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NOTE

Effect of the External Surface on the Reaction Rate and Selectivity of Isothermal Catalyst Particles

At small values of the Thiele modulus, the selectivity of isothermal porous catalyst particles for two consecutive first-order chemical reactions has been shown to be equivalent to that of plane surfaces (*1*, *2*). As the particle radius and Thiele modulus increase and become very large, catalyst selectivity again should approach that of a plane surface since this is the limiting case for a sphere with a very large radius. Weisz (*3*, *4*) considered selectivity within isothermal porous catalyst particles and obtained an expression which does not predict behavior similar to that of plane surfaces at large values of the Thiele modulus because the catalytic activity of the external surface had been neglected. The present study examines the influence of the external surface on the over-all rate of reaction and yield of the intermediate component.

Weisz (*3*, *4*) investigated the two consecutive first-order chemical reactions

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

occurring isothermally within porous spherical catalysts of radius R. For this case, the yield of component B, that is, the fraction of component A which has reacted and is converted to component B, is

$$Y_p = -\frac{d[B]}{d[A]} = \frac{S}{S-1} - \left(\frac{S}{S-1} + \frac{[B]^0}{[A]^0}\right) \frac{(\phi/\sqrt{S}) \coth (\phi/\sqrt{S}) - 1}{\phi \coth \phi - 1} \quad (1)$$

In Eq. (1), $S = K_1/K_2$, $\phi = R(K_1/D)^{1/2}$, D is the effective intraparticle diffusivity of components A and B, $[A]^0$ and $[B]^0$ are the bulk concentrations of components A and B that are present at the external surface of the particle, and K_1 and K_2 are the intrinsic chemical reaction rate constants per unit surface of catalyst.

At low values of the Thiele modulus (ϕ), the yield of component B approaches 1.0 when $[B]^0/[A]^0 = 0$. Wheeler (*1*, *2*) has shown that at sufficiently low values of the Thiele modulus ($\phi < 0.1$), catalyst selectivity is equivalent to that of plane surfaces. At these conditions, diffusion is rapid compared to the rate of reaction causing the concentrations to be uniform throughout the interior of the particle and the same as the bulk concentrations that are present at the external surface of the particle.

As the particle radius increases and ϕ becomes very large, the selectivity of porous catalyst particles again should approach that of plane surfaces since they are the limiting case for spheres with very large radii. Physically this is analogous to solid particles or to porous particles with such a low intraparticle diffusivity that only the external surface "sees" the reactant, and all the conversion occurs on the external surface. Under these conditions, intraparticle mass diffusion should have no effect on catalyst selectivity since the effective catalytic surface "sees" the reactant at the bulk concentrations. Consequently, selectivity should be the same as that of plane surfaces. Equation (1) does not predict this behavior because the catalytic activity of the external surface has been neglected.

The intraparticle Thiele effectiveness factor (*5*) for the first reaction in a series of consecutive reactions occurring within isothermal porous catalysts is the same as that for a single reaction occurring at the same conditions (*1*, *6*) and is

$$\eta_p = \frac{3}{\phi}\left[\frac{1}{\tanh \phi} - \frac{1}{\phi}\right] \qquad (2)$$

The influence of the catalytic activity of the external surface can be included by observing that the total rate of reaction of component A per unit surface of catalyst is the sum of the intraparticle and surface rates of reaction. Therefore,

$$-\,d[\mathrm{A}]/dt = (1-f)K_1[\mathrm{A}]^0\eta_p + fK_1[\mathrm{A}]^0$$

where f is the ratio of the external surface area to the total surface area of the catalyst particle.

The over-all effectiveness factor for the first reaction is the ratio of the total rate of reaction to that rate which would occur if the entire particle were exposed to the concentration of component A that is present at the external surface, and is

$$\eta = \frac{(1-f)K_1[\mathrm{A}]^0\eta_p + fK_1[\mathrm{A}]^0}{K_1[\mathrm{A}]^0} = (1-f)\eta_p + f \qquad (3)$$

Equation (3) reduces to the intraparticle Thiele effectiveness factor given by Eq. (2) when $f = 0$, which corresponds to no external surface area. However, for most porous catalyst particles f is between 10^{-3} and 10^{-7}. Figure 1 shows the dependence of the over-all effectiveness factor on ϕ for five values of f. When ϕ is sufficiently large, the catalytic activity of the external surface predominates, and the over-all effectiveness factor attains a constant value that is equal to f.

