2}\right) - 1\right] \tag{5}$$

yielding as a solution

$$C = C_o \frac{\cosh(z\sqrt{A})}{\cosh(L\sqrt{A})} \tag{6}$$

where C_o is the external reactant concentration in the absence of mass transfer limitation. Reaction rate per unit volume of the diluted pellet is given by

$$R = \frac{D_e C_o}{L} \sqrt{A} \tanh(L\sqrt{A}) \tag{7}$$

A relation for overall effective diffusivity D_e, in terms of D_1 and D_2, the diffusivities in the inert and active media respectively is now sought. DeLancey (1974) proposed a relation linking overall diffusivity to individual diffusivities in the porous media via a linear relationship of the form

$$D_e = f_1 D_1 + f_2 D_2 \tag{8}$$

where f_1 and f_2 represented the volume fractions of the respective porous media. A third term due to the macroporous interparticle spaces was also included in his analysis, but in the event that such interparticle space is reduced to insignificant levels by high pelleting pressures, or that interparticle volume is identical for pellets composed solely of medium one or two and as such is included in estimates of D_1 and D_2, Equation (8) should satisfactorily represent the overall diffusivity in a diluted catalyst pellet. The same author (DeLancey, 1974) has listed the assumptions that such a relationship entails in terms of both the parallel pore and random pore models, and has shown that it provides an adequate representation of the limited data available on systems qualitatively similar to the diluted pellet. For our purposes, Equation (8) becomes

$$D_e = f D_2 + (1 - f) D_1 \tag{9}$$

where f is the volume fraction of active material present.

The rate of reaction in an undiluted catalyst composed only of active material is

$$R_{f=1} = \frac{D_2 C_o}{L} \sqrt{k/D_2} \tanh(L\sqrt{k/D_2}) \tag{10}$$

If the model so far developed is to represent accurately the diluted catalyst, Equation (7) must, in the limit $f = 1$, reduce to Equation (10), the expression for an undiluted catalyst. Such will be the case when, for $f = 1$, $A = k/D_2$. Using the relation $f = m4\pi a^3/3$ and the series expansion of $\coth(a\sqrt{k/D_2})$ in Equation (5), it can be shown that Equation (7) satisfies the stated limit when the Thiele modulus of the microspheres $a\sqrt{k/D_2} << 1$. This indicates that the individual microspheres must in fact not be diffusion limited for an analytical solution of the kind developed here to be a valid representation of the diluted pellet, and that comparisons involving cases where the Thiele modulus of the active particles $a\sqrt{k/D_2}$ is not $<< 1$, as have been attempted earlier (Ruckenstein, 1970), are not permitted. In the limit $a\sqrt{k/D_2} << 1$, the rate of reaction in the diluted catalyst given by Equation (7) reduces to

$$R = \frac{kfC_o}{L} \sqrt{D_e/kf} \tanh\left(L\sqrt{kf/D_e}\right) \tag{11}$$

representing simple diminution of the rate constant k within the catalyst.

A comparison of the diluted catalyst with an undiluted one is afforded by the expression

