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Effectiveness Factors for Molecular Sieve Catalysts

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The classical analysis of kinetic data for diffusion limited heterogeneous catalytic reactions in terms of effectiveness factors is based upon the assumption that the effective diffusivity is independent of concentration. Zeolitic diffusivities are, however, concentration dependent, so that the classical analysis is not, in general, applicable to molecular sieve catalysts. In this paper theoretical concentration profiles and the corresponding effectiveness factors are calculated from the steady-state solution of the differential equation for diffusion with first order reaction for systems in which the concentration dependence of the effective diffusivity arises from the nonlinearity of a Langmuir equilibrium isotherm. Both the concentration profiles and the effectiveness factors show considerable differences from the classical solutions for systems with constant diffusivity. A simple expression, which gives a useful approximation for the effectiveness factor in the limiting case of high diffusional resistance, is derived. It is suggested that the approximations involved in the analysis should be reasonable for certain molecular sieve catalysts.

NOMENCLATURE

a	radius of spherical particle
b	Langmuir equilibrium constant
c	sorbate concentration
c_c	sorbate concentration at center of zeolite particle
c_0	sorbate concentration at zeolite surface
c_s	sorbate concentration at saturation
D	sorbate diffusivity
D_*	RT/κ = diffusivity as $c \rightarrow 0$
k	first order rate constant
L	half-thickness of slab
p	equilibrium sorbate pressure
r	radial coordinate
R	gas constant
T	absolute temperature
x	distance measured from center of slab
y	x/L = dimensionless distance
z	r/a = dimensionless radial distance
α	sorbate activity
κ	drag coefficient [defined by Eq. (1)]
θ	c/c_s, $\theta_0 = c_0/c_s$, $\theta_c = c_c/c_s$
ϕ_L	$L(k/D)^{1/2}$ or $L(k/D_*)^{1/2}$ = Thiele modulus for slab
ϕ_s	$a(k/D)^{1/2}$ or $a(k/D_*)^{1/2}$ = Thiele modulus for sphere
η	effectiveness factor
ρ	reaction rate

INTRODUCTION

Owing to their desirable properties of high selectivity and activity, molecular sieve catalysts have gained considerable importance in the petroleum and allied industries. Although the significance of diffusional resistance in the interpretation of kinetic data for such catalysts has been recognized, there has been little theoretical analysis (*1*, *2*). Molecular sieve catalysts consist of small crystals of zeolite pelleted with a clay binder. Two distinct diffusional processes are therefore involved: diffusion through the macropores of the pellet and diffusion within the micropores of the zeolite crystals. Studies of diffusion in such systems have, however, shown that the diffusional resistance of the macropores is often insignificant in comparison with the micropore resistance (*3*, *4*). Under these conditions the problem of the analysis of kinetic data for a chemical reaction becomes formally similar to the classical problem of simultaneous diffusion and reaction in a porous catalyst, but with the significant difference that the relevant particle is the zeolite crystal and the overall dimensions of the pellet are not important. It has been assumed that the classical analysis given by Thiele (*5*) and Wheeler (*6*) may be applied directly to molecular sieve catalysts with the Thiele modulus based on the crystal radius rather than the pellet radius (*7*). Recent studies of diffusion in molecular sieves have, however, shown that the effective diffusivities are often strongly concentration dependent so that the classical analysis, which assumes a constant diffusivity, is not, in general, applicable to zeolite catalysts (*3*, *8*). It is therefore pertinent to consider the way in which the analysis must be modified to take account of the concentration dependence of the diffusivity.

