EFFECTIVE DIFFUSIVITY OF BIDISPERSE POROUS CATALYSTS UNDER REACTION CONDITIONS*

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The importance of pore diffusion resistance in gas-solid catalytic reactions has resulted in a number of investigations of diffusion rate within porous media. One approach compares the diffusion rates derived from kinetic studies with those calculated from theory. Another approach measures the diffusion rate in the absence of reaction and uses the results of the non-reacting system to predict the transport rates under reacting conditions. The final purpose is to establish a method for predicting catalyst performance from information concerning pore structure as well as reaction rate.

Several methods have been proposed so far for the measurement of diffusivities in porous materials, such as the Wicke-Kallenbach diffusion cell, adsorption balance, and chromatography. However the relationship among the values obtained by different methods has not been well discussed. In some cases the observed diffusion rate in the presence of reaction disagreed with that obtained from the diffusion cell7-12. In other cases the diffusivity under reaction conditions agreed with that without reaction8. Several investigations have been concerned with this discrepancy9-13.

Many catalysts employed for industrial processes are bidisperse because they are prepared by compressing particles of catalyst powder, which themselves are porous. Thus, the resulting pellet has two pore systems; micropores within the powder crystals and macropores corresponding to the space between the powder particles. Single effective diffusivity models have sometimes been employed to describe the performance of such catalysts. However, it has been shown9 that a single, effective diffusivity extracted from dynamic adsorption data for a bidisperse catalyst can have unreal values.

The purpose of the present investigation is to: 1), derive the effective diffusivity for a steady-state reacting system as a function of macropore and micropore diffusivities, on the basis of a real pore model for bidisperse catalysts, and 2), to decide what values of the diffusivity should be employed for description of catalyst performance.

Effective Diffusivity in Bidisperse Pellet

Several pore models are proposed to describe bidisperse catalysts. The model first proposed by Mingle and Smith6 and later employed by Carberry11 and Komiyama4 assumes that the pellet comprises an aggregate of porous micro spheres containing the micropores. The macropores are located between these micro spheres. Thus the micropores exist in series with macropores, and this is a more real pore structure for bidisperse catalysts compared with the model based upon parallel structure of micro and macropores, at least under reaction conditions.

Significant reaction occurs only on the micropores, because the surface area in macropores is relatively small. The following assumptions also are employed for this model.

1) The catalytic active crystals, which are regarded as spheres having an average radius of 2r, are dispersed homogeneously in a catalyst pellet, whose radius is R. The rest of the pellet consists of inactive binding material such as clay.

2) The spaces between these crystals and the binder are regarded as macropores9. The pathway through the crystals is considered to be micropores. It is assumed that the reactant diffuses first through macropores and then penetrates into the microporous crystals.

Thus the material balance for micro crystals may be written as

$$D_m \left( \frac{d^2 C_{A\mu}}{dr^2} + \frac{2}{r} \frac{dC_{A\mu}}{dr} \right) = k_i C_{A\mu}$$  \hspace{1cm} (1)

