The Micro-Macro Effectiveness Factor for the Reversible Catalytic Reaction

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In the wake of the classic work of Thiele (*10*) considerable attention has been devoted to the influence of species diffusion within porous catalyst particles upon activity and selectivity (*1, 9, 13, 14*). While the major effort had been focused upon irreversible reactions, Smith and Amundson (*9*) analyzed reversible catalytic reactions in terms of both inter and intraparticle mass diffusion. Recently a series of papers have appeared which treat the more complex problem encountered when uniformity of temperature within the catalyst becomes an unwarranted assumption (*2, 3, 5, 6, 8, 11, 12*).

Most of the cited treatments presume a simple pore structure (macro or micropore) or that an experimentally determined diffusivity characterizes diffusion during catalysis. Catalyst pellet pore structure is known to be of a complex nature. When, for example, small (micro) pores exist in parallel with large (macro) pores, diffusivity coefficients determined by measurement of net transport through the pellet (*13*) do not reflect the existence of micropores. During catalysis however micropores are indeed engaged in the diffusion-reaction process. When micropores exist in series with macropores, net diffusion measurements are of value (*7*).

Both experimental data (macro and micropore diffusivities) and a mathematical model are required for an assessment of effectiveness and selectivity when a parallel network of micro and macropores is known to characterize a catalyst pellet. For irreversible reaction Mingle and Smith (*6*) and Harriott (*4*) considered a catalyst pore model of the complex type discussed above. The pellet is assumed to comprise an aggregate of porous microspheres; hence the entire catalyst particle is characterized by macropores created via pelleting of the porous microspheres. Viewed in an idealized fashion this macro-micropore model is equivalent to a cylindrical main (macro) pore from which small (micro) pores are branched along the wall and at right angle (on the average) to the main pore.

For this relatively complex pore network the effectiveness factor has been derived for irreversible reaction (*6, 4*) and under nonisothermal conditions (*6*).

The treatment presented here is an elementary extension of the isothermal effectiveness factor for first-order reversible reaction as catalyzed by pellets composed of micropores branched from macropores. Intraparticle diffusion is assumed to obey Fick's law; hence the model is limited to Knudsen diffusion and/or molecular diffusion under circumstances of dilute solution. Knudsen diffusion would most certainly prevail in the micropores, while molecular transport may exist in the main or macropores. In the absence of a high degree of reactant dilution the more rigorous law of molecular diffusion (Stefan-Maxwell) must be invoked (*5*). The influence of diffusion in the fluid film surrounding the particle is included on this analysis, and the results are presented in concise graphical form.

The effect of temperature gradients in either phase is neglected in this simple treatment. For reversible reactions, heat generation or abstraction within a given phase exerts an influence upon effectiveness which is less pronounced than in irreversible cases. This result follows from the fact that the equilibrium constant varies with temperature in a manner such as to compensate for the rate coefficient temperature dependency. In consequence the net rate of reversible reaction is less temperature sensitive than in the irreversible case.

SOLUTION

For the reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

the governing equation for the microsphere is, when one assumes $D_a = D_b$

$$D_a \nabla^2 a = (k_1 + k_{-1})a - k_{-1}\,[B_o/A_o + 1] \quad (1)$$

Invoking the analysis of Aris (*1*) one may deal with a flat-plate geometry by defining the pore length in terms of the volume to external surface area of the particle. For micropores of length y Equation (1) is expressed in reduced dimensions as

$$\frac{d^2 a}{d\rho^2} = \overline{\psi}^2 a - \overline{\psi}^2 \frac{[B_o/A_o + 1]}{K + 1} \quad (2)$$

$$\rho = 1, a = \overline{a} \qquad \rho = 0, da/d\rho = 0$$

The solution is

$$a = \overline{a}\,\frac{[K - B_o/A_o]\cosh \overline{\psi}\rho}{(K+1)\cosh \overline{\psi}} + \frac{(B_o/A_o + 1)}{(K + 1)} \quad (3)$$

where $K = k_1/k_{-1}$. The micropore effectiveness $\overline{\eta}$ is therefore

$$\overline{\eta} = \frac{\tanh \overline{\psi}}{\overline{\psi}} \quad (4)$$

where

$$\overline{\psi} = y\sqrt{\frac{k_1}{D_a}\left(\frac{K+1}{K}\right)} \quad (5)$$

For large values of the equilibrium constant K the above relationship reduces to the usual first-order irreversible effectiveness factor definition.