For many systems the concentration dependence of zeolitic diffusivity is related to the nonlinearity of the sorption equilibrium isotherm;

$$D = \frac{RT}{\kappa} \cdot \frac{\partial \ln a}{\partial \ln c} = \frac{RT}{\kappa} \cdot \frac{\partial \ln p}{\partial \ln c}, \qquad (1)$$

where κ is a coefficient which is independent of concentration. If the equilibrium isotherm can be approximated by a Langmuir equation:

$$\theta = c/c_s = bp/(1 + bp), \qquad (2)$$

Eq. (1) becomes:

$$D = (RT/\kappa) \cdot [1/(1 - \theta)] = D_*/(1 - \theta), \qquad (3)$$

where

$D_* = RT/\kappa$
= diffusivity at zero sorbate concentration.

Although not exact, the Langmuir equation does provide a useful approximate description of the equilibrium isotherms for many zeolites and, for such systems, Eq. (3) may therefore be expected to give a reasonable approximation for the concentration dependence of the diffusivity. The rapid increase in diffusivity as saturation is approached has been observed experimentally (*3*, *8*) although the ultimate limit ($\theta \rightarrow 1$, $D \rightarrow \infty$) is not physically meaningful. In the present paper theoretical concentration profiles and the corresponding effectiveness factors are calculated for a first order irreversible reaction occurring in a zeolite in which the concentration dependence of reactant diffusivity is governed by Eq. (3). The solutions, which are obtained both for an infinite slab of zeolite and for spherical particles, show substantal deviations from the standard solutions for systems with constant diffusivity.

THEORETICAL ANALYSIS

The specific problem considered is the diffusion of a sorbate within a zeolite crystal in which it is continuously destroyed according to an irreversible first order reaction. It is assumed that the system is isothermal, that the diffusion of the products of reaction is rapid, and that the diffusivity of the reactant depends only on its concentration and is unaffected by the counterdiffusion of the products of reaction. For an infinite slab of zeolite of thickness $2L$, the steady-state concentration profile is given by the solution of the differential equation:

$$(d/dx)[D \cdot (dc/dx)] = kc, \qquad (4)$$

subject to the boundary conditions:

$$x = 0,\ dc/dx = 0;\ x = L,\ c = c_0. \qquad (5)$$

The corresponding equation for a sphere of radius a is:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \cdot D \cdot \frac{dc}{dr}\right) = kc, \qquad (6)$$

with the boundary conditions:

$$r = 0,\ dc/dr = 0;\ r = a,\ c = c_0. \qquad (7)$$

For systems in which the diffusivity is independent of concentration the solutions of Eqs. (4) and (6) are well known (*1*):

Slab: $c/c_0 = \cosh(\phi_L \cdot y)/\cosh \phi_L$; (8)

Sphere: $c/c_0 = \sinh(\phi_s \cdot z)/z \sinh \phi_s$. (9)

The corresponding expressions for the effectiveness factor η, which may be obtained from Eqs. (8) and (9) by integration are:

Slab: $\eta = (1/\phi_L) \cdot \tanh \phi_L;$ (10)

Sphere: $\eta = (3/\phi_s)[(1/\tanh \phi_s) - (1/\phi_s)].$ (11)

For systems in which the diffusivity varies with concentration according to Eq. (3), the relevant dimensionless differential equations corresponding to Eqs. (4) and (6) are:

Slab: $$\frac{d^2\theta}{dy^2} + \frac{1}{1-\theta}\left(\frac{d\theta}{dy}\right)^2 = \phi_L^2\,\theta\,(1-\theta); \qquad (12)$$

Sphere: $$\frac{d^2\theta}{dz^2} + \frac{2}{z}\cdot\frac{d\theta}{dz} + \frac{1}{1-\theta}\left(\frac{d\theta}{dz}\right)^2 = \phi_s^2\cdot\theta(1-\theta), \qquad (13)$$

where

$\phi_L = L(k/D_*)^{1/2}$ (Modified Thiele Moduli),

$\phi_s = a(k/D_*)^{1/2}$,

with the boundary conditions:

Slab: $y = 0,\ d\theta/dy = 0;\ y = 1.0,\ \theta = \theta_0;$ (14)

Sphere: $y = 0,\ d\theta/dz = 0;\ z = 1.0,\ \theta = \theta_0.$ (15)

For any given values of θ_0 and ϕ these equations (12 or 13) may be solved numerically to obtain the dimensionless concentration profile and the effectiveness factor may then be calculated from the integrals $\eta = \int_{y=0}^{1}\theta\cdot dy$ (slab) and $\eta = 3\int_{z=0}^{1}\theta\cdot z^2\,dz$ (sphere).

