JOURNAL OF CATALYSIS 28, 33-38 (1973)

Inter-Intraphase Diffusion Affected Catalytic Yield

The Case Involving Finite External and Internal Area

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Received April 11, 1972

Isothermal catalytic activity and yield alteration in a consecutive reaction are analyzed in terms of interphase (external) and intraphase (internal) diffusional intrusions for the general case of a porous catalyst of finite external as well as internal area. The point yield of intermediate in a consecutive reaction network is shown to pass through a minimum, then a maximum, before falling to zero as the Thiele modulus of the first reaction step increases. It is shown that under no realistic circumstance can yield become unity when the zone of reaction retreats to the external surface in a porous solid catalyzed reaction, save for the rather extraordinary circumstance in which the Mach number of the flowing fluid is far greater than unity (supersonic flow).

NOMENCLATURE

A_0,B_0	Species concentrations in bulk fluid
a	External surface per unit volume, cm^{-1}
Bi	External Mass Transport Biot number, Eq. 4
Da	Damköhler number
$\mathfrak{D}$	Intraphase diffusivity, cm^2/sec
f	External to total surface area, $a/(a + S)$
k	Intrinsic rate coefficient cm/sec
kS	Internal rate coefficient sec^{-1}
kf	External rate coefficient sec^{-1}
k_g	External Mass Transfer coefficient cm/sec
K	Rate coefficient ratio, k_1/k_2
L	Volume to external area, $1/a$
m	External mass transfer-reaction function, Eq. 9
S	Internal catalyst area/volume, cm^{-1}
tanh	Hyperbolic tangent
u	Fluid velocity, cm/sec
Y	Yield

Subscripts

i	internal
x	external
o	overall

Greek Notation

η	Catalytic effectiveness
ϕ	Thiele modulus
γ	Diffusivity ratio $\mathfrak{D}_B/\mathfrak{D}_A$
θ	Contact time, sec

INTRODUCTION

It would seem that the topics of diffusion-affected catalytic activity and yield or selectivity have been exhaustively treated in the decades following Thiele's classic revelations (*1-3*). Yet, with two exceptions (*4*, *5*), previous analyses rest upon the *implicit* assumption that all of the active catalytic area resides *within* the porous catalytic pellet, particle, or extrusion. Further, many analyses ignore mass diffusional gradients in the fluid boundary layers bathing the catalyst formulation.

When external fluid film mass-transport

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and external catalytic surface area are both ignored, analyses predict that the first-order catalytic effectiveness, η, at values of the Thiele modulus

$$\phi_1 = L[(kS)/\mathfrak{D}]^{1/2} \qquad (1)$$

greater than about 3 is

$$\eta = 1/\phi. \qquad (2)$$

The general solution for flat plate geometry is

$$\eta = \tanh \phi/\phi. \qquad (3)$$

An external mass transport resistance can be anticipated with the result (*6*):

$$\eta = \frac{\tanh \phi}{\phi\{1 + [\phi \tanh \phi/(\mathrm{Bi})]\}}, \qquad (4)$$

where

$$(\mathrm{Bi}) = \frac{k_g L}{\mathfrak{D}} = \frac{\text{internal gradient}}{\text{external gradient}} \text{ of mass.}$$

For large values of ϕ, Eq. (4) reduces to

$$\eta = (\mathrm{Bi})/\phi^2 = k_g/k, \qquad (5)$$

where k is the catalytic rate coefficient (cm/sec). Equations (3) and (4) follow from the assumption that external catalytic area is virtually zero relative to internal area, S. In the first-order case, we note that the usual linear kinetic rate coefficient is

$$k\left(\frac{\text{catalytic area}}{\text{volume of catalyst}}\right) = \frac{1}{\text{sec}} = kS = k_1. \qquad (6)$$

[Obviously only some fraction of total (internal plus external) area is "catalytic"; however, specification of that fraction is not at hand–hence rate coefficients for, say linear kinetics, are given in terms of the homogeneous counterpart, i.e., $k(a + S) = 1/\text{sec}$.]

