R & D NOTES

A Method for the Study of Performance of a Single Spherical Particle with Nonuniform Catalytic Activity

WILLIAM R. ERNST
and
DUNCAN J. DAUGHERTY

School of Chemical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

In recent years, there has been increasing interest in porous catalysts which contain nonuniform activity. For example, Kasaoka and Sakata (1968), Villadsen (1976), Corbett and Luss (1974), Shadman-Yazdi and Petersen (1972), and Becker and Wei (1977*a*, *b*) have recently developed theoretical models to describe the performance of catalysts with nonuniform activity. Some catalysts contain nonuniform activity as a result of preparation methods employed, while others develop this feature because of poisoning. The deliberate inclusion of nonuniform activity in porous catalysts provides a means of tailoring a catalyst to a specific process to improve activity or selectivity, or to reduce the rate of poisoning.

This note develops the theoretical basis for an experimental study of the effect of catalyst activity distribution on selectivity. The reaction examined is the deuterium exchange with neopentane on supported platinum. It is a series reaction with many steps and resembles industrially important reactions such as the isomerization of certain olefins (see Haag and Pines, 1960) and the hydrogenolysis of polynuclear aromatics (see Sullivan et al., 1964; Germain, 1969). It was used as a test reaction in previous experimental studies of laboratory flow reactors (Zahner, 1970) and diffusion effects in porous catalysts (Dwyer et al., 1968; Ernst and Wei, 1975) because of several desirable features: negligible heat of reaction, single step surface exchange mechanism, and first order in neopentane.

THEORY

In a mass spectrometer, neopentane undergoes fragmentation such that the major peak corresponds to a *t*-butyl fragment, and the parent neopentane peak is negligible. Kemball (1954) has provided a means of following the course of the deuterium-neopentane exchange reaction via the deuterium exchanged *t*-butyl fragments. Thus, there are nine deuterated products that must be monitored during the course of the reaction.

For brevity, the model will be developed for the single-step exchange of methane:

$$CH_4 \underset{r}{\overset{q}{\rightleftharpoons}} CH_3D \underset{r}{\overset{q}{\rightleftharpoons}} CH_2D_2 \underset{r}{\overset{q}{\rightleftharpoons}} CHD_3 \underset{r}{\overset{q}{\rightleftharpoons}} CD_4 \qquad (1)$$

The model can be readily extended to the reaction of neopentane. The following assumptions will be made: a large excess of D_2 is used so that q is approximately equal to 1, and all reverse reactions are insignificant; the reaction occurs within a spherical catalyst particle containing the activity distribution

$$k(x) = k_s x^{\alpha} \qquad (2)$$

where k_s is the catalytic activity at the particle surface (Shadman-Yazdi and Petersen, 1972); diffusion coefficients $\mathcal{D}$ for all species are equal and independent of concentration; desorption (or β) effects are negligible (Zahner, 1970); and steady state conditions exist. The following differential equations in matrix form represent diffusion and reaction within the particle:

$$\nabla^2 \mathbf{a}(x) = (R^2 k_s/\mathcal{D}) x^{\alpha} \, \mathbf{B} \, \mathbf{a}(x) \qquad (3)$$

In our example (1), $n = 4$ and $i = 0, 1, 2, 3, 4$; $\mathbf{B}$ is the stoichiometric matrix:

$$\mathbf{B} = \begin{bmatrix} 4 & 0 & 0 & 0 & 0 \\ -4 & 3 & 0 & 0 & 0 \\ 0 & -3 & 2 & 0 & 0 \\ 0 & 0 & -2 & 1 & 0 \\ 0 & 0 & 0 & -1 & 0 \end{bmatrix} \qquad (4)$$

Following the uncoupling procedure developed by Wei and Prater (1962) and Wei (1962*a*, *b*), the equations can

---

Correspondence concerning this note should be addressed to William R. Ernst.

0001-1541-78-1544-0935-$00.75.

