An Example of the Influence of Intraparticle Diffusion on the Kinetics of Consecutive Heterogeneous Catalytic Reactions

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In mathematical language is described how diffusion in the pore structure of a solid catalyst can influence the over-all kinetics of a series of consecutive first order reactions. Expressions are derived in which the maximum conversion to the first intermediate product is related to the resistance to intraparticle diffusion. The maximum conversion, *i.e.* the selectivity of the process, decreases with increasing diffusion resistance and approaches a lower limit, whereas the time of reaction required to reach the maximum conversion increases steadily.

The pioneer workers in the field of diffusion and heterogeneous catalysis, Thiele¹, Wagner², Wicke and Brötz³, Smith and Amundson⁴, and others, have been concerned mainly with the influence of intraparticle diffusion on the rate of simple reactions such as

For more complex reaction schemes the mathematical development rapidly becomes quite involved and such reactions apparently have not been treated in greater detail.

Wheeler^{5,6} studied several cases of simultaneous reactions and concluded that diffusion in the pore structure can markedly influence catalyst selectivity. He thus examined a case of two consecutive first order reactions

catalyzed at the wall of a cylindrical pore and found that the maximum conversion to the unstable intermediate decreases with increasing resistance to axial diffusion of reactant.

The subject of the present paper is the first order reaction sequence

The purpose is to evaluate concentrations as functions of residence time in a fixed bed flow reactor and quantitatively to determine the influence of the diffusion process in the porous catalyst pellets.

The catalytic reactor is operated under isothermal conditions. Flow rates are assumed constant throughout the reactor and longitudinal mixing and diffusion is neglected. Only the steady state will be considered.

The catalyst is used in the form of spherical, homogeneous pellets. It is assumed that the reactions are not accompanied by volume changes, that diffusion coefficients remain constant, that the individual catalyst pellet is surrounded by a reaction mixture of constant composition, that pressure drop across the catalyst pellet can be disregarded, and that there is no resistance to mass transfer at the pellet surface.

The concentration distributions inside the catalyst must be determined before the rate equations can be derived.

NOTATION

$C'_1, C'_2, \dots$	concentrations in catalyst pore
$C_1, C_2, \dots$	concentrations at pellet surface
$C_{1,0}$	concentration of M_1 at reactor entrance
$C_{2, \max}$	maximum concentration of M_2
$D_1, D_2, \dots$	coefficients of diffusion in catalyst pellet
$E_1, \dots$	dimensionless factors as defined by eqn. (6)
$k'_1, k'_2, \dots$	reaction rate constants per unit volume of catalyst pellet
$k_1, k_2, \dots$	reaction rate constants per unit volume of catalyst bed
$m_1, m_2, \dots$	Thiele moduli as defined by eqn. (3)
R_p	radius of catalyst pellet
S	selectivity ratio
t	residence time in flow reactor
x	distance from center of catalyst pellet
ρ_p, ρ_b	density of catalyst pellet and of catalyst bed
τ	dimensionless residence time

CONCENTRATION DISTRIBUTIONS

The components of the reaction mixture are subjected to a diffusion process into the catalyst and to a chemical reaction at the intrinsic catalytic surface. The material balance in a spherical element of catalyst volume of radii x and $x + dx$ comprises the following equations:

$$D_1 (d^2C'_1/dx^2 + (2/x) dC'_1/dx) = k'_1C'_1 \quad (1.1)$$

$$D_2 (d^2C'_2/dx^2 + (2/x) dC'_2/dx) = k'_2C'_2 - k'_1C'_1 \quad (1.2)$$

$$D_n (d^2C'_n/dx^2 + (2/x) dC'_n/dx) = k'_nC'_n - k'_{n-1}C'_{n-1} \quad (1.n)$$

The first of these equations was solved by Thiele¹. The others can be solved by the method of variation of parameters. In determination of the arbitrary constants use is made of the initial conditions:

$$C'_1 = C_1; C'_2 = C_2; \dots C'_n = C_n; \dots$$

when

$$x = R_p$$

and of the physically obvious condition that concentrations must remain finite at the center of the pellet.