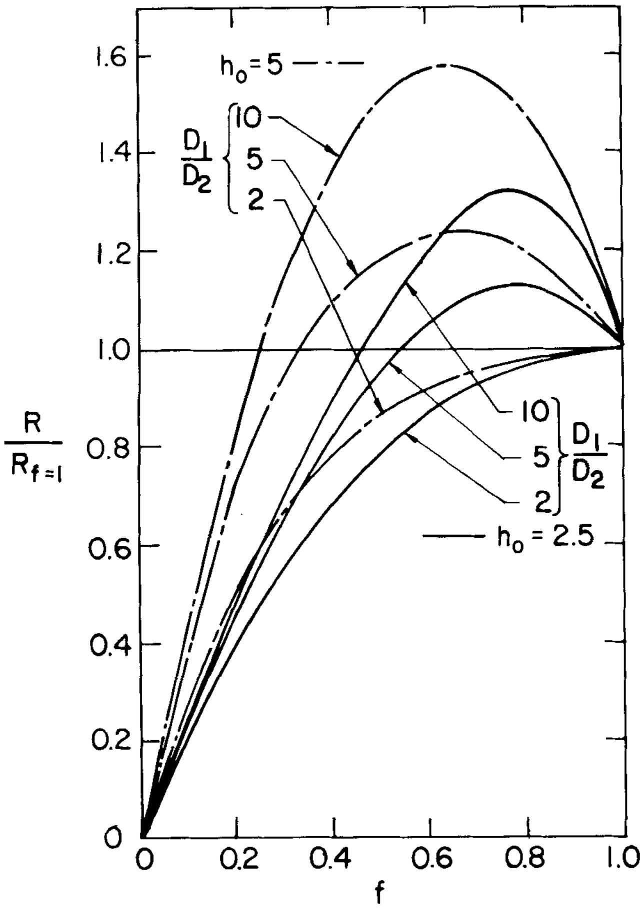

Figure 2. Reaction rate of the diluted catalyst relative to the reaction rate of the undiluted catalyst versus the fraction of active metal.

$$R/R_{f=1} = \sqrt{fD_e/D_2}\,\frac{\tanh(h_o\sqrt{fD_2/D_e})}{\tanh(h_o)} \qquad (12)$$

where $h_o = L\sqrt{k/D_2}$ is the Thiele modulus of the undiluted catalyst. The above quantity plotted in Figure 2 for various values of h_o and D_1/D_2 shows that, even when the undiluted catalyst is only marginally diffusion limited ($h_o = 2.5$), values of D_1/D_2 higher than 1 can yield diluted catalysts of higher activity with a consequent saving of active material. Previous analysis (Ruckenstein, 1970) predicted unrealistically, that activity would drop to zero when there was no dilution of the catalyst ($f = 1$), a consequence of the assumed relation $D_e = (1 - f)D_1$.

For a given value of h_o and D_1/D_2, Equation (12) is only a function of f and exhibits a maxima given by the solution of the equation

$$(D_1/D_2 + 2f(1 - D_1/D_2))\sinh(2h_o\sqrt{fD_2/D_e}) + 2h_o(D_1/D_2)\sqrt{fD_2/D_e} = 0 \qquad (13)$$

Figure 3 shows the variation of this optimum dilution level with h_o, for two selected diffusivity ratios.

POISONING BEHAVIOR

When a pore mouth or shell-progessive type of poisoning occurs, the catalyst can be visualized as divided into two regions. From the external surface to a depth $\bar{z}$, the catalyst is completely poisoned and, therefore, inactive; reaction occurs only in the remaining fraction of half-thickness $(L - \bar{z})$. An expression for reaction rate per unit volume may be obtained from

$$R = kfC(\bar{z})\xi(\bar{z})\frac{(L - \bar{z})}{L} \qquad (14)$$

where

$$\xi(\bar{z}) = \frac{\tanh[(L - \bar{z})\sqrt{fk/D_e}]}{(L - \bar{z})\sqrt{fk/D_e}}$$

$C(\bar{z})$ is determined by equating the rate of diffusion of reactant through the poisoned region to the rate of reaction in the unpoisoned region. Thus,

$$C(\bar{z}) = \frac{C_o}{1 + \bar{z}\sqrt{kf/D_e}\tanh[(L - \bar{z})\sqrt{kf/D_e}]} \qquad (16)$$

Defining $\Delta = \bar{z}/L$ and substituting Equations (15) and (16) into Equation (14), we obtain

$$R = \frac{kC_o}{h_o}\,\frac{(D_e/D_2)\tanh[h_o(1 - \Delta)\sqrt{fD_2/D_e}]}{\{(D_e/fD_2)^{1/2} + \Delta h_o\tanh[h_o(1 - \Delta)\sqrt{fD_2/D_e}]\}} \qquad (17)$$

