REACTION AND MASS TRANSFER IN A MACRORETICULAR RESIN CATALYST

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A model is proposed for a macroreticular resin catalyst to give the overall effectiveness factor in terms of the micro- and macro-effectiveness factors and the fraction of the surface layer active sites. Different values of the fraction can represent some possible cases of porous catalysts; i.e., a single or uniform pore and a bidisperse pore structure.

Introduction

Most heterogeneous catalysts are made by pelletizing active powders and show a bidisperse pore structure of micro- and macropores. Various models¹⁾ have been proposed to explain diffusion and reaction in such porous catalysts. Macroreticular ion exchange resins, which consist of very small randomly packed gelular microparticles with continuous non-gel pores, might be analyzed in a similar manner by taking the microparticles as having micropores.

Mingle and Smith⁴⁾, Carberry²⁾, and Örs and Dogu⁶⁾ have derived expressions for the micro- and macro-effectiveness factor. In their calculations the resulting overall effectiveness factor was essentially the product of the micro- and macro-effectiveness factors and the contribution from macro-pore walls to reaction is assumed to be negligible. Tartarelli *et al.*⁸⁾ analyzed a second-order reaction by introducing a generalized Thiele modulus and calculated the effectiveness factor for an isothermal condition by a numerical method.

For resin catalysis, Frisch³⁾ proposed a model with radially oriented cylindrical macropores in the gel structure and considered diffusion-limited first-order reversible reactions catalyzed by macroreticular ion exchange resins in which both macropore and matrix diffusion in the polymer were taken into account. Ruckenstein *et al.*⁷⁾ developed a similar macro-micro pore model for transient sorption in solids having bidisperse pore structures which showed the influence of the competing effects of macropore and micropore diffusion.

From the viewpoint of the scanning electron micrograph the cylindrical geometry of the macropore may not be adequate for describing the macro-

reticular ion exchange resin catalyst. The present study proposes a more generalized model which would be of aid in understanding the intraparticle mass transfer and its interaction with reaction, especially for macroreticular resins.

1. A Model for the Macroreticular Ion Exchange Resin

A macroreticular ion exchange resin particle is composed of spherical microparticles with free space between them, which accounts for the porosity of the resin. Therefore, the macroreticular resin can be envisaged as two phases, i.e., microspheres of uniform size and pores formed by the space between the microspheres. It is assumed that the radius of the microspheres is uniform and much smaller than that of the resin particle.

Two different kinds of active sites exist in the microsphere of macroreticular resin. The fraction γ of total active sites are located on the surface of the microparticle, providing easy access for the reactants. The reaction can proceed on these external active groups without being preceded by permeation into the microparticle. However, the remaining functional groups of fraction $1 - \gamma$ are located within the polymer matrix of the microparticle. The molecules from the external phase must penetrate through the polymer matrix in order to gain access to the inner active functional groups.

The external active groups and a large surface area due to high crosslinking are the characteristics of macroreticular resins, which can catalyze reactions even among nonpolar molecules while gelular resins cannot. The active acidic sites are uniformly distributed over the pore walls (surface of the microsphere) and also in the inner gelular phase of the microsphere. Reaction occurs on the pore walls as well as inside the gelular microspheres. A schema-

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tic diagram of a macroreticular resin catalyst is shown in Fig. 1.

2. Governing Equations

For the pore space, diffusional flux is balanced by disappearance due to reaction on the walls and diffusion into the microspheres, and for the microsphere diffusional flux is balanced by reaction only.