Then the effectiveness factor of the micro crystals may become

$$\eta_m = \frac{4\pi r^3 D_m (dC_{A\mu}/dr)|_{r=r}\mu}{(4/3)\pi r^3 k_i C_{A\mu}} = f(h_m)$$ \hspace{1cm} (2)
where
\[ h_f = r_f \sqrt{k_i D_m} \] (3)
The mass balance for catalyst pellet is
\[ D_m \left( \frac{d^2 C_{AM}}{dx^2} + \frac{2}{x} \frac{dC_{AM}}{dx} \right) = k_i \eta_f (1 - \varepsilon_m - \varepsilon_e) C_{AM} \] (4)
Thus, catalyst pellet effectiveness factor is
\[ \eta_f = -4\pi R D_m \left( \frac{dC_{AM}}{dx} \right)_{x=R} \] (5)
where
\[ h_f = R \sqrt{k_i \eta_f (1 - \varepsilon_m - \varepsilon_e)} / D_m \] (6)
If the total effectiveness is defined as
\[ \eta_{total} = -\frac{4\pi R^2 D_m (dC_{AM}/dx)_{x=R}}{(4/3) \pi R^3 / \eta_f} \] (7)
we obtain
\[ \eta_{total} = \eta_f \eta_M \] (8)
If the catalyst performance is described by a single effective diffusivity, the effectiveness can be written as
\[ \eta_{total} = \frac{3}{h} \left( \frac{1}{\tanh(h)} - \frac{1}{h} \right) \] (9)
where
\[ h = R \sqrt{\frac{k_l}{D_s}} \] (10)
The condition where \( h_M, h \gg 1 \) is often encountered in practice. For such condition the Eqs. (8) and (10) can be approximated as
\[ \eta_{total} = (3/h) \eta_f \] (11)
\[ \eta_{total} = 3/h \] (12)
Equating Eqs. (11) and (12) results in
\[ D_s = D_m \eta_f / [k_i (1 - \varepsilon_m - \varepsilon_e)] \] (13)
The reaction rate constant of Eqs. (9) and (10) must be obtained by experiments. The following cases are possible.
(A) The case where \( k_i \) is obtained experimentally. This reaction rate would be converted to the reaction rate in Eqs. (9) and (10) by
\[ V_s (1 - \varepsilon_m - \varepsilon_e) k_i \equiv V_s' k \] (14)
Thus
\[ k = (1 - \varepsilon_m - \varepsilon_e) \cdot k_i \] (15)
Putting the Eq. (15) into (13) gives
\[ D_s = D_m \eta_f \] (16)
(B) In the case where \( k_i \eta_f \) is obtained experimentally, Eq. (16) becomes
\[ D_s = D_m \] (17)
(C) The case where the experimentally obtained reaction rate is based upon the void volume of both micropores and macropores.

This case may occur for the catalyst whose microcrystal size cannot be clearly defined. For such a catalyst, the relationship between \( k \) and \( k_i \) of Eq. (13) is given as
\[ k = k_i \] (19)
Thus
\[ k = k_i \] (18)
From Eq. (13), we obtain
\[ D_s = D_m \eta_f / (1 - \varepsilon_m - \varepsilon_e) \] (20)

Discussion

While results shown by the previous equations seem easily obtained, examples are not common in the literature. The micropore effectiveness factor for some kinds of catalysts, such as zeolites, is known to be less than unity\(^9\). For such a catalyst, the effective diffusivity employed in Eq. (10) becomes a function of the reaction rate because of the effect of the change of physical properties due to reaction.

The micropore effectiveness factor is considered to be unity for the common catalysts. If this is true, the effective diffusivity which should be employed for prediction of catalyst performance as well as for the extraction of intrinsic reaction rate should be a function of macropore diffusivity, and not overall diffusivity including effects of both macropore and micropore diffusion. A number of investigations have compared the diffusivity under reaction conditions with that measured in a steady-state counter cell of the Wicke-Kallenbach type. If the diffusivity obtained in such a diffusion cell includes the micropore diffusion effects\(^11\) it will not be an adequate diffusivity to use under reaction conditions. If the diffusivity obtained by the diffusion cell reflects only the macropore diffusion, it should be a proper value to use for a reacting system with a bidisperse catalyst.

The above discussion supposes that rate parameters for each rate process are available. It should be mentioned that recently developed measuring techniques, such as chromatography and frequency response, provide rapid, simple methods for evaluating diffusion and reaction-rate parameters\(^3,5\).

