\[ E'_{av_t} = \sum_{k=1}^{\infty} E_{b_k} \cdot \frac{2J(a_k)}{m \cdot a_k^2} \left( 1 + 2m - \frac{4}{a_k^2} \right) \quad (A-13) \]

For sphere
\[ E_{av_t} = \frac{3E_{av_t} + 2E_{o_t}}{5} \quad (A-14) \]
\[ E'_{av_t} = \frac{3E'_{av_t} + 2E'_{o_t}}{5} \quad (A-15) \]
\[ E_{av_s} = \sum_{k=1}^{\infty} E_{b_k} \frac{3\sin(a_k)/a_k}{m \cdot a_k^2} \quad (A-16) \]
\[ E'_{av_s} = \sum_{k=1}^{\infty} E_{b_k} \frac{3\sin(a_k)/a_k}{m \cdot a_k^2} \left( 1 + 2m - \frac{6}{a_k^2} \right) \quad (A-17) \]

The values of \( E_{av_t}, E'_{av_t}, E_{av_s} - E_{av_s} \) and \( E'_{av_s} - E'_{av_s} \) are presented in Table 4.

Table 3 and 4 are also of use for the check points of calculation.

**Nomenclature**

- \( c_p \) = specific heat of solid [kcal/kg·°C]
- \( E_{av} \) = approximate value of \( E \) for \( t_0 \) (\( r = 0 \)) [-]
- \( E_{o_t} \) = approximate value of \( E' \) for \( t_0 \) (\( r = 0 \)) [-]
- \( E_{av_s} \) = approximate value of \( E \) for \( t_s \) (\( r = R \)) [-]
- \( E'_{av_s} \) = approximate value of \( E' \) for \( t_s \) (\( r = R \)) [-]
- \( h \) = heat transfer coefficient [kcal/m²·hr·°C]
- \( m \) = \( \lambda / Rk \) [-]
- \( P \) = \( (t_o - t_o)/(t_o - t_s) \) [-]
- \( R \) = radius or thickness of solid [m]
- \( r \) = distance from center [m]
- \( T \) = \( \alpha \theta / R^2 \) [°C]
- \( \theta \) = time [hr]
- \( \lambda \) = thermal conductivity [kcal/m·hr·°C]
- \( \rho \) = density [kg/m³]

\(<\text{Subscripts}>\)

- \( A \) = approximate value
- \( av \) = average value
- \( i \) = initial value
- \( o \) = center value
- \( s \) = surface value
- \( * \) = equilibrium value

**Literature Cited**


**INTRAPARTICLE DIFFUSIVITY OF POROUS CATALYSTS UNDER CONDITIONS WITH CHEMICAL REACTION**

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Department of Chemical Engineering, Kogakuin University, Tokyo, 160

Intraparticle diffusion models derived for the non-reacting condition have been applied to the expression of reaction kinetics for given systems. These are either successful or unsuccessful depending upon the systems. Several investigators also derived intraparticle diffusivity for the condition with chemical reaction. Although various models have been developed, there is no base to select the appropriate model for a given catalytic reaction system. In this study, the aim was to develop a simple pore model by which the application of the models proposed previously may be roughly explained.

**Structural Model for Bidisperse Catalyst**

Fig. 1 shows a pore model by which the intraparticle diffusivity for the reacting system may be obtained. In this model, it is assumed that the bidisperse pore network is composed of two kinds of pore network.

One of these will be called "macropore network" and the other "micropore network", according to the range of pore size exhibited by the networks. The external appearances of these networks are identical to that of the catalyst pellet.

Following assumptions may be utilized to derive the intraparticle diffusivity from proposed model:

1) The reaction is isothermal and irreversible first order with respect to the concentration of reactant gas A. The reaction rate per unit volume of catalyst pellet is given by

One of these will be called "macropore network" and the other "micropore network", according to the range of pore size exhibited by the networks. The external appearances of these networks are identical to that of the catalyst pellet.

Following assumptions may be utilized to derive the intraparticle diffusivity from proposed model:

1. The reaction is isothermal and irreversible first order with respect to the concentration of reactant gas A. The reaction rate per unit volume of catalyst pellet is given by

\[
\frac{dC_A}{dt} = -k \cdot C_A
\]

where

- \( dC_A/dt \) = reaction rate per unit volume of catalyst pellet
- \( k \) = reaction rate constant
- \( C_A \) = concentration of reactant gas A

The reaction rate constant \( k \) is related to the intraparticle diffusivity \( D \) and the rate of mass transfer \( m \) as follows:

\[
k = \frac{D}{m}
\]

**Fig. 1 Structural model of porous pellet**

Bidisperse catalyst pellet C is composed of micropore network A and macropore network B

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504 JOURNAL OF CHEMICAL ENGINEERING OF JAPAN
In each network, diffusivities under reacting condition are essentially the same as those for non-reacting condition, because of pore size uniformity or complete mixing of reactants between the pores in the networks. The diffusivities are estimated by means of the conventional method.