Δ represents the extent of penetration of the poison front into the catalyst. The initial rate of an unpoisoned ($\Delta = 0$), undiluted ($f = 1$), catalyst of the same dimensions is given by

$$R_o = kC_o\frac{\tanh(h_o)}{h_o} \qquad (18)$$

For a given depth of poison penetration Δ, the activity of the diluted catalyst relative to the undiluted unpoisoned catalyst is given by

$$\frac{R}{R_o} = \frac{(D_e/D_2)\tanh[h_o(1 - \Delta)\sqrt{fD_2/D_e}]}{\tanh(h_o)\{(D_e/fD_2)^{1/2} + \Delta h_o\tanh[h_o(1 - \Delta)\sqrt{fD_2/D_e}]\}} \qquad (19)$$

The above equation reduces to Equation (12) when

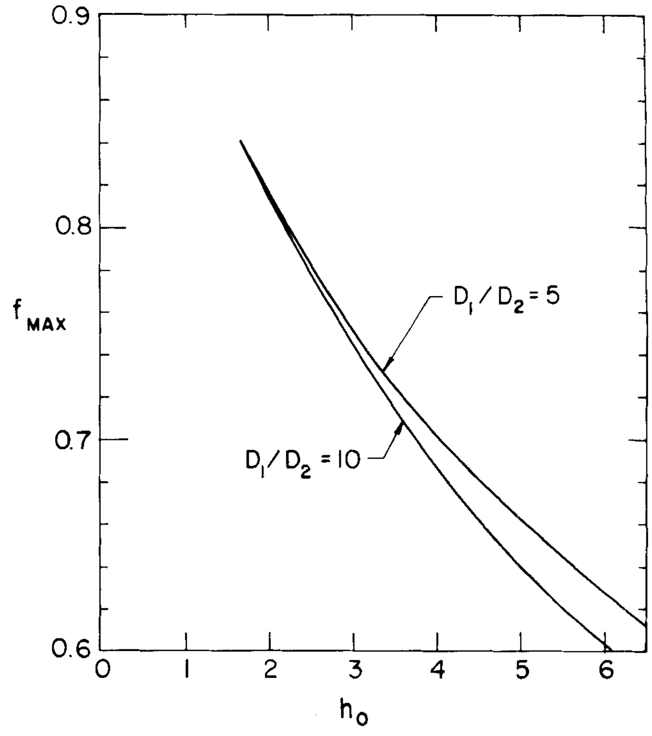

Figure 3. Fraction of active metal that gives maximum relative rate as a function of Thiele modulus.

$\Delta = 0$, and to the typical expression for pore mouth deactivation of an undiluted catalyst (Balder and Petersen, 1968), when $f = 1$.

To obtain the relation between activity and time, Δ must be related to time on stream. Carberry and Gorring (1966) obtained the relation between poison depth $\bar{z}$ and time $t_{\bar{z}}$, for the case where the poisoning reaction is very fast and diffusion of poison precursors through the poisoned shell is rate controlling

$$t_{\bar{z}} = \frac{CW_e \bar{z}^2}{2Dp_e Cp_o} \tag{20}$$

where CW_e is the poison getter capacity of the support, Dp_e the effective diffusivity of poison precursor in the support, and Cp_o the poison precursor concentration at the external pore mouth. In the case of the diluted catalysts Dp_e and CW_e are defined analogously to Equation (9) as

$$Dp_e = fDp_2 + (1 - f)Dp_1 \tag{21}$$

$$CW_e = fCW_2 + (1 - f)CW_1 \tag{22}$$

A dimensionless time can be defined by taking as a reference the time required to completely poison the undiluted catalyst, i.e.,

$$\tau = t_{\bar{z}}/t_{\bar{z}=L,f=1} = \left(\frac{CW_e}{CW_2}\right)\left(\frac{Dp_2}{Dp_e}\right)\Delta^2 \tag{23}$$

Eliminating Δ between Equations (23) and (19), one may obtain a relation between the declining relative activity R/R_o and dimensionless time τ.