Point yield (or selectivity) of intermediate B in the linear network

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

is readily derived for negligible external mass transfer resistance as (*2, 3*), where $K = k_1/k_2$ and $\gamma = \mathfrak{D}_B/\mathfrak{D}_A$:

$$Y_B = \left(\frac{dB}{dA}\right) = -\gamma \frac{\phi_2 \tanh \phi_2}{\phi_1 \tanh \phi_1}\left(\frac{B_0}{A_0} + \frac{K}{\gamma K - 1}\right) + \gamma\left(\frac{K}{\gamma K - 1}\right). \qquad (7)$$

The limiting value of Y_B at large values of ϕ_1 is, when $B_0 = 0$, and $\gamma = 1$:

$$Y_B = \left[\frac{1}{\phi_1}\left(\frac{K}{K-1} - \frac{1}{\sqrt{K}}\right)\right] \bigg/ \frac{1}{\phi} = \left(\frac{K}{K-1} - \frac{1}{\sqrt{K}}\right). \qquad (8)$$

Anticipating external resistance Eq. (7) is:

$$Y_B = -\gamma \frac{m_1 \phi_2 \tanh \phi_2}{m_2 \phi_1 \tanh \phi_1}\left(\frac{B_0}{A_0} + \frac{K}{K - 1}\right) + \gamma\left(\frac{K}{\gamma K - 1}\right), \qquad (9)$$

where

$$m_1 = 1 + [\phi_1 \tanh \phi_1/(\mathrm{Bi})]; \quad m_2 = 1 + [\phi_2 \tanh \phi_2/(\mathrm{Bi})].$$

The limiting value for large ϕ and finite Biot number is ($\gamma = 1$):

$$Y_B = \left(\frac{K}{K-1} - \frac{[1 + \phi_1/(\mathrm{Bi})]}{[1 + \phi_1/\sqrt{K}(\mathrm{Bi})]} \cdot \frac{1}{\sqrt{K}}\right). \qquad (10)$$

Equations (7) and (9) are rooted in the assumption of zero external surface area.

Kramers and Westerterp (*4*) developed an isothermal effectiveness factor as a function of both internal–external area and fluid film resistance. Kramer (*5*) considered selectivity in the consecutive reaction network in terms of internal–external catalyst area and concluded that at high values of the Thiele modulus yield the intermediate passes from a minimum to unity. In point of fact, as the following analysis demonstrates, such behavior is not possible unless the Biot number approaches infinity, which is another impossibility.

ANALYSIS

Assume a porous pellet of external area per unit volume a, and internal area per unit volume S. Following Kramer, let

$$f = a/(a + S).$$

The point yield of B is in the consecutive linear reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

is

$$\frac{dB}{dA} = Y_B$$
$$= \frac{[(dA/d\theta)(dB/dA)]_i + [(dA/d\theta)(dB/dA)]_x}{(dA/d\theta)_i + (dA/d\theta)_x}, \tag{11}$$

where subscript i refers to the internal reaction and x to that occurring on the external catalyst surface. A general solution results by specifying the internal–external yield-activity functions in terms of *both* internal and external diffusion of mass.

Noting that k_1 is based on the total area, $a + S$, then

$$(dA/d\theta \mathrm{l}) = \eta_i(1 - f)k_1A_0;$$
$$(dA/d\theta_x) = \eta_x f k_1 A_0;$$
$$(dB/dA)_i = Y_i, \text{ internal yield};$$
$$(dB/dA)_x = Y_x, \text{ external yield},$$

and η_i and η_x are, respectively, the internal and external effectiveness factors.

Equation (11) can thus be written as

$$Y_B = \frac{(1 - f)k_1A_0\eta_iY_i + f\eta_xk_1A_0Y_x}{(1 - f)k_1A_0\eta_i + fk_1A_0\eta_x},$$

or

$$Y_B = \frac{(1 - f)\eta_iY_i + f\eta_xY_x}{(1 - f)\eta_i + f\eta_x}. \tag{12}$$

Equation (12) is not general if it be assumed that η_x is unity, which is implicit in previous developments. This assumption is tantamount to the assertion that external fluid film mass transport is always rapid in contrast with other events, in particular the external surface reaction. The terms in Eq. (12) may now be rendered explicit.