The solutions to eqns. (1) are:

$$C'_1 = \frac{R_p}{x} C_1 \frac{\sinh(xm_1/R_p)}{\sinh m_1} \quad (2.1)$$

$$C'_2 = \frac{R_p}{x} \left(C_2 \frac{\sinh(xm_2/R_p)}{\sinh m_2} + C_1 \frac{k'_1}{k'_2} \left(\frac{m_2^2}{m_2^2 - m_1^2} \frac{\sinh(xm_1/R_p)}{\sinh m_1} + \frac{m_2^2}{m_1^2 - m_2^2} \frac{\sinh(xm_2/R_p)}{\sinh m_2} \right) \right) \quad (2.2)$$

$$C'_n = \frac{R_p}{x} \left(C_n \frac{\sinh(xm_n/R_p)}{\sinh m_n} + C_{n-1} \frac{k'_{n-1}}{k'_n} \left(\frac{m_n^2}{m_n^2 - m_{n-1}^2} \frac{\sinh(xm_{n-1}/R_p)}{\sinh m_{n-1}} + \frac{m_n^2}{m_{n-1}^2 - m_n^2} \frac{\sinh(xm_n/R_p)}{\sinh m_n} \right) + \dots \right. \\ \left. + C_1 \frac{k'_1}{k'_n} \left(\frac{m_2^2 m_3^2 \dots m_n^2}{(m_2^2 - m_1^2) \dots (m_n^2 - m_1^2)} \frac{\sinh(xm_1/R_p)}{\sinh m_1} + \dots \frac{m_2^2 m_3^2 \dots m_n^2}{(m_1^2 - m_2^2) \dots (m_{n-1}^2 - m_n^2)} \frac{\sinh(xm_n/R_p)}{\sinh m_n} \right) \right) \quad (2.2)$$

$m_1, m_2, \dots, m_n$ are the dimensionless Thiele moduli:

$$m_i = R_p \sqrt{k'_i/D_i} \quad (3)$$

REACTION RATES

The differential rate of formation of M_n is calculated as the rate of diffusion out of a catalyst pellet multiplied by the number of pellets in unit volume of catalyst bed:

$$dC_n/dt = -(3D_n \rho_b / R_p \rho_p) (dC'_n/dx)_{x=R_p} \quad (4)$$

dC'_n/dx is derived from eqns. (2) and inserted into (4).

The result is the following system of equations:

$$dC_1/dt = -k_1 E_1 C_1 \quad (5.1)$$

$$dC_2/dt = -k_2 E_2 C_2 + k_1 E_{1,2} C_1 \quad (5.2)$$

...

$$\begin{aligned} dC_n/dt = & -k_n E_n C_n + k_{n-1} E_{n-1,n} C_{n-1} \\ & + \dots + k_1 E_{1,2} \dots_n C_1 \\ & \dots \end{aligned} \quad (5.n)$$

where

$$\begin{aligned} E_i &= (3/m_i^2)(m_i \coth m_i - 1) \\ E_{i,i+1,\dots,n} &= -m_{i+1}^2 m_{i+2}^2 \dots m_n^2 \left(\frac{m_i^2 E_i}{(m_{i+1}^2 - m_i^2) \dots (m_n^2 - m_i^2)} \right. \\ &\quad \left. + \dots \right. \\ &\quad \left. + \frac{m_n^2 E_n}{(m_i^2 - m_n^2) \dots (m_{n-1}^2 - m_n^2)} \right) \end{aligned} \quad (6)$$

and

$$k_i = k'_i \rho_b / \rho_p$$

By solution of eqns. (5) by a standard method for linear first order differential equations concentrations become expressed as functions of residence time in the reactor. The initial conditions (the concentrations at the reactor entrance) are:

$$C_1 = C_{1,0}; C_2 = C_3 = \dots C_n = 0$$

when

$$t = 0$$

For the first three equations (5) are obtained the solutions:

$$C_1 = C_{1,0} \exp(-k_1 E_1 t) \quad (7.1)$$

$$C_2 = C_{1,0} k_1 E_{1,2} \left(\frac{\exp(-k_1 E_1 t)}{(k_2 E_2 - k_1 E_1)} + \frac{\exp(-k_2 E_2 t)}{(k_1 E_1 - k_2 E_2)} \right) \quad (7.2)$$

$$\begin{aligned} C_3 = C_{1,0} k_1 E_{1,2} k_2 E_{2,3} & \left(\frac{\exp(-k_1 E_1 t)}{(k_2 E_2 - k_1 E_1)(k_3 E_3 - k_1 E_1)} \right. \\ & + \frac{\exp(-k_2 E_2 t)}{(k_1 E_1 - k_2 E_2)(k_3 E_3 - k_2 E_2)} \\ & + \frac{\exp(-k_3 E_3 t)}{(k_1 E_1 - k_3 E_3)(k_2 E_2 - k_3 E_3)} \Big) \\ & + C_{1,0} k_1 E_{1,2,3} \left(\frac{\exp(-k_1 E_1 t)}{(k_3 E_3 - k_1 E_1)} + \frac{\exp(-k_3 E_3 t)}{(k_1 E_1 - k_3 E_3)} \right) \end{aligned} \quad (7.3)$$

It is assumed that all the Thiele moduli and all the reaction rate constants are of different magnitude. If this is not the case the expressions can still be derived in the way described, the results becoming somewhat different. An example is presented below.

Fig. 1.

SELECTIVITY

As residence time is increased the concentration of any intermediate product in a series of consecutive reactions passes through a maximum. It is of technical importance to determine the magnitude of this maximum concentration as well as of the residence time required to reach the maximum. It is also of interest to examine how these factors are influenced by intraparticle diffusion.

Fig. 2.

This can be done analytically only for the first intermediate product, M_2 .
The condition:

$$d(C_2/C_{1,0})/dt = 0$$

is fulfilled when

$$\tau = k_2 t = \ln(SE_1/E_2)/(SE_1 - E_2) \quad (8)$$

τ being a dimensionless time of reaction and

$$S = k_1/k_2$$

Insertion of (8) into (7.2) yields the following expression for the maximum fraction of initial reactant which can be converted to the first intermediate product:

$$(C_2/C_{1,0})_{\max} = (E_{1,2}/E_1)(SE_1/E_2)^{-1/(SE_1/E_2 - 1)} \quad (9)$$

If $S = 1$ and $m_1 = m_2$ (i.e. $D_1 = D_2$) eqns. (8) and (9) are transformed into

$$\tau = 1/E_2 \quad (8a)$$

$$(C_2/C_{1,0})_{\max} = (E'_{1,2}/E_1) \exp(-1) \quad (9a)$$

where

$$E'_{1,2} = \frac{3}{2} (1 + (\coth m_2)/m_2 - \coth^2 m_2)$$

The relationships expressed in eqns. (8), (8a), (9), and (9a) are shown graphically in Figs. 1 and 2. It has been assumed that $D_1 = D_2$ and, consequently, $m_1 = \sqrt{S}m_2$. $(C_2/C_{1,0})_{\max}$ decreases from an upper limit, $S^{-1/(S-1)}$ when diffusion has no rate determining influence, to a lower limit, $(\sqrt{S}/(\sqrt{S} + 1))(\sqrt{S})^{-1/(\sqrt{S}-1)}$. The residence time required to reach the maximum conversion increases steadily with increasing diffusion resistance.

CONCLUSION

The influence of intraparticle diffusion upon the reaction kinetics of a series of n consecutive first order reactions catalyzed by spherical catalyst pellets can be evaluated analytically, reaction conditions being idealized to some extent.

The selectivity of the first reaction step, defined as the maximum conversion to M_2 , depends only upon the dimensionless factors S , m_1 and m_2 . For fixed values of S and increasing values of m the selectivity decreases towards a lower limit. This relationship is illustrated in Fig. 1.

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