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>( C_{AM} )</td>
<td>[g-mol/cm(^3)]</td>
</tr>
<tr>
<td>( C_{AP} )</td>
<td>[g-mol/cm(^3)]</td>
</tr>
<tr>
<td>( C_o )</td>
<td>[g-mol/cm]</td>
</tr>
<tr>
<td>( D_m )</td>
<td>[cm/( \text{sec} )]</td>
</tr>
<tr>
<td>( D_s )</td>
<td>[cm/( \text{sec} )]</td>
</tr>
<tr>
<td>( D_i )</td>
<td>[cm/( \text{sec} )]</td>
</tr>
<tr>
<td>( h )</td>
<td>Thiele modulus defined by Eq. (6)</td>
</tr>
<tr>
<td>( h_f )</td>
<td>Thiele modulus defined by Eq. (3)</td>
</tr>
</tbody>
</table>

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\[ k_i = \text{intrinsic reaction rate constant, based upon intracrystalline volume} \quad [1/\text{sec}] \]
\[ R = \text{pellet radius} \quad [\text{cm}] \]
\[ r = \text{coordinate in the direction of diffusion in microporous crystal} \quad [\text{cm}] \]
\[ r_p = \text{radius of microcrystal} \quad [\text{cm}] \]
\[ x = \text{coordinate in the direction of diffusion in pellet} \]
\[ V_e = \text{catalyst pellet volume} \quad [\text{cm}^3] \]
\[ \varepsilon = \text{porosity; } \varepsilon_p, \varepsilon_M \text{ and } \varepsilon_C \text{ denote void fractions of micropore and macropore, and fraction of clay} \]
\[ \eta = \text{effectiveness factor; } \eta_p \text{ and } \eta_M \text{ denote effectiveness factor of microcrystal and macropore diffusion, } \eta_{\text{total}} \text{ denotes effectiveness factor of a pellet} \]

**Literature Cited**


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**A NOTE ON CHROMATOGRAPHIC PARAMETER ESTIMATION**

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It is well understood that chromatographic technique is useful for parameter estimation. Several methods, different in weighting function, have been proposed.

Anderssen and White\(^1\) examined several estimation methods and have concluded that the best is to fit a signal in the time domain.

Similar conclusion is reached in this note, in which the time solution for the output signal \( C_{II} \) is computed by a convolution integral on the input signal \( C_i \) and Fourier inverting of the transfer function. This method of inversion transfer function in Fourier series is powerful when it is difficult to apply the ordinary Laplace inversion.

In the following transfer function,

\[
C_{ne} = F(s) \quad (1)
\]

the \( C_{II} \) is given by a convolution integral as

\[
C_{II} = \int_0^\infty C_i(t)e^{-s_t}dt = F(s) \quad (2)
\]

Substitution of \( s = \pi n/T \) into Eq. (3) gives

\[
\int_0^\infty f(t) \cos (n\pi t/T)dt = \text{Real } [F] = R_n
\]

\[
\int_0^\infty f(t) \sin (n\pi t/T)dt = \text{Imag } [F] = I_n \quad (4)
\]

When \( f(t) \) is expressed in Fourier series over a time range from \( t=0 \) to a time \( t=T \) long enough to let the tail of \( C_{II} \) vanish,

\[
f(t) = \sum_{n=0}^\infty \left[a_n \sin (n\pi t/T) + b_n \cos (n\pi t/T)\right] \quad (5)
\]

where

\[
a_n = (1/T) \int_0^T f(t) \sin (n\pi t/T) dt = -I_n/T
\]

\[
b_n = (1/T) \int_0^T f(t) \cos (n\pi t/T) dt = R_n/T
\]

\[
b_0 = (1/2T) \int_0^T f(t) dt = R_0/2T \quad (6)
\]

Then,

\[
f(t) = R_0/2T + \frac{1}{T} \sum_{n=1}^\infty \left[R_n \cos \frac{n\pi t}{T} - I_n \sin \frac{n\pi t}{T}\right] \quad (7)
\]

and the output signal may be calculated from Eqs. (2) and (7).

If \( f(t) \) is a delta shot, \( C_{II} \) is

\[
C_{II} = f(t) \quad (8)
\]

Let us take a look at an example shown in Wakao, Iida and Tanisho\(^3\), in which chromatographic