paratus to Simulate Absorber and to Predict the Effect of Chemical Reaction," *AIChE J.*, **20**, 1029 (1974).

Charpentier, J. C., "Gas-liquid Reactors," *Chem. React. Eng. Reviews*, D. Luss and V. W. Weetman, ed., ACS Symposium Series, **72**, 223 (1978).

Danckwerts, P. V., and A. J. Gillham, "The Design of Gas Absorbers: Part I, Method for Predicting Rates of Absorption with Chemical Reaction in Packed Columns and Tests with 1.5 in Raschig Rings," *Trans. Inst. Chem. Engrs.*, **44**, 42 (1966).

———, and E. Alper, "Design of Gas Absorbers; Laboratory Point Model of Packed Column Absorber," *Trans. Inst. of Chem., Engrs.*, **53**, 34 (1975).

Fonteix, C., "Hydrodynamique et Transfert de Matière dans un Laveur Pilote de Type Jet dans un Venturi: Simulation de son comportement par un Modèle de Laboratoire. Intérêt et Limites actuelles de la Technique," Thesis, Institut National Polytechnique de Lorraine, Nancy, France (1978).

Harris, L. S., and G. R. Haun, "The Ejector Venturi Scrubber," *Chem. Eng. Progr.*, **60**, 100 (1964).

Hoffmann, R., H. Kurten, and O. Nagel, "Stoffaustauschfläche und Hydrodynamik in Strahl-bzw. Venturi-Wäschern," *Chemie Ing. Technik*, **45**, 881 (1973).

Krotzsch, P., "Abgasreiningung durch Chemisorption mittels Strahlwäschern am Beispiel der Cl_2—Absorption in wässriger Natriumthiosulfat-Lösung," *ibid.*, **47**, 213 (1975).

Laurent, A., C. Prost, and J. C. Charpentier, "Bestimmung des Stoffübergangs in einem Laborrührwerksbehälter mit Stoffübergangs widerstanden in beiden Phasen," *Chemische Technik*, **26**, 471, *réf.* 52/74 (1974).

Laurent, A., and J. C. Charpentier, "Le Rôle et l'Utilité des Modeles Expérimentaux de Laboratoire dans la Prévision des Performances d'un Réacteur Gaz-Liquide Industriel," *J. Chimie Physique*, **10**, 1001 (1977).

Laurent, A., C. Fonteix, G. Besson, and J. C. Charpentier, "Pilot-Scale study of Absorption with Chemical Reaction in a Venturi-Jet Scrubber," *Atmosphere Pollution 1978*, M. M. Benarie, ed., *Studies in Environmental Science*, I, 251 (1978*a*).

Laurent, A., C. Fonteix, G. Besson, and J. C. Charpentier, "Gas-liquid Absorption with Chemical Reaction in a Liquid-Motivated Ejector Venturi-Scrubber," Congress CHISA '78, *Section Distillation and Absorption*, Praha, Tchecoslovaquie (Aug. 21-25, 1978*b*).

Nagel, O., H. Kurten, and B. Hegner, "Die Stoffaustauschfläche in Gas-Flüssigkeits-Kontaktapparaten Auswahlkriterien und Unterlagen zur Vegrösserung," *Chemie Ing. Technik*, **45**, 913 (1973).

Manuscript received February 21, 1979; revision received April 9, and accepted April 19, 1979.

A General Criterion to Test the Importance of Diffusion Limitations in Bidisperse Porous Catalysts

GÜLSEN DOĞU
and
TIMUR DOĞU

Chemical Engineering Department
Middle East Technical University
Ankara, Turkey

In the analysis of solid catalyzed reactions, it is very important to know whether transport processes within the micro- and macropore regions have any effect on the observed reaction rate. Since the kinetic rate expression is usually nonlinear, it is difficult to determine the regions of kinetic control and diffusion control by solving the controlling differential equations of the model, as was done originally by Thiele (1939) for a first-order reaction. A detailed review of diffusion and reaction processes in porous catalysts was done by Aris (1975).