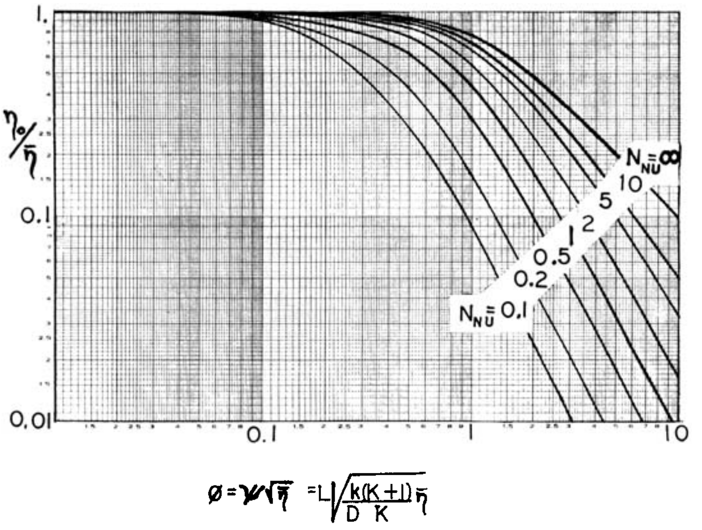

Fig. 1. Ratio of overall to micropore effectiveness factors, first-order reversible reactions.

The macropore concentration profile follows from solution of the equation

$$\frac{D_A}{L^2}\frac{d^2\bar a}{dz^2} = \bar\eta k_1 \bar a - \bar\eta k_{-1}(B_o/A_o + 1 - \bar a) \quad (6)$$

Hence

$$\frac{d^2\bar a}{dz^2} = L^2\frac{k_1}{D_A}\bar\eta\left(\frac{K+1}{K}\right)\bar a - L^2\frac{k_1}{D_A}\bar\eta\frac{(B_o/A_o+1)}{K} \quad (7)$$

or

$$\frac{d^2\bar a}{dz^2} = \phi^2\left[\bar a - \frac{(B_o/A_o+1)}{(K+1)}\right] \quad (8)$$

where

$$\phi^2 = L^2\frac{k_1}{D_A}\left(\frac{K+1}{K}\right)\bar\eta = \psi^2\bar\eta \quad (9)$$

The boundary conditions are

$$z = 1 \quad \bar a = 1 - \frac{1}{N_{Nu}}\left.\frac{d\bar a}{dz}\right|_{z=1}$$

$$z = 0 \quad \frac{d\bar a}{dz} = 0$$

where

$$N_{Nu} = \frac{k_g L}{D_A} = \frac{\text{fluid phase diffusivity}}{\text{porous solid diffusivity}} \quad (10)$$

The solution is readily found to be

$$\bar a = \frac{(K - B_o/A_o)\cosh\phi z}{\left(1 + \frac{\phi\tanh\phi}{N_{Nu}}\right)\cosh\phi} + \frac{(B_o/A_o+1)}{(K+1)} \quad (11)$$

The resulting overall effectiveness is the product of the micro $(\bar\eta)$ and macropore (η) effectiveness factors and a bulk mass transport function:

$$\eta_o = \frac{\phi\tanh\phi}{\left(1+\frac{\phi\tanh\phi}{N_{Nu}}\right)\psi^2} = \frac{\bar\eta\,\eta}{\left(1+\frac{\psi^2\bar\eta\,\eta}{N_{Nu}}\right)} \quad (12)$$

The ratio of the overall to micropore effectiveness $\eta_o/\bar\eta$ is concisely expressed as

$$\eta_o/\bar\eta = \frac{\tanh\phi}{\phi\left(1+\frac{\phi\tanh\phi}{N_{Nu}}\right)} \quad (13)$$

This relationship is displayed graphically in Figure 1, where the parameter is the Nusselt number expressed in terms of the fluid and porous solid mass transport coefficients as defined in Equation (10).

