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A Note on Diffusion Limitations for Multiple Reaction Systems in Porous Catalysts

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Diffusion of species through the pores of solid catalysts is very often the rate-limiting step in catalytic reactions. Diffusion limitations also have a very important effect on the selectivity in multiple reaction systems. Since the kinetic rate expressions are usually nonlinear, it is usually very difficult to determine the effect of transport processes on the observed rates by solving the controlling differential equations of the model.

A number of criteria were derived to predict the importance of diffusion limitations on the overall rate of catalytic reactions (Weisz and Prater, 1954; Peterson, 1964; Hutchings and Carberry, 1966; Schneider and Mitschka, 1966; Bischoff, 1967; Narshimhan and Guha, 1972). The criterion developed by Hudgins (1968) is applicable for reactions having other than power-type rate expressions. Dogu and Dogu (1980) extended the criterion derived by Hudgins to bidisperse systems. Effect of diffusion on the observed rate in bidisperse systems was also investigated by Ors and Dogu (1979). In all of these studies a single independent reaction is considered. A detailed review of diffusion and reaction processes in porous catalysts is given by Aris (1975).

More often than not, solid-catalyzed reactions are multiple reactions. Reactions occur in parallel and the products of these decompose further. A general consecutive reaction system is investigated by Van De Vusse (1966). Luss and Golikeri (1971) and Roberts (1972) investigated multiple reaction systems under isothermal conditions and obtained asymptotic solutions. In stoichiometrically complex systems it is usually impossible to derive analytical expressions for the observed rates. In this work, a very general criterion is developed for detecting the presence of significant intraparticle mass transport effects for multiple fluid-porous solid reaction systems. The criterion is applicable to any multiple reaction system and to reactions conforming to any rate law.

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Here, a system containing m species and n independent solid catalyzed reactions is considered. In this system, the rate of generation of species j can be expressed as:

$$R_j = \sum_{i=1}^{n} R_{(i)} V_{ij}; \; j = 1, 2, 3 \ldots, m \tag{1}$$

Here, V_{ij} is the stoichiometric coefficient of the j'th species in i'th reaction, and it is positive for products and negative for reactants. $R_{(1)}$ is $1/V_{1j}$ times the rate of production of species j which is accompanied by the production of V_{1k}/V_{1j} moles of the other species k, as distinguished from that production of j'th species accompanied by production of other species k in ratios given by the other V_{ik}/V_{ij}'s. In other words, the intrinsic rate of reaction i, $R_{(i)}$, is simply $1/V_{ij}$ times the rate of generation of j'th species from the i'th independent reaction.

Following the procedure used by Anderson (1963) and Dogu and Dogu (1980), the intrinsic rate of reaction i, $R_{(i)}$, is expanded in a Taylor series about the external surface concentrations of species, $C_{j,s}$, and the Taylor's series is truncated after the linear term.

$$R_{(i)} = R_{(i)_s} + \sum_{j=1}^{m} \left(\frac{\partial R_{(i)}}{\partial C_j} \right)_{r=r_o} (C_j - C_{j,s}) \tag{2}$$

It is also assumed that the concentration profiles of all the species within the catalyst pellet can be approximated by parabolic functions.

$$C_j - C_{j,s} = -\beta_j \left(1 - \frac{r^2}{r_o^2} \right) \tag{3}$$

The apparent rate of reaction i in a porous spherical catalyst can be written as:

$$R_{(i)_a} = \left[\int_o^{r_o} R_{(i)} \cdot 4\pi r^2 dr \right] \Big/ \left[\int_o^{r_o} 4\pi r^2 dr \right] \tag{4}$$

Defining,

$$\rho = \frac{r}{r_o} \tag{5}$$

and combining the $R_{(i)}$ expression given by Eqs. 2 and 4, the apparent rate of reaction can be written as:

$$R_{(i)_a} = 3 \int_o^1 \left\{ R_{(i)_s} + \sum_{j=1}^{m} \left[\frac{\partial R_{(i)}}{\partial C_j} \right]_{r=r_o} (C_j - C_{j,s}) \right\} \rho^2 d\rho \tag{6}$$

The concentration of species j expressed by Eq. 3 is introduced into Eq. 6 and this equation is integrated to give

$$\frac{R_{(i)_a}}{R_{(i)_s}} = 1 - \frac{2}{5} \left(\frac{1}{R_{(i)_s}} \right) \sum_{j=1}^{m} \beta_j \left[\frac{\partial R_{(i)}}{\partial C_j} \right]_{r=r_o} \tag{7}$$