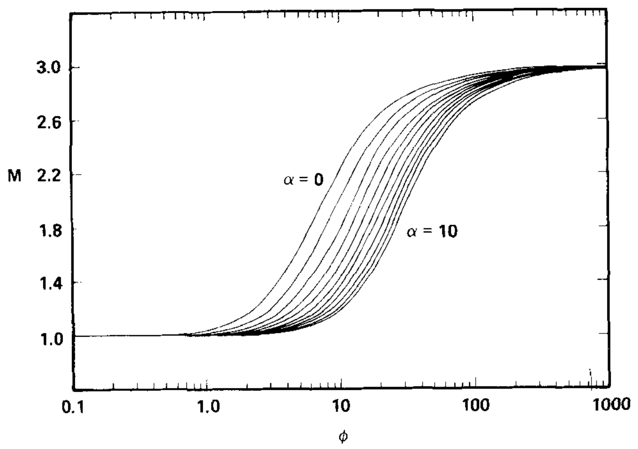

Fig. 1. Selectivity versus Thiele modulus for $\alpha = 0$ to 10.

be written in terms of characteristic species. The matrix **B** is diagonalized:

$$\mathbf{B} = \mathbf{X}\,\boldsymbol{\Lambda}\,\mathbf{X}^{-1} \tag{5}$$

where **X** *is the eigenvector matrix of* **B** *and* $\boldsymbol{\Lambda}$ *is the* matrix of eigenvalues of the form

$$\lambda_i = i \tag{6}$$

A characteristic species vector **b** is defined as

$$\mathbf{b} = \mathbf{X}^{-1}\,\mathbf{a} \tag{7}$$

where b_i represents the concentration of the i^{th} characteristic species. Equation (3) can be written as

$$\nabla^2 \mathbf{b}(x) = (R^2 k_s/\mathfrak{D})x^\alpha\,\boldsymbol{\Lambda}\,\mathbf{b}(x) \tag{8}$$

Equations (8) are uncoupled; hence the equation for the i^{th} species can be written

$$\nabla^2 b_i(x) = \phi_i^2\, x^\alpha\, b_i(x) \tag{9}$$

where

$$\phi_i = \text{a Thiele modulus} = R\sqrt{\frac{ik_s}{\mathfrak{D}}} \tag{10}$$

The boundary conditions are

$$\frac{db_i}{dx} = 0 \quad \text{at} \quad x = 0 \tag{11}$$

and

$$b_i = b_i(1) \quad \text{at} \quad x = 1 \tag{12}$$

Solution to Equation (9) involves modified Bessel functions of the first kind

$$b_i = \frac{x^{-1/2} I_p(2p\phi_i\, x^{1/2p})}{I_p\,(2p\phi_i)}\, b_i(1) \tag{13}$$

where

$$p = \frac{1}{\alpha + 2} \tag{14}$$

This equation which expresses the concentration of characteristic species for the deuterium exchange reaction is identical to the result of Shadman-Yazdi and Petersen for the concentration of species for the series reaction $A \rightarrow B \rightarrow C$.

Following the method of Wei (1962*a*), the observed rate of change of the real species a_i in the gas can be expressed in matrix form as

$$\frac{d}{dt}\,\mathbf{a} = -\,k_s\,\mathbf{X}\,\boldsymbol{\Lambda}^\dagger\,\mathbf{X}^{-1}\,\mathbf{a} \tag{15}$$

where $\boldsymbol{\Lambda}^\dagger$ $(= \boldsymbol{\Lambda}\,\boldsymbol{\eta})$ is a diagonal matrix which has elements, $\lambda_i^\dagger$ $(= i\,\eta_i)$. The following expression for effectiveness factor η_i can be derived by proceeding from Equation (13):

$$\eta_i = \frac{3}{\phi_i}\left[\frac{I_{p+1}\,(2p\phi_i)}{I_p\,(2p\phi_i)}\right] \tag{16}$$

The ratio of eigenvalues $\lambda_1^\dagger$ and $\lambda_n^\dagger$ is proportional to the average number of deuterium atoms in the initial hydrocarbon product, hence a measure of selectivity. The selectivity parameter M was originally presented by Kemball (1954). It has the form

$$M = \text{initial}\left[\,\sum_{i=1}^{n} ia_i \Big/ \sum_{i=1}^{n} a_i\,\right] \tag{17}$$

$$= \frac{n\lambda_1^\dagger}{\lambda_n^\dagger} = \frac{\eta_1}{\eta_n} \tag{18}$$

Figure 1 shows the selectivity-Thiele parameter profile as a function of catalyst activity distribution for the deuterium exchange with neopentane ($n = 9$). The value of M can vary from 1 to 3. The Thiele parameter ϕ refers to ϕ_{12}. This figure shows that there is a region approximately between $\phi = 1$ and $\phi = 100$ where selectivity is greatly influenced by activity distribution.