In order to permit those who work with catalysts to estimate the importance of diffusion limitations on the overall rate, a number of criteria have been derived: Weisz and Prater (1954), Bischof (1967), Narshimhan and Guha (1972). Petersen (1965), Hutchings and Carberry (1966), and Schneider and Mitschka (1966) extended the Weisz-Prater criterion to systems where product inhibition is important. Hudgins (1968) developed a more general criterion for absence of appreciable diffusion effects, applicable for reactions having other than power-type rate expressions

$$\bar{r}_s \frac{R_0^2}{C_0 D} < \frac{1}{C_0} \frac{r_s(C_0)}{r_s'(C_0)} \tag{1}$$

Most of the industrially used catalysts have a bidisperse pore structure. In some cases, the intraparticle diffusion might be at least as important as interparticle diffusion and chemical kinetics. Brown (1972) discussed the intraparticle diffusion effects in branched-pore systems. Örs and Doğu (1979) show that the effectiveness of bidisperse porous catalysts which are formed by the agglomeration of porous particles depends not only upon the Thiele Modulus, but also upon another modulus, that they call α, which is proportional to the ratio of diffusion times in the macro- and micropore regions. In this work, we derive a general criterion for negligible macro- and micro-pore diffusion effects on the observed rate of catalytic reactions in bidisperse porous catalysts.

The effectiveness factor of a spherical bidisperse porous catalyst can be expressed as

$$\eta = \frac{9}{R_0^3 r_0^3 r_s(C_0)} \int_0^{R_0} \int_0^{r_0} [r_s(C_i) r^2 dr] R^2 dR \tag{2}$$

where R_0 and r_0 are the radius of the catalyst pellet and the average radius of the particles which make up the pellet, respectively, and C_i is the concentration of reactant in the micropores.

Following the procedure used by Anderson (1963), the rate is expanded in a Taylor series about the surface concentration of particles, C_a, which is the concentration of reactant in the macropores, and second-order and higher order terms are neglected. The concentration profile within the particles is approximated by a simple parabolic function.

0001-1541-80-2763-0287-$00.75. © The American Institute of Chemical Engineers, 1980.

$$r_s(C_i) = r_s(C_a) + r_s'(C_a)[C_i - C_a] \tag{3}$$

$$C_i = C_a - \beta_i\left(1 - \frac{r^2}{r_0^2}\right) \tag{4}$$

Substituting Equations (3) and (4) into Equation (2) and carrying out the integration gives,

$$\eta = \frac{3}{R_0^3 r_s(C_0)} \int_0^{R_0} \left[r_s(C_a) - \frac{2}{5} r_s'(C_a)\beta_i\right] R^2 dR \tag{5}$$

By expanding $r_s(C_a)$ and $r_s'(C_a)$ in Taylor series about the surface concentration of the pellet, C_0, and assuming a parabolic profile for concentration C_a,

$$C_a = C_0 - \beta_a\left(1 - \frac{R^2}{R_0^2}\right) \tag{6}$$

and setting up that $\eta > 0.95$ for negligible diffusion effects Equation (5) reduces to

$$\left(\frac{2}{5}\right) \frac{r_s'(C_0)}{r_s(C_0)} (\beta_i - \beta_a) - \left(\frac{2}{5}\right)^2 \frac{r_s''(C_0)}{r_s(C_0)} \beta_i\beta_a < 0.05 \tag{7}$$

In this procedure, an average and constant value for β_i is assumed to hold throughout the pellet. By equating the diffusion rate at the surface of the pellet to extensive observed reaction rate, an expression for β_a is obtained. By a similar procedure an expression for β_i is obtained.

$$\beta_a = \frac{R_0^2 \bar{r}_s \rho_p'(1 - \epsilon_a)S}{6D_a} \tag{8}$$

$$\beta_i = \frac{r_0^2 \bar{r}_s \rho_p' S}{6D_i} \tag{9}$$

where ρ_p' is the particle density, ϵ_a is the macropore porosity, and D_a and D_i are the effective macropore and micropore diffusion coefficients. By substituting β_i and β_a expressions into Equation (7), a general citerion for bidisperse porous catalysts is obtained.

$$\frac{r_s'(C_0)}{r_s(C_0)} \left[\bar{r}_s \rho_p S \frac{R_0^2}{D_a}\right](1 + G) - \frac{1}{15} \frac{r_s''(C_0)}{r_s(C_0)} \left[\bar{r}_s \rho_p S \frac{R_0^2}{D_a}\right]^2 G < \frac{3}{4} \tag{10}$$

where

$$G = \left(\frac{r_0}{R_0}\right)^2 \frac{D_a}{D_i(1 - \epsilon_a)} \tag{11}$$

The parameter G is proportional to the reciprocal of parameter defined by Örs and Doğu (1979), and its magnitude is determined by the ratio of diffusion times in the micro and macropores. G is equal to zero, which corresponds to negligible diffusion resistance in the micropores, and this criterion reduces to the criterion suggested by Hudgins in 1968 (Equation 1). Considering the order of magnitudes of effective macro- and micropore diffusivities and particle and pellet dimensions reported in the literature (Örs and Doğu 1979, Doğu and Smith 1975, Hashimoto and Smith 1974), it can be predicted that for most practical catalysts, the value of parameter G lies between 10 and 10^{-3}.