In order to evaluate the value of parameter β_j, the diffusion rate of species j at the surface of the pellet is equated to the observed rate of generation

$$-D_j (4\pi r_0^2) \left(\frac{\partial C_j}{\partial r} \right)_{r=r_o} = \frac{4}{3} \pi r_o^3 \sum_{i=1}^{n} R_{(i)_a} V_{ij} \tag{8}$$

Then, taking the derivative of Eq. 3 with respect to r and substituting the expression for $(dC_j/dr)_{r=r_o}$ into Eq. 8 yields:

$$\beta_j = -\frac{r_o^2}{6D_j} \sum_{i=1}^{n} R_{(i)_a} V_{ij}; \; j = 1, 2, 3, \ldots m \tag{9}$$

By substituting β_j from Eq. 9 into Eq. 7 the following expression is obtained for $R_{(i)_a}$.

$$R_{(i)_a} = R_{(i)_s} + \frac{r_o^2}{15} \sum_{j=1}^{m} \frac{1}{D_j} \left(\frac{\partial R_{(i)}}{\partial C_j} \right)_{r=r_o} \times \left[\sum_{i=1}^{n} R_{(i)_a} V_{ij} \right]; \; i = 1, 2 \ldots n \tag{10}$$

For negligible diffusion effects the ratio $R_{(i)_a}/R_{(i)_s}$ should be close to one. By setting up $R_{(i)_a}/R_{(i)_s} > 0.95$ a general criterion is obtained for negligible diffusion effects in multiple reaction systems.

$$\alpha_i = -r_o^2 \sum_{j=1}^{m} \frac{\left(\dfrac{\partial R_{(i)}}{\partial C_j} \right)_{r=r_o}}{R_{(i)_s} D_j} \left[\sum_{i=1}^{n} R_{(i)_a} V_{ij} \right] < 0.75 \tag{11}$$

This criterion can be used for any multiple reaction system containing n independent reactions whose rates are any function of concentrations of m species. Similar expressions can be derived for slab and infinite cylinder geometries. For slab and cylinder the right hand side of inequality in Equation 11 becomes 0.15 and 0.40 respectively, r_o being the half thickness of the slab and the radius of cylinder.

A typical multiple reaction system, which is also industrially important, is the catalytic oxidation of ethylene to ethylene oxide by use of silver catalysts deposited on low surface area supports. The major chemical reactions that take place in this system are:

$$C_2H_4 + \frac{1}{2} O_2 \rightarrow C_2H_4O \tag{R.1}$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \tag{R.2}$$

$$C_2H_4O + \frac{5}{2} O_2 \rightarrow 2CO_2 + 2H_2O \tag{R.3}$$

For this system it is shown by Dogu (1981) that at 245°C the rates of R.1 and R.2 can be expressed as:

$$R_{(1)} = 6.69 \, C_{C_2H_4}^{1/2} C_{O_2} \, (\text{mol/cm}^3 \cdot \text{s}) \tag{12}$$

$$R_{(2)} = 3.18 \, C_{C_2H_4}^{1/2} C_{O_2} \, (\text{mol/cm}^3 \cdot \text{s}) \tag{13}$$

with a supported silver catalyst containing 5% Ag. Rate of Reaction 3 is reported to be negligible at these conditions and for conversion values of C_2H_4 less than 0.3. Using this information, and predicting the effective diffusivities of C_2H_4 and O_2 using Wakao and Smith (1962) model ($D_{C_2H_4} = 0.115$ cm^2/s, $D_{O_2} = 0.136$ cm^2/s for the catalyst particles of 0.095 cm in diameter and having a porosity of 0.53) the left hand side of inequality in Equation 11 is found to be 10^{-3}. This indicates that diffusion effects are completely negligible in Dogu's work and this result is consistent with Dogu's conclusion.

Another example of a multiple reaction system is the hydrogenation of methyl linoleate to methyl oleate and methyl stearate.

$$\text{L (methyl linoleate)} \xrightarrow{H_2} \text{O(methyl oleate)} \tag{R.4}$$

$$\text{O (methyl oleate)} \xrightarrow{H_2} \text{S(methyl stearate)} \tag{R.4}$$

Tsuto et al. (1978) and Cordova and Harriot (1975) investigated this system with 1 per cent Pd-carbon catalyst (pore volume = 1.3 cm^3/g; porosity = 0.7; surface area = 343 m^2/g) and observed different effectiveness factors with catalyst particles having different sizes. Tsuto et al. (1978) estimated the effective diffusivity

