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Diffusivities in Catalyst Pellets with Bidisperse Pores

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Recently (Dogu and Smith, 1975), a dynamic version of the Wicke-Kallenbach method was developed for measuring effective diffusivities (D_e) in single catalyst pellets. The theory was derived for diffusion through the macropores surrounding the particles from which the pellet was produced. Hence, the method was strictly applicable only to pellets made from nonporous particles. However, first moment measurements for a pellet made from alumina particles, which contained micropores, indicated that the method was also applicable to such bidisperse pellets. Verification was sought by obtaining data for pellets of the same macro (α) and micro (β) porosities but prepared from different size particles. These data resulted in the same values of D_e even though the length of the diffusion path in the micropores was presumably changed. On this basis it was concluded that micropore diffusion did not affect application of the method for obtaining macropore diffusivities. Here we show theoretically that the conclusion is correct by extending the original development to bidisperse pellets. This is important because the experimental test is uncertain. Even though different size particles were used, the pelletting process may have reduced the particles to about the same dimensions.

For a bidisperse pellet it is supposed that diffusion occurs through the macropores surrounding the particles and in series fashion into the micropores. Then, instead of the single mass conservation equation [Equation (4) of Dogu and Smith, 1975], separate expressions are written for the macropores (interparticle region)

$$D_e \frac{\partial^2 C}{\partial x^2} = \alpha \frac{\partial C}{\partial t} + D_{ei} \frac{3(1-\alpha)}{r_o} \left(\frac{\partial C_i}{\partial r} \right)_{r=r_o} \tag{1}$$

and for the micropores (intraparticle region)

$$D_{ei} \left[\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \left(\frac{\partial C_i}{\partial r} \right) \right] = \beta \frac{\partial C_i}{\partial t} \tag{2}$$

with the boundary condition

$$C_i(r_o, t) = C(t) \tag{3}$$

relating the concentrations of diffusing component in the intraparticle and interparticle regions. The particles are assumed to be spherical of radius r_o and to have a micropore effective diffusivity D_{ei}. The pellet is cylindrical with diffusion in the axial direction (x) and with a length L. Initial and boundary conditions for the pulse experiments are the same as presented by Dogu and Smith (1975).

Linear Equations (1) and (2), with the boundary and initial conditions, were solved in the Laplace domain to give $\overline{C}(L, s)$. Then the first moment (retention time) of the response peak to an input pluse of diffusing substance is obtained from the expression

$$\mu_1 = \frac{m_1}{m_o} \tag{4}$$

where

$$m_1 = -\lim_{s \to 0} \frac{d\overline{C}(L, s)}{ds} \tag{5}$$

and

$$m_o = \lim_{s \to 0} \overline{C}(L, s) \tag{6}$$

Carrying out the indicated operations yields

$$\mu_1 = \frac{L^2}{6D_e} [\alpha + \beta(1-\alpha)] \frac{3\dfrac{AD_e}{L} + F}{\dfrac{AD_e}{L} + F} \tag{7}$$

This result is identical to that obtained by Dogu and Smith [their Equation (9)], since the term in brackets is the total porosity of the pellet.

An important feature of Equation (7) is that it does not contain the micropore diffusivity D_{ei}. Hence, micropore diffusivities cannot be obtained by this dynamic method, at least not from first moment information. The situation is analogous to pulse-response methods applied to fixed beds of particles through which a fluid is flowing. It has been shown (Schneider and Smith, 1968) that the first moment for that case is a function of the fluid

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velocity and capacity (void space) but not of intraparticle transport rate coefficients.

In contrast, the second central moment does become function of D_{ei}, as in the fixed-bed case. This can be shown by writing μ'_2 as

$$\mu'_2 = \frac{m_2}{m_o} - \left(\frac{m_1}{m_o}\right)^2 \tag{8}$$

where m_1 and m_o are given by Equations (5) and (6), and

$$m_2 = \lim_{s\to 0} \frac{d^2\overline{C}(L,s)}{ds^2} \tag{9}$$

Evaluating m_2 from the solution in the Laplace domain and using the previously obtained results for m_o and m_1, we get

$$\mu'_2 = \left\{ \frac{L^2}{6D_e}[\alpha + (1-\alpha)\beta] \right\}^2 \frac{\left(3\frac{AD_e}{L} + F\right)^2}{\left(\frac{AD_e}{L} + F\right)^2} - \frac{L^2}{90D_e}\left(\frac{r_o^2}{D_{ei}}\right)(1-\alpha)\beta^2 \frac{3\frac{AD_e}{L} + F}{\frac{AD_e}{L} + F} - \frac{1}{60}\left\{ \frac{L^2}{D_e}[\alpha + (1-\alpha)\beta] \right\}^2 \frac{5\frac{AD_e}{L} + F}{\frac{AD_e}{L} + F} \tag{10}$$

The second term of Equation (10) gives the contribution of intraparticle diffusion to μ'_2. When the particles are nonporous, $\beta = 0$, Equation (10) becomes identical to that given by Dogu and Smith (1976).

In principle, first moment data could be used with Equation (7) to obtain D_e, and then this result along with data for μ'_2 could be used with Equation (10) to obtain D_{ei}. An accurate result would depend on the second term of Equation (10) being relatively large with respect to the first and third terms. Use of a short pellet (small L) and large particles (large r_o) would favor this situation.

For a linear rate of adsorption on the intraparticle pore surface, the previous development can be readily extended to gases that adsorb as well as diffuse. The rate of adsorption is written

$$\frac{\partial n}{\partial t} = k\left(C_i - \frac{1}{K}n\right) \tag{11}$$

Equation (2) must be modified by adding to the right side the term $\rho(\partial n/\partial t)$. Then the solution of Equations (1) and (2) and Equation (11) gives for the first moment

$$\mu_1 = \frac{L^2}{6D_e}[\alpha + (1-\alpha)(\beta + \rho K)] \frac{3\frac{AD_e}{L} + F}{\frac{AD_e}{L} + F} \tag{12}$$

As in Equation (7), the bracketed term is a measure of the total capacity of the pellet for the adsorbable gas.

NOTATION

A = area of end face of cylindrical pellet, cm^2
C = concentration of diffusing gas in interparticle region; C_i = concentration in intraparticle region, mole/cm^3
$\overline{C}$ = Laplace transform of $C(x, t)$
D_e = effective diffusivity in macropores, cm^2/s
D_{ei} = effective diffusivity in micropores (intraparticle region), cm^2/s
F = volumetric flow rate through lower chamber of pellet holder, cm^3/s
K = adsorption equilibrium constant, cm^3/g
k = first-order adsorption rate constant, cm^3/(s) (g cat)
L = pellet length, cm
m_o, m_1, m_2 = elements of zero, first and second moments defined as $m_{n'} = \int_0^\infty C t^{n'} dt$
n = concentration of diffusing gas adsorbed on micropores, mole/(g cat)
r = radial coordinate in spherical particle; r_o = radius of particle, cm
s = Laplace variable, s^{-1}
t = time, s
x = coordinate in diffusion direction (axial direction) in cylindrical pellet, cm

Greek Letters

α = interparticle porosity in pellet
β = intraparticle porosity in pellet
μ_1 = first absolute in cylindrical pellet, s
ρ = particle density, g/cm^3
μ'_2 = second, central moment, s^2

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A Note on Gas Solid Noncatalytic Reactions

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Heterogeneous reactions between gases and solids play an important role in chemical and metallurgical industry. Mathematical modeling of these processes begins with the description of reaction of a single solid pellet. A