Some discussion of the physical constraints on the diffusivity and poison getter capacity ratios is appropriate here. It is immediately apparent that if the porous medium 1 possesses a higher reactant diffusivity ($D_1/D_2 > 1$) then one may also expect poison precursor diffusivity to be enhanced ($Dp_1/Dp_2 > 1$). Under certain restricted conditions, these diffusivity ratios also bear a relation to the poison getter capacity ratio. If both supports 1 and 2 possess a mono-modal distribution of pore sizes, then support area is inversely proportional to average pore radius r. Then, since poison getter capacity is proportional to the support surface area,

$$CW_1/CW_2 \propto r_2/r_1$$

Furthermore if Knudsen diffusivity prevails then

$$Dp_1/Dp_2 \propto r_1/r_2$$

so that

$$CW_1Dp_1/CW_2Dp_2 \simeq 1$$

This relation indicates that, for mono-modal pore size distributions, the requirement that both CW_1/CW_2 and Dp_1/Dp_2 be greater than unity is not realizable.

It is quite possible however to use supports of a bimodal pore size distribution in which case the limitations imposed by Equation (26) will have been circumvented. Indeed, data from Hegedus and Summers (1977) shows that for a support of such bimodal pore size distribution, it was possible to obtain simultaneous increases in poison getter capacity *and* diffusivity (e.g., $CW_1/CW_2 = 1.75$ and $Dp_1/Dp_2 = 1.85$) by appropriate modification of the total pore volume and macro-micropore distribution of the support.

Another approach to increasing the poison getter capacity of the inert support material is via the chemical nature of the support itself. Experimental studies indicate (McArthur, 1975) that saturation concentrations of poisons on a surface often coincide with that representative of a stoichiometric monolayer of poisoning product on the support surface. Variation of the chemical nature of the support may conceivably result in higher uptakes of poison precursor per unit area of support.

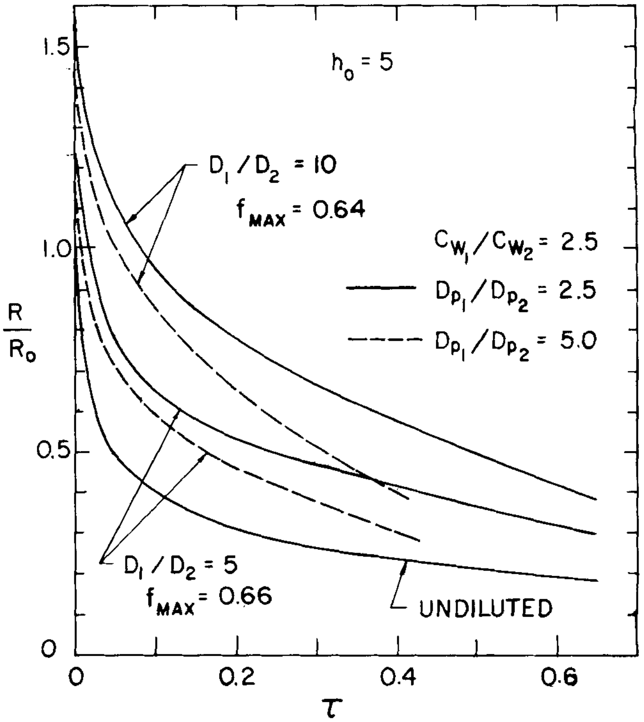

Figure 4. Reaction rate of the diluted catalyst relative to the initial rate of the undiluted catalyst (R/R_0), versus dimensionless time τ.