The part of the reactant diffusing into macropore network, penetrates into and also reacts on micropore network. The reverse process also exists. As a result the following reactivities are applicable to the reactants in macropore and micropore networks, respectively.

\[
\begin{align*}
  \kappa_{v,a} &= \kappa_a S_a + \eta \alpha_B \kappa_i S_i - \eta \beta_B \kappa_a S_a \\
  \kappa_{v,i} &= \kappa_i S_i - \eta \alpha_B \kappa_s S_s + \eta \beta_B \kappa_s S_s
\end{align*}
\]

where \( \eta \alpha_B \) is the fraction of surface area in micropore network occupied by the reactant in macropore network. \( \eta \beta_B \) is that for the reactant in micropore network. \( \gamma \) refers to the mass transfer resistance between the networks, and if the reactants are mixed completely between them, \( \gamma \) equals unity. Note that macropore reactivity is generally negligible compared to micropore reactivity for the commercial catalyst.

The parameters \( \gamma, \alpha_B \) and \( \beta_B \) are independent of the concentration of reactant so that \( \kappa_{v,a} \) and \( \kappa_{v,i} \) are constant within the pore networks.

Based upon the assumptions, the intraparticle diffusivity will be expressed in terms of \( D_a \) and \( D_i \). Considering a catalyst pellet in the form of a sphere, the catalyst effectiveness factor of the pellet can be shown to be as follows:

\[
E_p = 3 \sqrt{\frac{D_p}{\kappa_a S_a}} \quad (\phi_p > 3)
\]

Similarly, the effectiveness factor of the macropore and micropore networks may also be as follows:

\[
E_a = 3 \sqrt{\frac{D_a}{\eta \alpha_B \kappa_i S_i}} \quad (\phi_a > 3)
\]

\[
E_i = 3 \sqrt{\frac{D_i}{(1-\eta \alpha_B) \kappa_s S_s}} \quad (\phi_i > 3)
\]

When the reactants within the networks are mixed completely, that is \( \eta = 1.0 \), \( E_a \) equals \( E_i \) since the concentration profiles of the networks are identical with each other. Therefore,

\[
\frac{k_{v,a}}{k_{v,i}} = \frac{\alpha_B}{1-\alpha_B} = \frac{D_a}{D_i}
\]

where

\[
\begin{align*}
  k_{v,a} &= \alpha_B \kappa_i S_i \\
  k_{v,i} &= (1-\alpha_B) \kappa_s S_s
\end{align*}
\]

The apparent rate constant of the pellet, \( E_p \kappa_{v,p} \) can be expressed as the sum of those of the networks.

\[
E_p \kappa_{v,p} = E_a \kappa_{v,a} + E_i \kappa_{v,i}
\]

From these equations, Eq. (11) is obtained.

\[
\sqrt{D_p} \kappa_{v,p} = \sqrt{D_a} \eta \kappa_{v,a} + \sqrt{D_i} \kappa_{v,i} \left[ 1 + \frac{\alpha_B (1-\eta)}{1-\alpha_B} \right]
\]

Taking into account \( k_{v,p} = k_{v,a} + k_{v,i} \) and Eq. (7), one gets the following equation from Eq. (11).

\[
D_p = \frac{D_a \sqrt{\eta} + D_i \sqrt{1+(D_a/D_i)(1-\gamma)^2}}{D_a + D_i}
\]

**Extreme Cases of Intraparticle Diffusion Processes**

In the extreme cases of hypothetical intraparticle diffusion processes, Eq. (12) may be reduced to simple forms. When the reactants within the macropore and micropore networks are mixed so completely that concentration profiles within the networks are identical, \( \gamma \) in Eq. (12) is unity. Consequently,

\[
D_p = D_a + D_i
\]

Eq. (13) essentially agrees with the parallel pore model, if the macropore and micropore have uniform pore sizes, respectively.

However, if there is no mixing of reactants between the networks, \( \gamma \) is zero, and then,

\[
D_p = D_i
\]

This result roughly coincides with the model derived by Wakao et al.13).

If \( D_i \) is negligibly small compared with \( D_a \), though \( \gamma \) is zero to one, \( D_p \) becomes:

\[
D_p = \gamma D_a
\]
Table 1 Catalytic reacting conditions under which the experimental data in Fig. 2 were obtained