For the case of the slab, an analytic solution may be obtained, in parametric form, by change of variable. With the substitution $u = [1/(1-\theta)]\,(d\theta/dy)$, Eq. 12 becomes:

$$u\cdot(du/d\theta) = \phi_L^2\cdot[\theta/(1-\theta)]. \qquad (16)$$

The boundary condition at the center of the slab, where the dimensionless concentration is θ_c, becomes:

$$y = 0,\ d\theta/dy = 0,\ u = 0, \qquad (17)$$

and Eq. 16 may thus be integrated to give:

$$\frac{u^2}{2} = \phi_L^2\left\{(\theta_c - \theta) + \ln\left(\frac{1-\theta_c}{1-\theta}\right)\right\} \qquad (18)$$

or

$$\frac{1}{1-\theta}\cdot\frac{d\theta}{dy} = \phi_L \cdot\sqrt{2}\left[\theta_c - \theta + \ln\left(\frac{1-\theta_c}{1-\theta}\right)\right]^{1/2} \qquad (19)$$

The expression for the effectiveness factor is thus given by:

$$\eta = \frac{D}{kLc_0}\cdot\left(\frac{dc}{dx}\right)_{x=L} = \frac{1}{\phi_L^2\theta_0(1-\theta_0)}\cdot\left(\frac{d\theta}{dy}\right)_{y=1} \qquad (20)$$

$$= \frac{\sqrt{2}}{\theta_0\phi_L}\left[\theta_c - \theta_0 + \ln\left(\frac{1-\theta_c}{1-\theta_0}\right)\right]^{1/2}\cdot \qquad (21)$$

Integration of Eq. 19 gives:

$$\sqrt{2}\cdot\phi_L\cdot y = \int_{\theta=\theta_c}^{\theta}\frac{d\theta}{(1-\theta)\left[\theta_c - \theta + \ln\left(\frac{1-\theta_c}{1-\theta}\right)\right]^{1/2}} \qquad (22)$$

and for $y = 1$, $\theta = \theta_0$ we obtain:

$$\sqrt{2}\,\phi_L = \int_{\theta=\theta}^{\theta_0}\frac{d\theta}{(1-\theta)\left[\theta_c - \theta + \ln\left(\frac{1-\theta_c}{1-\theta}\right)\right]^{1/2}}. \qquad (23)$$

Equations (21)–(23) thus provide expressions for the effectiveness factor and the concentration profile in terms of the independent variables, ϕ_L and θ_0, and the parameter θ_c. When θ_c is small, Eq. 21 becomes:

$$\eta \simeq (\sqrt{2}/\theta_0\phi_L)[-\theta_0 - \ln(1-\theta_0)]^{1/2} \qquad (24)$$

This expression provides a useful approximation for the effectiveness factor which is valid when $\eta < \sim 0.5$. It may be shown, by expansion of the logarithm, that

$$\lim_{\theta_0 \to 0}\eta = 1/\phi_L,$$

the same as for the constant diffusivity case (Eq. 8) at large values of ϕ_L.