Figure 4 shows the deactivation behavior of diluted catalysts with some selected poisoning and diffusivity parameters. Comparisons are made with a catalyst which, in undiluted form, would possess a Thiele modulus of 5; the deactivation of this undiluted catalyst is also shown in the same figure. In each case, the value of f selected for the diluted catalysts corresponds to f_{max}, i.e., that obtained as a solution to Equation (13). It is seen that, even when the poison precursor shares the same diffusional advantage through the inert support as the reactant, the diluted catalysts display higher activity and hence longer effective lifetimes. For instance, the diluted catalyst with $D_1/D_2 = Dp_1/Dp_2 = 5$ takes 3.75 times as long as the undiluted catalyst to decline to a relative activity R/R_o of 0.5. Given the extent of dilution, it is thus clear that both, savings in active material, and substantially increased catalyst lifetimes are realizable in a diluted catalyst.

The advantages accruing to a diluted catalyst are uniquely a result of two circumstances: first, the diffusional limitation in the conventional catalyst, which renders all but the outer layers of active material ineffective in reaction, and second, the pore-mouth poisoning, which succeeds in deactivating preferentially these very layers of the catalyst. By dispersing the effective activity more uniformly over the catalyst volume, the susceptibility of the diluted pellet to pore-mouth poisoning is reduced, which results in savings in active material. Catalyst pellets impregnated only to a finite depth with active material, although representing savings in the use of active agent (Hegedus and Summers, 1977), would be most susceptible to pore-mouth poisoning. The advantages shown by the diluted pellet over conventional catalyst designs, would be even more pronounced in cases where the Thiele modulus of the conventional catalyst is higher than it is in our calculations.

NOTATION

a = radius of active particles, cm
C = reactant concentration inside diluted pellet, moles/cm^3
C_o = reactant concentration at external surface of pellet, moles/cm^3
$C_{\bar{z}}$ = reactant concentration at poison front, moles/cm^3
Cp_o = poison precursor concentration at external surface of pellet, moles/cm^3
CW_i = saturation poison capacity in support i, moles/cm^3
CW_e = saturation poison capacity in diluted pellet, moles/cm^3
D_i = reactant effective diffusivity in support i, cm^2/sec
D_e = reactant effective diffusivity in diluted pellet, cm^2/sec.
Dp_i = poison precursor effective diffusivity in support i, cm^2/sec.
Dp_e = poison precursor effective diffusivity in diluted pellet, cm^2/sec.
f = fraction of volume occupied by active particles
h_o = Thiele modulus of undiluted pellet of same dimensions
k = reaction rate constant, sec^{-1}
L = half-thickness of catalyst pellet, cm
r = radial distance inside active particle, cm
R = reaction rate in diluted pellet, moles/cm^3-sec.
R_o = initial reaction rate in undiluted pellet, moles/cm^3-sec.
t = time, sec.
u = reactant concentration inside active particle, moles/cm^3
u_o = reactant concentration at surface of active particle, moles/cm^3
z = distance inside pellet, cm
$\bar{z}$ = depth of poison penetration, cm

Greek Letters

Δ = fractional depth of poison penetration, $\bar{z}/L$
ξ = effectiveness factor
τ = dimensionless time

Subscripts

1 = identify the inert support or diluent
2 = identify the support containing active material

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The Co-current Reactor-Heat Exchanger

A reactor of four crossflow monolithic blocks is used to approximate a cocurrent and a countercurrent reactor-heat exchanger. Essentially isothermal reaction pass profiles are produced by flowing the coolant and reactant streams cocurrent to each other according to the criteria set down in Part I of this paper. A multiplicity of steady states is shown to exist for the autothermal countercurrent mode, but not for the autothermal cocurrent mode, under identical conditions.

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Part II. Experimental Results

SCOPE

Four crossflow monolith blocks are used to carry out an oxidation reaction in which heat is simultaneously generated and transferred to a coolant stream. The crossflow design is of particular interest because of its high heat transfer area-to-volume ratio.

Two cases are considered. In one, cylindrical catalyst pellets fill the volume through which the reactant stream flows. In the second case, a similar catalyst is coated on the walls of the reaction pass. The remaining monolith volume is comprised of coolant channels that run perpendicular to the reaction pass.

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