Internal Effectiveness and Yield

The internal (intraphase) effectiveness, η_i, is easily phrased in terms of the Thiele modulus, ϕ, and the external mass transport Biot number (Bi). For even if external surface, a, is negligible relative to total surface, $a + S$, the limiting value of η_i must reflect external transport to the pore mouth (*6*):

$$\eta_i = \frac{\tanh \phi}{\phi\{1 + [\phi \tanh \phi/(\mathrm{Bi})]\}}. \tag{4'}$$

The internal (intraphase) diffusion-affected point yield in terms of external mass transport for consecutive reaction is (*7*):

$$Y_i = -\gamma \frac{m_1}{m_2} \frac{\phi_2 \tanh \phi_2}{\phi_1 \tanh \phi_1} \left(\frac{B_0}{A_0} + \frac{K}{\gamma K - 1}\right) + \gamma\left(\frac{K}{\gamma K - 1}\right). \tag{9'}$$

External Effectiveness and Yield

Here we deal with effectiveness and yield for the external catalytic surface. Fluid film-affected reaction upon a nonporous catalytic surface is our model. For effectiveness (*8*):

$$\eta_x = 1/1 + \mathrm{Da}, \tag{13}$$

where $\mathrm{Da} = k/k_g$ = Damköhler number.

The external catalytic point yield is (*8*):

$$Y_x = \frac{1}{1 + (\mathrm{Da})_2} - \left(\frac{k_2}{k_1}\right) \frac{[1 + (\mathrm{Da})_1]}{[1 + (\mathrm{Da})_2]} \left(\frac{B_0}{A_0}\right). \tag{14}$$

In Eqs. (4) and (9) we note that the mass Biot number and its magnitude reflects the extent of external diffusional intrusions upon internal effectiveness and yield. Its importance in governing the external effectiveness and yield is suggested by an examination of the Damköhler number in terms of the Thiele modulus and Biot number:

$$\mathrm{Da}_1 = \frac{k}{k_g} = \frac{k_1[a/(a + S)]}{k_g a} = \frac{\phi_i^2}{(\mathrm{Bi})} f. \tag{15}$$

It follows that the importance of external area and its ratio to total area is critically dependent upon the square of the magnitude of the internal Thiele modulus and the external to total surface area, f, divided by the mass Biot number, (Bi). Thus, even for large values of (Bi) at large values of ϕ_i and realistic values of f, the resulting Damköhler number can be significant and, therefore, external–internal effectiveness and yield are affected by the existence of a finite external area.

General effectiveness is then given in terms of f, the mass Biot number and Thiele modulus, for finite external-internal area, by:

$$\eta = \frac{(1-f)\tanh\phi}{\phi\{1+[\phi\tanh\phi/(\mathrm{Bi})]\}} + \frac{f}{\{1+[\phi^2 f/(\mathrm{Bi})_m]\}}. \qquad (16)$$

For large values of ϕ:

$$\eta = [(\mathrm{Bi})/\phi^2](2-f), \qquad (17)$$

while neglect of external mass transport leads to the limiting result for large ϕ (*5*):

$$\eta = f. \qquad (18)$$

Neglect of both external area and external mass transfer leads to a limiting effectiveness of:

$$\eta = 1/\phi. \qquad (2)$$

The point yield of the intermediate in terms of finite f and the Biot number is, by substituting Eqs. (4), (9), (13), and (14) into (12):

$$Y_B = \frac{(1-f)(\text{Eq 4})(\text{Eq 9}) + f(\text{Eq 13})(\text{Eq 14})}{(1-f)(\text{Eq 4}) + f(\text{Eq 13})} \qquad (19)$$