Plots of effectiveness factor vs modified Thiele modulus are shown, for various values of θ_0, in Figs. 1 and 2. Also shown in these figures are the curves for the

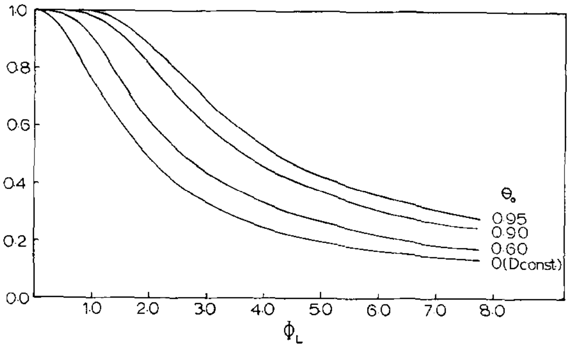

FIG. 1. Effectiveness factors for a slab with concentration dependent diffusivity.

constant diffusivity case calculated from Eqs. (10) and (11). It is evident that the effect of the concentration dependent diffusivity is quite large.

For the constant diffusivity case it has been shown that the effect of particle shape can be accounted for by using a modified Thiele modulus in which the length parameter is taken as the ratio of volume to external area (*9*). Thus, the curves for the slab and sphere become nearly coincident when $\phi_L = \phi_s/3$. This conclusion appears to be equally valid for the variable diffusivity system as may be seen from Fig. 3, in which the η vs ϕ curves for slab and sphere are compared for the constant diffusivity case and for the variable diffusivity case with $\theta_0 = 0.90$. The limiting expression for the effectiveness factor calculated from Eq. 24 is also shown and it is evident that this expression is a reasonable approximation for the low effectiveness factor region ($\eta < 0.5$).

Typical concentration profiles are shown in Figs. 4 and 5 for both slab and sphere at comparable values and Thiele modulus ($\phi_s = 12$; $\phi_L = 4.0$). It is evident that the profiles for slab and sphere differ significantly although the corresponding effectiveness factors are quite similar. The difference between the concentration profiles for constant and variable diffusivity is also indicated.

It is pertinent to consider how the overall kinetics of reaction are affected by pore diffusional resistance when the effective diffusivity shows this type of concentration dependence. Assuming that adsorption equilibrium is maintained at the surface of the zeolite, the overall reaction rate ρ will be given by:

$$\rho = kc_0\eta = kc_s\,[bp/(1 + bp)]\,\eta \qquad (25)$$

Under conditions of high pore diffusional resistance the effectiveness factor, for the variable diffusivity case, is given by Eq. 24, with $\theta_0 = bp/(1 + bp)$, and for the constant diffusivity case, by $\eta \simeq 1/\phi_L$.

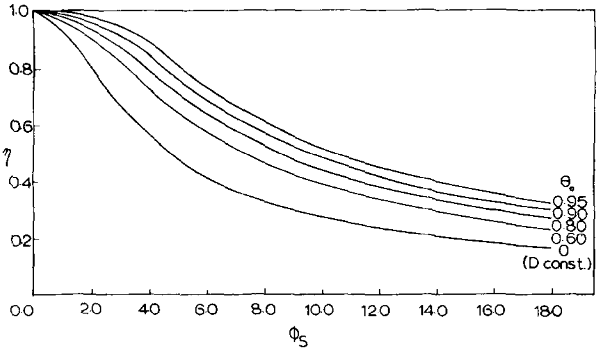

FIG. 2. Effectiveness factors for spherical particles with concentration dependent diffusivity.

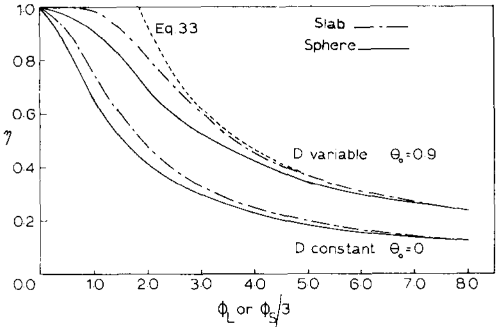

FIG. 3. Comparison of effectiveness factors for slab and sphere.