<table>
<thead>
<tr>
<th>Sample Nos.</th>
<th>Reactions</th>
<th>Catalysts</th>
<th>Temp. [°C]</th>
<th>$S_p$ [m²/g]</th>
<th>Properties of pellet</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>o-H₂⇒p-H₂</td>
<td>ferric oxide gel</td>
<td>-196</td>
<td>222</td>
<td>0</td>
<td>0.4</td>
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<tr>
<td>2</td>
<td>o-H₂⇒p-H₂</td>
<td>NiO-Vycor</td>
<td>-196</td>
<td>107</td>
<td>0</td>
<td>0.31</td>
</tr>
<tr>
<td>3</td>
<td>cracking of gas oil</td>
<td>silica-alumina</td>
<td>480</td>
<td>338</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>480</td>
<td>154</td>
<td>0</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>480</td>
<td>266</td>
<td>0</td>
<td>52</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>480</td>
<td>310</td>
<td>0</td>
<td>51</td>
</tr>
<tr>
<td>7</td>
<td>hydrogenation of C₅H₁₀</td>
<td>Ni-kieselguhr</td>
<td>150</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>hydrogenation of C₅H₁₀</td>
<td>Ni-refractory oxide</td>
<td>90</td>
<td>17</td>
<td>0.24</td>
<td>0.046</td>
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<tr>
<td>9</td>
<td>hydrogenation of C₅H₁₀</td>
<td>copper-chromia</td>
<td>60</td>
<td>49</td>
<td>0.18</td>
<td>0.06</td>
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<tr>
<td>10</td>
<td>hydrogenation of C₅H₁₀</td>
<td>Ni-kieselguhr</td>
<td>60</td>
<td>110</td>
<td>0.4</td>
<td>0.03</td>
</tr>
<tr>
<td>11</td>
<td>oxidation of CO</td>
<td>NiO-alumina</td>
<td>370</td>
<td>256</td>
<td>0.50</td>
<td>0.73</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>&quot;</td>
<td>370</td>
<td>256</td>
<td>0.47</td>
<td>0.38</td>
</tr>
<tr>
<td>13</td>
<td>&quot;</td>
<td>&quot;</td>
<td>370</td>
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<td>0.41</td>
<td>0.20</td>
</tr>
<tr>
<td>14</td>
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<td>&quot;</td>
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<td>256</td>
<td>0.34</td>
<td>0.13</td>
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<tr>
<td>15</td>
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<td>activated carbon</td>
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<tr>
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<tr>
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<tr>
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<tr>
<td>19</td>
<td>&quot;</td>
<td>&quot;</td>
<td>150</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>o-H₂⇒p-H₂</td>
<td>NiO-kieselguhr</td>
<td>40</td>
<td>108</td>
<td>0.4</td>
<td>0.03</td>
</tr>
<tr>
<td>21</td>
<td>isomerization of o-xylene</td>
<td>Silica alumina</td>
<td>370</td>
<td>-</td>
<td>0.08</td>
<td>0.38</td>
</tr>
<tr>
<td>22</td>
<td>&quot;</td>
<td>&quot;</td>
<td>400</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>&quot;</td>
<td>&quot;</td>
<td>430</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>&quot;</td>
<td>&quot;</td>
<td>460</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Some of the data were obtained from the pore size distribution curves shown in the literature by the authors.

This is similar to the model derived by Mingle and Smith\(^b\) because the similarity of $\gamma$ and micropore effectiveness factor defined by these authors is considered.

Comparison of Experimental Data with Eq. (12)

In this section, Eq. (12) will be tested with the aid of published experimental data. In Fig. 2, Eq. (12) and the diffusivities for the extreme cases of diffusion processes mentioned above are expressed by the relation between $D_p$ and $D_{ia}+D_i$. In this figure, $D_p$ expressed by Eq. (12) is found in the area enclosed by the curves for the diffusivities of the extreme cases. It seems that most of the experimental data confirm this argument as shown in Fig. 2.

The definition of the characteristic dimension of the pore network is so difficult that $\gamma$ is left to be of somewhat indefinite character. For discussion of the validity of the parameter, more experimental data will be appreciated.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_A$</td>
<td>gas concentration</td>
<td>[g-mol/cm²]</td>
</tr>
<tr>
<td>$D$</td>
<td>intraparticle diffusivity</td>
<td>[cm²/sec]</td>
</tr>
<tr>
<td>$E$</td>
<td>= catalyst effectiveness factor</td>
<td>[-]</td>
</tr>
<tr>
<td>$k_s$</td>
<td>first-order reaction rate constant for surface reaction</td>
<td>[cm/sec]</td>
</tr>
<tr>
<td>$k_v$</td>
<td>first-order reaction rate constant per unit volume of catalyst pellet</td>
<td>[sec⁻¹]</td>
</tr>
<tr>
<td>$R$</td>
<td>radius of catalyst pellet</td>
<td>[cm]</td>
</tr>
<tr>
<td>$S$</td>
<td>surface area per unit volume of catalyst</td>
<td>[cm⁻¹]</td>
</tr>
</tbody>
</table>

$\sigma_p = \text{parameter defined by Eqs. (3) and (4)}$  
$\beta_p = \text{parameter defined by Eqs. (3) and (4)}$  
$\gamma = \text{parameter of mass transfer between macropore and micropore networks}$  
$\phi = \text{Thiele parameter for first order irreversible reaction on spherical catalyst}$

Literature Cited