For values of ϕ greater than 3, tanhϕ is unity and the point yield for $\gamma = 1$ and $B_0 = 0$ is:

$$Y_B = \frac{\left[\dfrac{(1-f)}{\phi_1[1+\phi_1/(\mathrm{Bi})]}\left(\dfrac{K}{K-1} - \dfrac{[1+\phi_1/(\mathrm{Bi})]}{[1+\phi_1/\sqrt{K}\,(\mathrm{Bi})]}\cdot\dfrac{1}{\sqrt{K}}\right) + \dfrac{f}{\{1+[\phi_1^2 f/(\mathrm{Bi})]\}\{1+[\phi_1^2 f/K(\mathrm{Bi})]\}}\right]}{\left[(1-f)\left(\dfrac{1}{\phi_1[1+\phi_1/(\mathrm{Bi})]}\right) + \dfrac{f}{\{1+[\phi_1^2 f/(\mathrm{Bi})]\}}\right]}. \qquad (20)$$

Note that both activity (Eq. 16) and point yield (Eqs. 19–20) are functions of external to total area, f, to the extent that the Damköhler number,

$$\mathrm{Da} = k/k_g = \phi_1^2 f/(\mathrm{Bi}).$$

is finite.

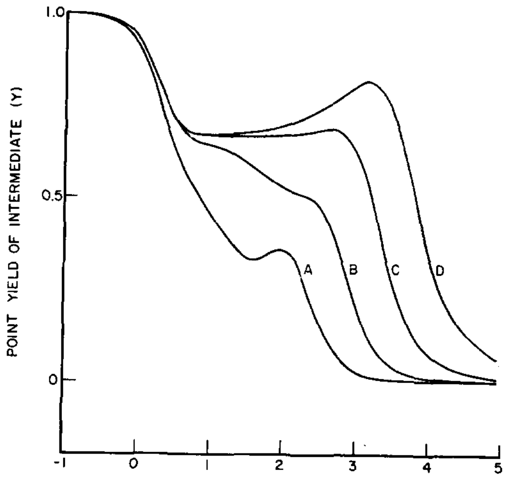

FIG. 1. Point yield of B vs the Thiele Modulus ϕ_1: $f = 10^{-3}$; $B_0 = 0$; $k_1/k_2 = 4$. Values of (Bi): A: 10; B: 10^2; C: 10^3; D: 10^4.

Equation (20) is to be contrasted with Eq. (8) for $f = 0$ and Bi = infinity, and Eq. (10) for finite Bi but $f = 0$. Kramer's result for $\phi > 3$ is:

$$Y_B = \frac{\left[(1-f)\dfrac{1}{\phi_1}\left(\dfrac{K}{K-1} - \dfrac{1}{\sqrt{K}}\right) + f\right]}{(1-f)\dfrac{1}{\phi_1} + f}. \qquad (21)$$

RESULTS

We illustrate the matter by a display of point yield vs ϕ_1 for cases of $f = 10^{-3}$ and 10^{-7} as shown in Figs. 1 and 2 when the intermediate is absent in the bulk stream ($B_0 = 0$). In Figs. 3 and 4, the point yield vs ϕ_1 for $f = 10^{-3}$ and 10^{-7}, where $B_0 = 0.1$, is displayed. In all cases $k_1/k_2 = 4$, a ratio of intrinsic rate coefficients utilized by Kramer (*5*). A wide and realistic range of

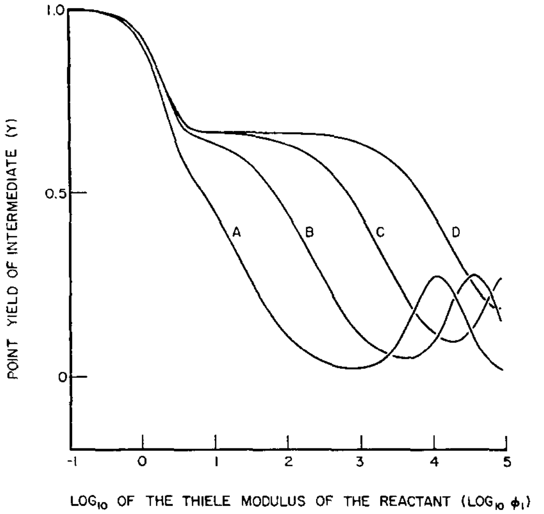

FIG. 2. Point yield of B vs the Thiele Modulus ϕ_1: $f = 10^{-7}$; $B_0 = 0$; $k_1/k_2 = 4$. Values of (Bi): A: 10; B: 10^2; C: 10^3; D: 10^4.