Especially for systems in which the value of G is in the order of magnitude of 10^{-1} or higher, diffusion effects in the micropores cannot be neglected. For example, for the pellets used by Hashimoto and Smith (1974), the order of magnitude of G is about one. The value of G strongly depends upon the pore size distributions of the catalysts, which determine the ratio of effective diffusivities in the micro- and macro-pore regions, and also upon the ratio of particle to pellet sizes.

Otani and Smith (1966) studied the oxidation of carbon monoxide in large catalyst pellets (10% NiO-on-alumina). For their pellets, the square of the ratio of particle to pellet diameters is about 2.5×10^{-5}. Assuming that the ratio of diffusivities D_a/D_i is on the order of magnitude of 10^2 (Hashimoto and Smith 1974) the order of magnitude of G for their system can be estimated to be 10^{-3}. This implies that for large pellet to particle size ratios, the effect of micropore diffusion can be negligible.

We can conclude that unless the value of G is very small, the criterion derived in this work is much more conservative than the previous criteria reported in the literature. By using this criterion, it is also possible to predict the importance of diffusion limitations in the micropores (with respect to diffusion in the macropores), in addition to reaction kinetics.

NOTATION

C_a = concentration of reactant in the macropores
C_i = concentration of reactant in the micropores
C_0 = external surface concentration of the reactant
D = effective diffusion coefficient
D_a = effective macropore diffusion coefficient
D_i = effective micropore diffusion coefficient
G = defined by Equation (11)
R = radial coordinate for the pellet
R_0 = radius of the pellet
r = radial coordinate for the particle
r_0 = radius of the particle
r_s = surface reaction rate
$\bar{r}_s$ = observed reaction rate
S = surface area per unit mass of the catalyst

Greek Letters

β_a = defined by Equation (8)
β_i = defined by Equation (9)
ϵ_a = macropore porosity
η = effectiveness factor
ρ_p = $\rho_p'(1 - \epsilon_a)$ = pellet density
ρ_p' = particle density

LITERATURE CITED

Anderson, J. B., "A Criterion for Isothermal Behavior of a Catalyst Pellet," *Chem. Eng. Sci.*, **18**, 147 (1963).

Aris, R., *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts*, Clarendon Press, Oxford, London (1975).

Bischoff, K.B., "An Extension of the General Criterion for Importance of Pore Diffusion with Chemical Reactions," *Chem. Eng. Sci.*, **22**, 525 (1967).

Brown, L. F., "Tests for Absence of Intraparticle Diffusion Effects in Branched-Pore Systems," *Chem. Eng. Sci.*, **27**, 213 (1972).

Doğu, G., and J. M. Smith, "A Dynamic Method for Catalyst Diffusivities," *AIChE J.*, **21**, 58 (1975).

Hashimoto, N., and J. M. Smith, "Diffusion in Bidisperse Porous Catalyst Pellets," *Ind. Eng. Chem. Fundam.*, **13**, 115 (1974).

Hudgins, R. R., "A General Criterion for Absence of Diffusion Control in an Isothermal Catalyst Pellet," *Chem. Eng. Sci.*, **23**, 93 (1968).

Hutchings, J., and J. J. Carberry, "The Influence of Surface Coverage on Catalytic Effectiveness and Selectivity. The Isothermal and Non-Isothermal Cases," *AIChE J.*, **12**, 20 (1966).

Narsimhan, G., and B. K. Guha, "Control Regimes in Experimentation of Heterogeneous Kinetics," *Chem. Eng. Sci.*, **27**, 703 (1972).

Otani, S., and J. M. Smith, "Effectiveness of Large Catalyst Pellets—An Experimental Study," *J. Catal.*, **5**, 332 (1966).

Örs, N., and T. Doğu, "Effectiveness of Bidisperse Catalysts," *AIChE J.*, **25**, 723 (1979).

Petersen, E. E., "A General Criterion for Diffusion Influenced Chemical Reactions in Porous Solids," *Chem. Eng. Sci.*, **20**, 587 (1965).

Schneider, P., and P. Mitschka, "Effect of Internal Diffusion on Catalytic Reactions," *Chem. Eng. Sci.*, **21**, 455 (1966).

Thiele, E. W., "Relation Between Catalytic Activity and Size of Particle," *Ind. Eng. Chem.*, **31**, 916 (1939).

Weisz, P. B., and C. D. Prater, "Interpretation of Measurements in Experimental Catalysis," *Adv. Catalysis*, **6**, 143 (1954).

Manuscript received October 30, 1978; revision received April 18, and accepted April 26, 1979.