Figure 1 may be utilized to evaluate the microeffectiveness factor $(N_{Nu} = \infty)$ by setting

$$\phi = y\sqrt{\frac{k_1}{D_A}\left(\frac{K+1}{K}\right)}$$

and then $\eta_o/\bar\eta$ is evaluated for given values of $\psi\sqrt{\bar\eta}$ and Nusselt number.

The potential existence of a microeffectiveness contribution to the overall effectiveness of a pelleted catalyst creates interesting problems. One would conclude that diffusion coefficients are required for both the microspheres and the gross pellet to facilitate a valid assessment of overall catalytic effectiveness, unless it can be shown that the micropore effectiveness is virtually unity for a given reaction within the temperature range of interest.

NOTATION

a = reduced concentration of reactant in micropore, A/A_o
$\bar a$ = reduced concentration of reactant in macropore, $\bar A/A_o$
A_o = bulk phase concentration of reactant
B_o = bulk phase concentration of product
D_a = diffusivity in micropores
D_A = diffusivity in macropores
k_1 = forward reaction rate constant
k_{-1} = reverse reaction rate constant
K = equilibrium constant, k_1/k_{-1}
k_g = bulk phase mass transfer coefficient
L = effective macropore length (volume to external surface area of pellet)
N_{Nu} = Nusselt number, $k_g L/D_A$
y = effective micropore length (volume to external surface area of particle)
z = reduced pore length, x/L

Greek Letters

ρ = reduced micropore length, y/L
$\bar\psi$ = micropore diffusion-reaction modulus defined by Equation (5)
ψ = macropore diffusion-reaction modulus defined by Equation (9)
ϕ = overall diffusion-reaction modulus defined by Equation (9)
η_o = overall pellet effectiveness factor
$\bar\eta$ = macropore effectiveness factor $= \frac{\tanh\bar\psi}{\bar\psi}$
η = macropore effectiveness factor $= \frac{\tanh\phi}{\phi}$

LITERATURE CITED

1. Aris, Rutherford, *Chem. Eng. Sci.*, **6**, 262 (1957).
2. Beek, John, *A.I.Ch.E. Journal*, **7**, 337 (1961).
3. Carberry, J. J., *ibid.*, p. 350.
4. Harriott, Peter, Unpublished paper, Cornell Univ., Ithaca, New York.
5. Hawthorn, R. D., Paper presented at A.I.Ch.E. meeting, New York (December, 1961).
6. Mingle, J. O., and J. M. Smith, *A.I.Ch.E. Journal*, **7**, 243 (1961).
7. Robertson, J. L., and J. M. Smith, paper presented at A.I.Ch.E. meeting, New York (December, 1961).
8. Schilson, R. E., and N. R. Amundson, *Chem. Eng. Sci.*, **13**, 226 (1961).
9. Smith, N. L., and N. R. Amundson, *Ind. Eng. Chem.*, **43**, 2156 (1951).
10. Thiele, E. W., *ibid.*, **31**, 916 (1939).
11. Tinkler, J., and A. B. Metzner, *ibid.*, **53**, 663 (1961).
12. Tinkler, J., and R. L. Pigford, *Chem. Eng. Sci.*, **15**, 326 (1961).
13. Weisz, P. B., *Z. Physik. Chem., Neue Folge*, **11**, 1 (1957).
14. Wheeler, Ahlborn, "Catalysis," Vol. 2, Reinhold, New York (1955).