This note has considered, for illustrative purposes, catalyst activity distributions with increasing activity toward the particle surface. It must be pointed out that for some commercial reactions, especially those in which catalyst poisoning starts at the pore mouth, activity distributions with increasing activity toward the particle center may be preferred (Villadsen, 1976). The theoretical discussion of the deuterium exchange reaction could be readily extended to such activity distributions.

NOTATION

a_i = mole fraction of species $CD_i\,H_{n-i}$
$\mathbf{a}(x)$ = real species vector
b_i = concentration of characteristic species i
$\mathbf{b}(x)$ = characteristic species vector
$\mathbf{B}$ = stoichiometric matrix, see Equation (4)
$\mathfrak{D}$ = diffusion coefficient
I_p = modified Bessel function of the first kind
k = catalytic activity
$k(x)$ = activity distribution function, see Equation (2)
M = selectivity parameter
q = atomic fraction of D in H_2, HD, and D_2
r = atomic fraction of H in H_2, HD, and D_2
R = particle radius
x = dimensionless distance from particle center
$\mathbf{X}$ = eigenvector matrix of **B**

Greek Letters

α = activity distribution
β = desorption parameter
$\boldsymbol{\Lambda}$ = eigenvalue matrix of **B**
$\boldsymbol{\Lambda}^\dagger$ = $(\boldsymbol{\Lambda}\,\boldsymbol{\eta})$
η_i = effectiveness factor
$\boldsymbol{\eta}$ = matrix of effectiveness factors
ϕ_i = Thiele modulus

Subscripts

i = species $CD_i\,H_{n-i}$ and i^{th} characteristic species
n = number of exchangeable hydrogens in the hydrocarbon
p = order of Bessel function
s = particle surface

LITERATURE CITED

Becker, E. R., and J. Wei "Non-uniform Distribution of Catalysts on Supports I. Bimolecular Langmuir Reactions," *J. Catalysis*, **46**, 365 (1977*a*).

———, "Non-uniform Distribution of Catalysts on Supports II. First Order Reactions with Poisoning," *ibid.*, **46**, 372 (1977*b*).

Corbett, W. E., and D. Luss, "The Influence of Non-Uniform Catalytic Activity on the Performance of a Single Spherical Pellet," *Chem. Eng. Sci.*, **29**, 1473 (1974).

Dwyer, F. G., L. C. Eagleton, J. Wei, and J. C. Zahner, "The Kinetics of Deuterium—Neopentane Exchange: Effects of Desorption and Diffusion," *Proc. Royal Soc.*, **A302**, 253 (1968).

Ernst, W. R., and J. Wei, "Deuterium—Hydride Exchange in a Single Catalyst Particle," *J. Catalysis*, **39**, 303 (1975).

Germain, J. E., *Catalytic Conversion of Hydrocarbons*, Academic Press, New York (1969).

Haag, W. O., and Herman Pines, "Alumina: Catalyst and Support. III. The Kinetics and Mechanisms of Olefin Isomerization," *J. Am. Chem. Soc.*, **82**, 2488 (1960).

Kasaoka, S., and Y. Sakata, "Effectiveness Factors for Non-Uniform Catalyst Pellets," *J. Chem. Eng. Japan*, **1**, 138 (1968).

Kemball, C., "The Exchange Reaction Between Neopentane and Deuterium on Evaporated Metallic Films," *Trans. Faraday Soc.*, **50**, 1344 (1954).

Shadman—Yazdi, F., and E. E. Petersen, "Changing Catalyst Performance by Varying the Distribution of Active Catalyst Within Porous Supports," *Chem. Eng. Sci.*, **27**, 227 (1972).

Sullivan, R. F., Clark J. Egan, and G. E. Langlois, "Hydrocracking of Alkylbenzenes and Polycyclic Aromatic Hydrocarbons on Acidic Catalysts. Evidence for Cyclization of the Side Chains," *J. Catalysis*, **3**, 183 (1964).