By defining the dimensionless variables as

$$y_a = \frac{C_a}{C_o}, y_i = \frac{C_i}{C_o}, x_a = \frac{r_a}{R_a}, x_i = \frac{r_i}{R_i} \quad (1)$$

and the parameters as

$$m_i = R_i \sqrt{\frac{(1-\gamma)ekC_o^{n-1}}{n'V_iD_i}} \quad (2)$$

$$m_a = R_a \sqrt{\frac{ekC_o^{n-1}}{V_aD_a\varepsilon}} \quad (3)$$

the governing equations at steady state can be written for an n -th order irreversible reaction for the pore space

$$\frac{d^2y_a}{dx_a^2} + \frac{2}{x_a} \frac{dy_a}{dx_a} = \gamma m_a^2 y_a^n + 3(1-\gamma) \frac{m_a^2}{m_i^2} \left(\frac{dy_i}{dx_i} \right)_{x_i=1} \quad (4)$$

and for the microsphere

$$\frac{d^2y_i}{dx_i^2} + \frac{2}{x_i} \frac{dy_i}{dx_i} = m_i^2 y_i^n \quad (5)$$

and the boundary conditions are

$$x_a=0; dy_a/dx_a=0 \quad (6a)$$

$$x_a=1; y_a=1 \quad (6b)$$

$$x_i=0; dy_i/dx_i=0 \quad (6c)$$

$$x_i=1; y_i=y_a(x_a) \quad (6d)$$

where parameter m_i represents the Thiele modulus for a microsphere and m_a the Thiele modulus for the pore space. If m_i is defined as the ratio of the time scales for the processes taking place in the resin pore and in the microparticle respectively,

$$m_i = \frac{t_a}{t_i} = \frac{(1-\varepsilon)D_i/R_i^2}{\varepsilon D_a/R_a^2} = (1-\gamma) \frac{m_a^2}{m_i^2} \quad (7)$$

where t_a represents the characteristic time required for diffusion through the pore of the resin particle and t_i the characteristic time required for permeating through the microparticle, Eq. (4) becomes

$$\frac{d^2y_a}{dx_a^2} + \frac{2}{x_a} \frac{dy_a}{dx_a} = \frac{m_i^2 m_a^2 \gamma}{1-\gamma} y_a^n + 3m_i^2 \left(\frac{dy_i}{dx_i} \right)_{x_i=1} \quad (8)$$

The microeffectiveness factor is defined as

$$\eta_i = \frac{3}{m_i^2 y_a^n} \left(\frac{dy_i}{dx_i} \right)_{x_i=1} \quad (9)$$

Introducing Eq. (9) into Eq. (4) results in a more general form, or

$$\frac{d^2y_a}{dx_a^2} + \frac{2}{x_a} \frac{dy_a}{dx_a} = m_a^2 [\gamma + (1-\gamma)\eta_i] y_a^n \quad (10)$$

Fig. 1 Schematic diagram of a resin particle

Before solving Eqs. (5) and (10) it can be shown that the overall effectiveness factor η_{ov} is expressed in terms of the average micro-effectiveness factor $\bar{\eta}_i$, the macro-effectiveness factor η_a and the fraction γ of active sites located on the pore walls as follows:

$$\eta_{ov} = \frac{3}{m_a^2} \left(\frac{dy_a}{dx_a} \right)_{x_a=1} \quad (11)$$

$$= [(1-\gamma)\bar{\eta}_i + \gamma]\eta_a \quad (12)$$

$$\bar{\eta}_i = \frac{\int_0^1 x_a^2 y_a^n \eta_i dx_a}{\int_0^1 x_a^2 y_a^n dx_a} \quad (13)$$

and

$$\eta_a = \frac{3}{M^2} \left(\frac{dy_a}{dx_a} \right)_{x_a=1} \quad (14)$$

where M is the modified Thiele modulus defined as

$$M^2 = m_a^2 [\gamma + (1-\gamma)\bar{\eta}_i] \quad (15)$$

$\bar{\eta}_i$ is the averaged value of the local effectiveness factor η_i for a microsphere which, except for a first-order reaction, depends upon the radial position of the resin particle as the concentration in the pore space varies along the radial position.