Constant Diffusivity: $\frac{\rho}{kc_s} = \frac{1}{\phi_L}\frac{bp}{1+bp}$ (26)

Variable Diffusivity:

$$\frac{\rho}{kc_s} = \frac{1}{\phi_L}\left\{\sqrt{2}\left[\ln(1+bp) - \frac{bp}{1+bp}\right]^{1/2}\right\}. \tag{27}$$

These expressions are compared, for the arbitrary value of $\phi_L = 5.0$, in Fig. 6 in which the dimensionless reaction rate is plotted against reactant pressure. Shown also in this figure is the curve which would be obtained in the absence of pore diffusional resistance, as given by Eq. 25 with $\eta = 1.0$. It is evident that the concentration dependence of diffusivity causes an appreciable modification of the rate–pressure curve thus affecting the apparent order of reaction. Since both b and ϕ_L will in general be functions of temperature, the temperature dependence of reaction rate in such a system will be complex.

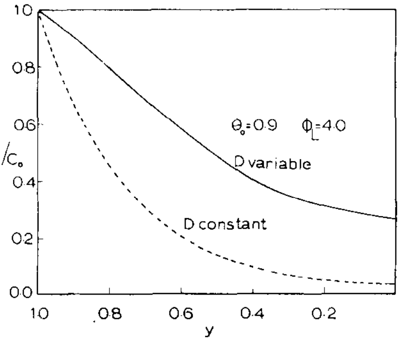

FIG. 4. Concentration profiles for a slab—comparison of constant and variable diffusivity cases.

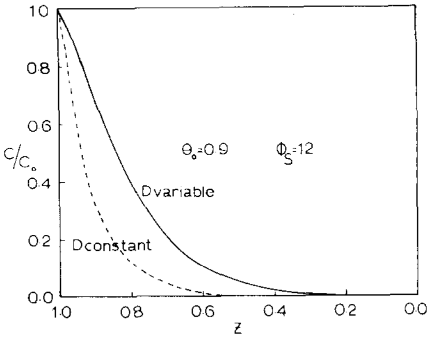

FIG. 5. Concentration profiles for spherical particles—comparison of constant and variable diffusivity cases.

CONCLUSION

The strong concentration dependence of zeolitic diffusion coefficients complicates the analysis and interpretation of kinetic data for molecular sieve catalysts. Nevertheless, under certain idealized conditions, theoretical effectiveness factors may be calculated and, in the region of high dif-

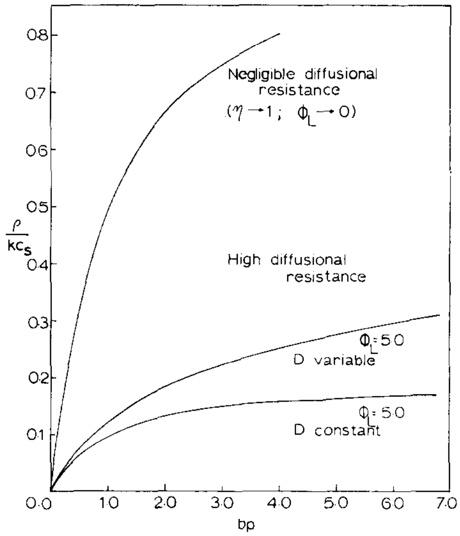

FIG. 6. Dependence of reaction rate on reactant partial pressure.

fusional resistance, a simple approximate analytical expression for the effectiveness factor is obtained. Although restrictive, the approximations involved in this analysis would appear to be reasonable for many practical systems, particularly for cracking or hydrocracking reactions in small port zeolites. The intrinsic kinetics of such reactions are often first order and, owing to the decrease in the molecule size, the diffusivity of the reaction products would be expected to be considerably larger than that of the reactants, in accordance with the basic postulates of the theory. For such systems the analysis presented should therefore be of value for the interpretation of kinetic data. Available kinetic data are, however, not sufficiently extensive to allow the theory to be tested experimentally so that it must, at present, be regarded as tentative.

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