Villadsen, J., "The Effectiveness Factor for an Isothermal Pellet with Decreasing Activity Towards the Pellet Surface," *Chem. Eng. Sci.*, **31**, 1212 (1976).

Wei, J., and C. D. Prater, "The Structure and Analysis of Complex Reaction Systems," *in Advances in Catalysis*, D. D. Eley, P. W. Selwood, and P. B. Weisz, ed., Vol. 13, p. 203, Academic Press, New York (1962).

Wei, J., "Intraparticle Diffusion Effects in Complex Systems of First Order Reactions, I. The Effects in Single Particles," *J. Catalysis*, **1**, 526 (1962*a*).

———, "Intraparticle Diffusion Effects in Complex Systems of First Order Reactions II. The Influence of Diffusion on the Performance of Chemical Reactors," *ibid.*, 538 (1962*b*).

Zahner, J. C., "Experimental Study of Laboratory Flow Reactors," *Proceedings of the First International Symposium on Chemical Reaction Engineering*, Washington, D.C. (1970).

Manuscript received September 26, 1977; revision received February 24, and accepted March 6, 1978.

Effect of Concentration on Partitioning of Polystyrene within Finely Porous Glass

CHARLES N. SATTERFIELD, CLARK K. COLTON,
BERNARD DE TURCKHEIM, and TERRY M. COPELAND

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusett 02139

We recently published a study (Colton et al., 1975) of diffusion and partitioning of solutions of nearly monodisperse polystyrene ($M = 600$ to 670 000) in leached borosilicate glass cubes having a narrow pore size distribution and pore radii of from 2.5 to 47.6 nm. In that work, bulk solute concentrations were equal to or less than 0.1% (w/v). Here we report an extension of that study in which the effect of solute concentration on the equilibrium partition coefficient is investigated, thereby making possible the extrapolation of the partition coefficient to infinite dilution for comparison with theory. The effect of solute concentration, which we have found to be surprisingly large, is in qualitative agreement with theory and may be of importance itself in connection with understanding various liquid phase reactions catalyzed by porous solids in which the size of the reacting molecules is comparable to that of the pores.

EXPERIMENTAL METHODS

The porous glass cubes employed were from our previous study. Physical properties of the cubes, denoted henceforth as types A, B, and C, were, respectively, as follows: volumetric mean pore radii (r_{P1}) from mercury porosimetry data, 18.5, 23.4, and 47.6 nm; specific pore volumes (V_P), 1.07, 0.62, and 0.68 cm^3/g; specific surface areas (S_P) from BET data (Quantachrome Co., Glenvale, N.Y.), 66.2, 31.5, and 14.9 m^2/g; equivalent cylindrical pore radiii ($r_{P2} = 2V_P/S_P$), 32.3, 39.4, and 91.3 nm. The ratio r_{P2}/r_{P1} was 1.75, 1.68, and 1.92 for cube types A, B, and C, respectively. Before use, the glass cubes were reacted under vacuum at 120°C with hexamethyl disilazane (HMDS) to prevent adsorption of polystyrene. After each run, the cubes were regenerated by rinsing with methylene chloride for 2 days in a soxhlet extractor, then dried in a vacuum oven and stored in sealed containers. Molecular weights and root mean square radii of gyration (calculated as described in our previous study) of the monodisperse polystyrene (Pressure Chemical Co., Pittsburgh, Pa.) were 37 000 (6.75 nm), 110 000 (12.7 nm), 200 000 (18.0 nm), 498 000 (30.6 nm), and 670 000 (36.3 nm). The solvent was reagent grade chloroform, a good solvent for polystyrene. Concentrated solutions of polystyrene in chloroform were prepared in advance and allowed to stand for a few days in darkness to permit complete solution in the solvent. The maximum concentration that could be studied was limited to about 20 to 25 mg/cm^3 because of the difficulty in working with the highly viscous liquids which formed in more concentrated solutions.

To measure the partition coefficient, polystyrene solution of

---

0001-1541-78-1227-0937-$00.75. © The American Institute of Chemical Engineers, 1978.