3. Results and Discussion

3.1. First-order reaction

For a first-order reaction ($n=1$), the analytical solutions of Eqs. (5) and (10) can easily be found, or

$$y_a = \frac{1}{x_a} \frac{\sinh M x_a}{\sinh M} \quad (16)$$

$$y_i = \frac{y_a}{x_i} \frac{\sinh m_i x_i}{\sinh m_i} \quad (17)$$

Effectiveness factors are given as

$$\bar{\eta}_i = \eta_i = \frac{3}{m_i} \left(\frac{1}{\tanh m_i} - \frac{1}{m_i} \right) \quad (18)$$

$$\eta_a = \frac{3}{M} \left(\frac{1}{\tanh M} - \frac{1}{M} \right) \quad (19)$$

and

$$\eta_{ov} = \frac{3}{m_a^2} \left(\frac{M}{\tanh M} - 1 \right) = \left[(1-\gamma) \frac{3}{m_i} \left(\frac{1}{\tanh m_i} - \frac{1}{m_i} \right) + \gamma \right] \frac{3}{M} \left(\frac{1}{\tanh M} - \frac{1}{M} \right) \quad (20)$$

Fig. 2 Effectiveness factors for 1st-order reaction

Fig. 3 Concentration gradient as a function of m_i and y_a

Figure 2 shows these effectiveness factors, η_i , η_a and η_{ov} for the case of $\gamma=0$ and $\gamma=0.528$ when $m_a=5.0$. As permeation becomes more difficult ($m_i \sim \infty$), the micro-effectiveness factor η_i approaches zero and as the reaction controls the rate process ($m_i \sim 0$), η_i becomes unity. It should be noted that the micro-effectiveness factor η_i is the same as the effectiveness factor of a uniformly porous catalyst particle with a Thiele modulus m_i .

3.2 Second-order reaction

For a second-order reaction ($n=2$), analytical solutions cannot be found and numerical integrations were performed by the fourth-order Runge-Kutta method with varying step size to solve the nonlinear boundary value problem.

From Eq. (5), $(dy_i/dx_i)_{x_i=1}$ can be approximated as a function of m_i and y_a to be introduced to Eq. (4).

$$\left(\frac{dy_i}{dx_i}\right)_{x_i=1} = \begin{cases} \frac{1}{3}m_i^2 y_a^2 & (m_i \ll 1) \end{cases} \quad (21a)$$

$$A y_a^B \quad (\text{intermediate}) \quad (21b)$$

$$\sqrt{2/\sqrt{3}} m_i y_a^{3/2} \quad (m_i \gg 1) \quad (21c)$$

and the micro-effectiveness factor becomes

$$\eta_i = \begin{cases} 1 & (m_i \ll 1) \end{cases} \quad (22a)$$

$$\frac{3}{m_i^2} A y_a^{B-2} \quad (\text{intermediate}) \quad (22b)$$

$$\sqrt{6} \frac{1}{m_i y_a^{1/2}} \quad (m_i \gg 1) \quad (22c)$$

Equation (21a) is derived from Eq. (9) because η_i becomes unity for $m_i \ll 1$, and Eq. (21c) can be derived from the asymptotic solution for $m_i \gg 1$.

By solving Eq. (5) for a given value of m_i , the concentration gradients at the external surface of the microsphere $(dy_i/dx_i)_{x_i=1}$ can be obtained. The log-log plot of $(dy_i/dx_i)_{x_i=1}$ versus y_a was found to give a straight line, as shown in Fig. 3, confirming the validity of the approximation by Eq. (21b), and the values of A and B obtained for the different values of m_i are also listed.

With Eqs. (21) or (22), Eq. (4) or (10) can be solved numerically and the concentration profile can be obtained at given values of γ , m_i , and m_a . Accordingly, the averaged micro-effectiveness factors are evaluated from the concentration profile. That is,

$$\bar{\eta}_i = \begin{cases} 1 & (m_i \ll 1) \end{cases} \quad (23a)$$

$$\frac{3A}{m_i^2} \frac{\int_0^1 x_a^2 y_a^B dx_a}{\int_0^1 x_a^2 y_a^2 dx_a} \quad (\text{intermediate}) \quad (23b)$$

$$\frac{\sqrt{6}}{m_i} \frac{\int_0^1 x_a^2 y_a^{3/2} dx_a}{\int_0^1 x_a^2 y_a^2 dx_a} \quad (m_i \gg 1) \quad (23c)$$

The effectiveness factors for the cases of $\gamma=0$ and $\gamma=0.528$ are plotted in Figs. 4 and 5 respectively in terms of m_a , and in Fig. 6 in terms of m_i and m_i .