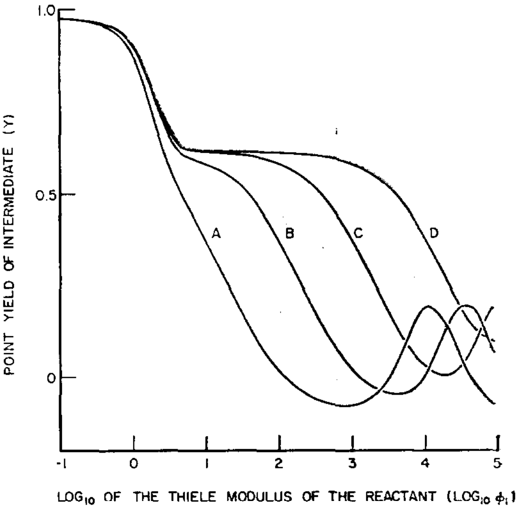

FIG. 4. Point yield of B vs the Thiele Modulus ϕ_1: $f = 10^{-7}$; $B_0 = 0.1$; $k_1/k_2 = 4$. Values of (Bi): A: 10; B: 10^2; C: 10^3; D: 10^4.

mass Biot numbers is embraced by our computations. The noteworthy result is that, contrary to earlier assertions, the point yield of the intermediate passes through a minimum, then a maximum (not equal to unity), and finally a zero (or less than zero) yield (when $B_0 \neq 0$) results.

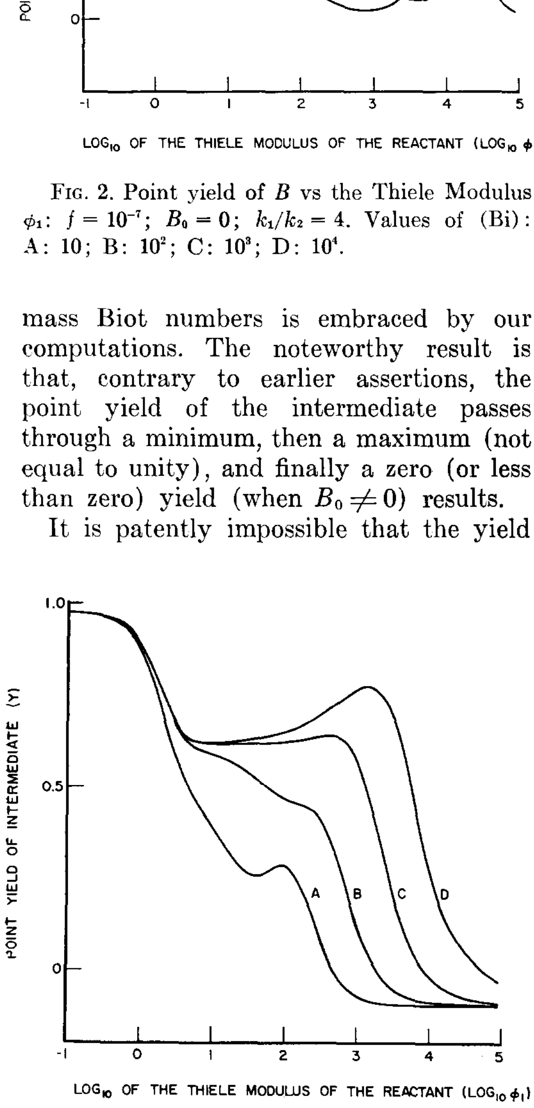

FIG. 3. Point yield of B vs the Thiele Modulus ϕ_1: $f = 10^{-3}$; $B_0 = 0.1$; $k_1/k_2 = 4$. Values of (Bi): A: 10; B: 10^2; C: 10^3; D: 10^4.