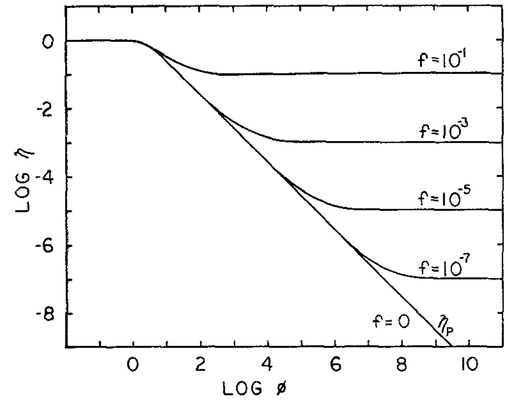

FIG. 1. The logarithm of the over-all effectiveness factor versus the logarithm of ϕ for $f = 0$, 10^{-7}, 10^{-5}, 10^{-3}, and 10^{-1}.

The yield of component B produced by the reactions occurring on the external surface of the particle is the same as that for plane surfaces or solid particles (*1*, *4*) and is

$$Y_s = -\frac{d[\mathrm{B}]}{d[\mathrm{A}]} = \frac{K_1[\mathrm{A}]^0 - K_2[\mathrm{B}]^0}{K_1[\mathrm{A}]^0} = \frac{S - [\mathrm{B}]^0/[\mathrm{A}]^0}{S}$$

The over-all yield of the intermediate component, Y, is the weighted mean of the intraparticle and surface yields

$$Y = \frac{(1-f)K_1[\mathrm{A}]^0\eta_p Y_p + fK_1[\mathrm{A}]^0 Y_s}{(1-f)K_1[\mathrm{A}]^0\eta_p + fK_1[\mathrm{A}]^0} = \frac{(1-f)\eta_p Y_p + fY_s}{(1-f)\eta_p + f} \qquad (4)$$

Equation (4) predicts the yield of component B as a function of the Thiele modulus ϕ, intrinsic selectivity ratio (S), ratio of the external surface area to the total surface area of the particle (f), and bulk concentrations that are present at the external surface of the particle ($[\mathrm{A}]^0$, $[\mathrm{B}]^0$). Equation (4) reduces to Weisz's Eq. (1) when $f = 0$, which corresponds to no external surface area.

Figure 2 shows the dependence of the yield of component B on ϕ when $S = 4.0$ and $[\mathrm{B}]^0/[\mathrm{A}]^0 = 0$ for five values of f. At low and intermediate values of ϕ, the intraparticle catalytic activity predominates, and the effect of the external surface is not observed. However, at sufficiently large values of ϕ, the catalytic activity of the external surface predominates, and the selectivity of the porous particles again approaches that of plane surfaces or solid particles.

Because f is very small for most porous catalysts, the catalytic effect of the external surface is not likely to be of practical significance except in the case of extremely fast reactions. However, it is interesting to observe that selectivity is the same at both very small and very large values of the Thiele modulus, and intraparticle mass

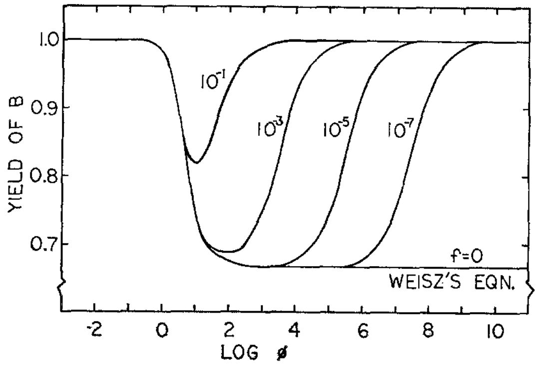

FIG. 2. The yield of component B versus the logarithm of ϕ when $S = 4.0$ and $[B]^0/[A]^0 = 0$ for $f = 0$, 10^{-7}, 10^{-5}, 10^{-3}, and 10^{-1}.

diffusion influences catalyst selectivity only at intermediate values of the Thiele modulus. Furthermore, this analysis shows the relationship between porous and solid catalyst particles and demonstrates how the Thiele modulus may be used to characterize the transition between porous and solid catalysts.

NOMENCLATURE

[A]	Concentration of component A (moles/cm^3)
[B]	Concentration of component B (moles/cm^3)
D	Effective intraparticle diffusivity of components A and B (cm^2/sec)
f	Ratio of the external surface area to the total surface area of the catalyst particle
K_1	Intrinsic first-order reaction rate constant per unit surface of catalyst for the first reaction (1/sec cm^2)
K_2	Intrinsic first-order reaction rate constant per unit surface of catalyst for the second reaction (1/sec cm^2)
R	Radius of catalyst particle (cm)
S	K_1/K_2, intrinsic selectivity ratio
t	Time (sec)
Y	Yield of component B expressed as the fraction of component A which has reacted and is converted to component B
ϕ	$R\sqrt{K_1/D}$, dimensionless Thiele modulus
η	Catalyst effectiveness factor

Subscripts

p	Referring to intraparticle conditions
s	Referring to surface conditions

Superscript

0	Referring to bulk conditions that are present at the external surface of the particle

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