As the microsphere Thiele modulus m_i increases, the diffusion rate into the microsphere becomes slow and the reactants tend to accumulate in the pore space. The uniform concentration profile in the pore results in the enhancement of the macro-effectiveness factor η_a . However, the overall effectiveness factor will decrease due to diffusion limitations in the microspheres.

If very few active sites are located on the pore walls (i.e., $\gamma=0$), there is little reaction on the pore walls. However, if a large portion of active sites is located on the pore walls (i.e., $\gamma \neq 0$), they play the role of sink for reactants in the pore space due to the wall reaction. Hence the overall effectiveness factor for

the case of $\gamma \neq 0$ is different from that for the case of $\gamma = 0$ showing a different asymptote.

If the diffusion resistance through the microsphere is negligible (or microsphere Thiele modulus m_i becomes smaller) reaction occurs in the entire range of the microsphere and the overall process depends only on diffusion through the pore space. Therefore, the overall effectiveness factor η_{ov} becomes a function of the Thiele modulus m_a alone.

Figure 6 shows that as m_i increases, the diffusion rate of the reactant molecules into the pore of the resin particle decreases and the overall effectiveness factor decreases.

3.3 Limiting cases of $\gamma = 0$ and $\gamma = 1$

If $\gamma = 0$, the present model is the same as the bidisperse porous catalyst models, and the effectiveness factor becomes simply the product of the micro- and macro-effectiveness factor, or

$$\eta_{ov} = \bar{\eta}_i \eta_a \quad (24)$$

The same relation can be obtained from the model proposed by Örs and Dogu⁶⁾ and also by Carberry²⁾.

If $\gamma = 1$, the governing equation reduces to that for a single pore or uniformly porous catalyst, for which numerous studies¹⁾ can be referenced.

It is the merit of the present model that three possibilities in typical heterogeneous catalysis, i.e. a single pore, a biporous catalyst and an ion exchange resin catalyst, can be explained by a single expression.

4. Experimental Examples—Temperature Effect

As an illustration, some experimental results obtained by the authors are explained in the following:

A) The liquid-phase esterification of phenol and acetic acid was performed in a batch reactor using macroreticular ion exchange resin catalysts (Amberlyst 15 and Amberlyst XN-1010) and experimental data on the initial reaction rate were analyzed by the present model⁸⁾. Under the experimental condition of $\eta_a = 1$ (i.e., when the variations in size of resin particle do not affect the overall rate), the overall initial reaction rate r_{ov} could be expressed as

$$r_{ov} = r_a \eta_{ov} = r_a [\gamma + (1 - \gamma) \bar{\eta}_i] \quad (25)$$

In the range of low reaction temperature most reaction occurs on the surface layer of the micro-particle (the pore walls) because the reactant cannot easily penetrate into the highly crosslinked gel phase of the microparticle. Therefore, micro-effectiveness factor $\bar{\eta}_i$ becomes very small. As the reaction temperature increases the gel phase can participate in the reaction due to increased swellability and this results in higher micro-effectiveness factor. In the extreme case of high reaction temperature where the mobility of the gel phase increases, the reactant molecules move easily into the microparticle and the

Fig. 4 Effectiveness factor vs. m_i and m_a ; $\gamma = 0$

Fig. 5 Effectiveness factor vs. m_i and m_a ; $\gamma = 0.528$

Fig. 6 Overall effectiveness factor

microsphere effectiveness factor becomes unity. These phenomena can be written in the following expression for $\eta_a = 1$,

$$\eta_{ov} = \begin{cases} \gamma & (\bar{\eta}_i = 0); \text{ low-temperature range} \end{cases} \quad (26a)$$

$$\begin{cases} \gamma + (1 - \gamma) \bar{\eta}_i \\ (0 < \bar{\eta}_i < 1); \text{ intermediate range} \end{cases} \quad (26b)$$

$$\begin{cases} 1 \\ (\bar{\eta}_i = 1); \text{ high-temperature range} \end{cases} \quad (26c)$$

and are illustrated as an Arrhenius plot in Fig. 7.