It is patently impossible that the yield of the intermediate be unity at high values of ϕ_1, as suggested earlier. Given a reasonable value of f (say 10^{-7}), and a tolerable value of (Bi) (say 10^2), then at a Thiele modulus of 10^5, for the first of a two-step series reaction, the resulting Damköhler number is, by Eq. (15):

$$(\mathrm{Da})_1 = [(10^5)^2 10^{-7}/6 \times 10^3] = 1.$$

Thus by Eq. (13), η_x is not 1 but ½; nor is Y_x that commensurate with a diffusion-uninhibited external surface reaction. The point is of some import since values of the Thiele modulus for consecutive reactions can assume large magnitudes indeed. For example, in a simulation of fixed-bed oxidation of naphthalene (*9*) employing published rate coefficients for a V_2O_5 catalyst, Thiele moduli of the order of 10^5 are found in the region of reactor hot spots. To be sure, at smaller values of ϕ_1, the Damköhler number is negligible, but at smaller values of ϕ_1, say 10, external area is of negligible importance.

It is of interest to compute the Biot number required to cause an intermediate yield of unity at high values of ϕ_1. The key parameter is the Damköhler number, $\phi_1^2 f/(\mathrm{Bi})$. Let us suppose that it must be 0.1 or less if external mass-transport effects are to be insignificant. Assuming $f = 10^{-7}$ and a ϕ_1 of 10^6, then it is necessary that

$$(\mathrm{Bi}) \geqq 10^6.$$

Assume a particle Reynolds number of 10^6, a 1-mm catalyst particle and kinematic viscosity (of air) of 2×10^{-2} cm^2/sec. Superficial velocity through the reactor then becomes *supersonic* at 2×10^5 cm/sec. The fluid film mass transport coefficient is, for a fixed bed (*10*):

$$k_g = \frac{1.15u}{[(d_p u/\nu)]^{1/2}} \cong 2 \times 10^2 \text{ cm/sec.}$$

For an intraparticle diffusivity of 10^{-3} cm^2/sec, the Biot number is:

$$(\mathrm{Bi}) = [(2 \times 10^2)(0.1)/6 \times 10^{-3}] = 3 \times 10^3,$$

a value far less than that minimum found necessary for a negligible external transport intrusion. A value of $f = 10^{-3}$ reduces the critical Biot number, but intraparticle diffusivity would be correspondingly higher than the value assumed above as a low BET area catalyst would be characterized by a higher diffusivity. In any case, Mach numbers well in excess of unity must prevail to secure very large values of (Bi).

Physical Implications

The characteristics of Figs. 1–4 reflect physical–chemical events which are best understood in terms of the Damköhler number:

$$\mathrm{Da} = [\phi_1^2 f/(\mathrm{Bi})] = [\phi_1/(\mathrm{Bi})](\phi_1 f).$$

At small values of ϕ_1, say less than unity, reaction occurs throughout the pellet and hence diffusion-unaffected activity and yield prevail. With the manifestation of diffusional retardation (increasing ϕ_1), the zone of reaction moves from within the total pellet towards the external surface. Internal yield drops as the term:

$$\phi_1/\mathrm{Bi}$$

in Eq. 20 becomes significant. However, because of the typically small values of f, the Damköhler number remains insignificant. With a further increase in ϕ_1, the zone of reaction moves to the external surface of the pellet. Yield will then increase *until* the Damköhler number becomes significant (large values of ϕ_1), beyond which point the yield must fall to zero as dictated by a complete external diffusion-controlled reaction. Thus a maximum is found in the Thiele modulus range of transition from an internal surface reaction to an external surface reaction regime.

Conclusions

Isothermal catalytic effectiveness and point yield of the intermediate in a consecutive reaction are each affected by external to total area ratio as well as the mass Biot number which characterizes external mass transport. These influences become manifest at high values of the reactant Thiele modulus. Under no realistic circumstance can the intermediate yield recover to a value of unity when the reaction zone retreats to the external surface. The critical parameter is the surface Damköhler number Da, which is related to the Thiele modulus ϕ_1 and external to total area ratio f and the Biot number by

$$\mathrm{Da} = k/k_g = \phi_1^2 f/(\mathrm{Bi}),$$

where the modulus must be less than about 0.1 if external mass transport retardation is to be ignored.

Acknowledgment

We are indebted to Mrs. John DeWilde for her invaluable editorial assistance.

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