TABLE 1. KINETIC DATA REPORTED BY TSUTO ET AL. (1978) FOR THE HYDROGENATION OF METHYL LINOLEATE AT 80°C

Particle Radius r_o, μm	Catalyst Charge, g. of Cat/ L of Oil	Thiele Modulus ϕ	Effective-ness Factor for R.4, η	Observed Rate of R.4 Based on Reactor Volume (mol/Lt·min)	Observed rate of R.5 based on reactor volume (mol/Lt·min)	$C_{H_2,s}$ (mol/L)
6	0.452	1.32	0.90	0.0315	0.0122	0.00381
12.5	0.453	2.75	0.70	0.0273	0.0116	0.00414
25	0.452	5.50	0.44	0.0195	0.0086	0.00457

TABLE 2. VALUES OF THE PARAMETER α FOR THE METHYL LINOLEATE HYDROGENATION REACTION (R.4)

Particle Radius, r_o (μm)	6	12.5	25
α_4	2.4	8	21

of H_2 in the catalyst pores as $D_{H_2} = 3.6 \times 10^{-5}$ cm^2/s and assumed that the effectiveness factor for reaction R.4 is equal to 0.90 for the smallest catalyst particle they have used ($r_o = 6\mu$m). They showed that the following rate expressions which are derived assuming a reaction mechanism with nonequilibrium adsorption, satisfy the experimental observations:

$$R_{(4)} = \frac{k_1 C_{H_2}}{1 + \dfrac{K_O}{K_L}\dfrac{C_O}{C_L}} \quad \text{(for reaction R.4)} \tag{14}$$

$$R_{(5)} = \frac{k_2 C_{H_2}}{\left(1 + \dfrac{K_L}{K_O}\dfrac{C_L}{C_O}\right)}\left(1 + \frac{k_1 C_{H_2}}{k_{des}}\frac{K_L}{K_O}\frac{C_L}{C_O}\right) \quad \text{(for reaction R.5)} \tag{15}$$

For this reaction system the criterion for negligible diffusion effects (Eq. 11) becomes:

$$\alpha_4 = r_o^2 \left\{ \frac{R_{(4)_a} + R_{(5)_a}}{C_{H_2,s} D_{H_2}} + \frac{R_{(4)_a} - R_{(5)_a}}{\left(C_{O,s} + \dfrac{K_L}{K_O} C_{L,s}\right) D_O} + \frac{R_{(4)_a}\dfrac{C_{O,s}}{C_{L,s}}}{\left(C_{O,s} + \dfrac{K_L}{K_O} C_{L,s}\right) D_L} \right\} < 0.75 \tag{16}$$

Tsuto et al. (1978) reported that $K_L/K_O = 20$, $D_{H_2}/D_L \simeq D_{H_2}/D_O = 100$; and $C_{O,s} \simeq 0.45$ mol/L, $C_{L,s} \simeq 2.2$ mol/L for experiments carried out with catalyst particles of 25 μm in radius. Their experimental rate and effectiveness factor values are given in Table 1. Using the observed rate values (based on catalyst volume) for different particle sizes and the values of the other parameters reported by Tsuto et al., the value of the dimensionless group α_4, expressed in Eq. 16, is calculated. These values are given in Table 2.

The values reported in Table II show that the diffusion effects are significant and cannot be neglected in this reaction system. Even for smallest particle size the value of α_4 is larger than 0.75. The conclusions reached from this analysis and the effectiveness factor values reported by Tsuto et al. (1978) are in very good agreement.

It is concluded that the criterion derived here is very useful to test the importance of diffusion resistance in any multiple reaction system and to reactions conforming to any rate law.

NOTATION

C_j = concentration
$C_{j,s}$ = concentration of species j at the external surface of the catalyst
D_j = effective diffusion coefficient of species j
k_1, k_2 = first order reaction rate constants
K_O, K_L = adsorption equilibrium constants of methyl oleate and methyl linoleate
m = number of species in the system
n = number of independent reactions
R_j = rate of generation of j'th species
$R_{(i)}$ = intrinsic rate of reaction i, based on catalyst volume
$R_{(i)_a}$ = apparent rate of reaction i, based on catalyst volume
$R_{(i)_s}$ = rate of reaction i evaluated at the external surface concentrations, based on catalyst volume
r = radial coordinate for the catalyst particle
r_o = radius of the catalyst particle
V_{ij} = stoichiometric coefficient of j'th species in i'th reaction

Greek Letters

α_i = defined by Eq. 11
β_j = parameter used in Eq. 3
ϕ = Thiele modulus, $\phi = \dfrac{r_o}{2}\left(\dfrac{k_1}{D_j}\right)^{1/2}$
η = effectiveness factor

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