B) Sucrose inversion was performed in a batch reactor, varying the particle sizes and the reaction

Fig. 7 Arrhenius plot of reaction rate for macroreticular resin catalyst with large γ

temperatures by using also Amberlyst 15 and Amberlyst XN-1010⁵⁾. In this case the overall initial reaction rate r_{ov} is written as

$$r_{ov} = k C_o \eta_{ov} \quad (27)$$

$$= k C_o [\gamma + (1-\gamma)\bar{\eta}_i] \eta_a \quad (28)$$

$$= k_{app} C_o \eta_a \quad (29)$$

where k_{app} is the apparent reaction rate constant, or

$$k_{app} = k[\gamma + (1-\gamma)\bar{\eta}_i] \quad (30)$$

It is reasonable to assume for isothermal conditions that as the intrinsic reaction rate constant k , the radius R_i of the microparticle and the diffusivity D_i in the microparticle are constant and independent of the resin sizes, the apparent reaction rate constant k_{app} is also constant and independent of the sizes of resin particles. The values of D_a and k_{app} were estimated from measurements of the overall reaction rate for given values of particle size and catalyst quantity, and the correlation between experimental data and the present model for η_a was found to be excellent.

Conclusion

Macroreticular ion exchange resin catalyst has been envisaged as two phases: the microspheres and the pore space formed between them. For an n -th-order irreversible reaction at steady state the overall effectiveness factor η_{ov} can be expressed in terms of the average micro-effectiveness factor $\bar{\eta}_i$, macro-effectiveness factor η_a and the fraction γ of active sites located on the pore walls, or

$$\eta_{ov} = [\gamma + (1-\gamma)\bar{\eta}_i] \eta_a$$

and has been evaluated analytically for a first-order reaction and numerically for a second-order reaction.

In addition to the case of a macroreticular resin catalyst with some fraction of the active sites on the pore walls, two other possible cases of heterogeneous catalysts can be explained by the present model in terms of different ranges of γ , i.e. a bidisperse porous

catalyst for $\gamma=0$ and a catalyst with uniform pore size for $\gamma=1$.

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Nomenclature

C	= concentration; C_a , in the pore; C_i in the microsphere; C_o in the bulk [mol/cm ³]
D	= effective diffusivity; D_a , in the pore; D_i , in the microsphere [cm ² /sec]
e	= total capacity of a resin particle [equivalent]
k	= reaction rate constant [cm ³ⁿ /sec·eq. mol ⁿ⁻¹]
M	= modified Thiele modulus defined by Eq. (15)
m	= dimensionless variable; m_i , defined by Eq. (2); m_a , defined by Eq. (3); m_t defined by Eq. (7)
n	= reaction order
n'	= number of microspheres in a resin particle
R	= radius; R_a , of a resin particle; R_i , of a microsphere [cm]
r	= radial position from the center; r_a , of a resin particle; r_i , of a microsphere [cm]
r_{ov}	= overall initial reaction rate
r_x	= intrinsic reaction rate
V	= volume, V_a , of a resin particle; V_i , of a microsphere [cm ³]
x	= dimensionless distance from the center; x_a , for a resin particle, defined by Eq. (1c); x_i , for a microsphere, defined by Eq. (1d)
y	= dimensionless concentration; y_a , in a resin particle, defined by Eq. (1a); y_i , in a microsphere, defined by Eq. (1b)
γ	= fraction of active sites distributed over the pore walls
ε	= porosity
η	= effectiveness factor; η_i , for a microsphere, η_a , for a resin particle; η_{ov} for overall resin

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