

Isomerization of Cyclopropane on Synthetic Faujasite by Pulse Technique

I. Mathematical Model

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A mathematical model is derived to describe the transient behavior of a continuous stirred tank reactor containing catalyst particles with a bipore distribution when a stimulus is introduced. The reaction taking place inside the catalyst is assumed to be isothermal, first order, and irreversible. The expressions for the zeroth-, first-, and second-order moments of the response curve are given in terms of the adsorption equilibrium constant, the intercrystalline and intracrystalline diffusion coefficients, and the first-order reaction rate constant. A method for the determination of these parameters is presented. The same method also leads to the determination of micro- and macropore effectiveness factors.

INTRODUCTION

When catalysts are used in pelletized forms, they sometimes exhibit a bidistribution of pores. For example, pelletized zeolites exhibit a bipore distribution because they contain both a micropore structure within the crystals and a macropore structure between crystals. Consequently, there will be an intracrystalline pore diffusion within the well-structured micropores and an intercrystalline diffusion in the randomly distributed macropores. Knowledge of the relative importance of these diffusion rates as compared to the sorption and reaction rates simultaneously taking place in the catalysts can be of importance in interpreting the experimental data and improving engineering design of catalytic conversion units.

The pioneering works of Damkohler (1), Thiele (2), Zeldovitch (3), and Wagner (4) on reaction and mass transfer started a new approach to the analysis of heterogeneous catalysis which led to the concept of effectiveness of a porous catalyst. The general approach has been discussed by mathematically modeling mass transfer in the pres-

ence of a reaction as described by various authors (5-7). Schilson and Amundson (8) presented methods to predict the rates of reaction from a single porous catalyst, assuming that the reaction kinetics were known and that Knudsen diffusion occurred in the pores. Smith and co-workers (9-11) considered the interaction of physical transfer processes and chemical reaction in porous pellets for isothermal and nonisothermal conditions. They also investigated the possible significance of surface diffusion on catalytic activity. A similar study was done by Foster and Butt (12).

A convenient way of obtaining "clean" reaction rate data is to use a continuous stirred tank reactor (CSTR). Because of the high recirculation rate in the reactor, it can be operated isothermally and external mass transfer resistance from the fluid phase to the catalyst can be minimized. These reactors were used in transient operations to investigate kinetics and diffusional effects in catalytic reactions (13-18). Relya and Perlmutter (18) presented experimental and analytical investigations on the characteristics of a well-stirred reactor with a porous catalyst wall for the ethylene hydrogenation

tion reaction. In their approach Balder and Petersen (19, 20) and Hegedus and Petersen (21, 22) studied the transient operation of a single-pellet reactor. Suzuki and Smith (23) provided a method to measure diffusion coefficients and adsorption equilibrium constants using one catalyst pellet, whereas Furusawa and Smith (24) presented a mathematical and experimental investigation on mass transfer rates in a well-stirred slurry by chromatography. Finally, Kelly (25) described sorption, diffusion, and reaction phenomena in a continuous stirred catalytic reactor containing a slab-shaped catalyst. It should be noted that most of these studies assumed a single-pore distribution in the catalyst.

The objective of the present study is to derive a model to describe the transient behavior of a continuous stirred tank reactor containing spherical catalyst pellets with a bipore distribution. The model includes a first-order irreversible chemical reaction with intraparticle and interparticle diffusion and adsorption. The model is then used to derive the equations for the moments of the response curve to a stimulus. By comparing the experimentally determined moments to those predicted from the model, the rate parameters and the micropore and macropore effectiveness factors can be evaluated.

BASIC EQUATIONS FOR SPHERICAL CRYSTALS WITH MICROPORES

A simplified diagram of the continuous stirred catalytic reactor is given in Fig. 1. Microporous crystals are placed in the reactor and rotated at high speed. In the derivation of the mathematical model, it is assumed that:

1. The crystals are spherical and uniform in size.
2. The gas-phase concentration in the reactor and around the crystals is well mixed and uniform.
3. The intracrystalline diffusion can be

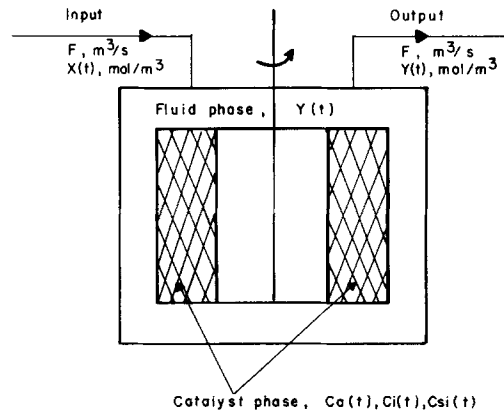


FIG. 1. Simplified diagram of the CSTR.

described by Fick's equation and the diffusion coefficient is constant.

4. An irreversible first-order reaction occurs within the micropores and the process is isothermal.

5. The adsorption isotherm is linear and adsorption equilibrium is attained at the boundary surface of the crystals.

With these assumptions, the differential equations describing the concentrations at the surface of the micropores and inside the pores are

$$\frac{k_a \epsilon_1}{A_v} \left(C_i - \frac{C_{si}}{K_p} \right) - k_s C_{si} = \frac{\partial C_{si}}{\partial t}, \quad (1)$$

$$\frac{D_i}{r_i^2} \left[\frac{\partial}{\partial r_i} \left(r_i^2 \frac{\partial C_i}{\partial r_i} \right) \right] - k_a \left(C_i - \frac{C_{si}}{K_p} \right) = \frac{\partial C_i}{\partial t}, \quad (2)$$

where $K_p = \epsilon_1 K_a / A_v$ and $D_i = D_{eff,i} / \epsilon_i$.

The initial and boundary conditions are

$$\begin{aligned} C_{si}(r_i, 0) &= 0, \\ \frac{\partial C_i}{\partial r_i}(0, t) &= 0, \\ C_i(R_i, t) &= C(t), \\ C_i(r_i, 0) &= 0. \end{aligned} \quad (3)$$

A mass balance for the fluid phase in the reactor gives

$$V \frac{dY}{dt} = F(X - Y) - D_1 4\pi R_1^2 n \epsilon_1 \left. \frac{\partial C_1}{\partial r_1} \right|_{r_1=R_1} \quad (4)$$

with the initial condition

$$Y(0) = 0.$$

After defining the new variables

$$\rho_i = r_i/R_1, \\ \xi_i = \xi_i(\rho_i, t) = C_i r_i$$

and applying the Laplace transform technique, the solution of Eqs. (1), (2), and (4) with associated boundary conditions in the Laplace domain is given by

$$\tilde{\xi}_i(\rho_i, S) = \frac{\tilde{Y}(S) R_1 \sinh \alpha(S) \rho_i}{\sinh \alpha(S)} \quad (5)$$

with

$$\alpha(S) = \frac{R_1}{(D_1)^{1/2}} \left(S + k_a - \frac{k_a^2}{K_a S + K_a k_s + k_a} \right)^{1/2}.$$

Thus, the transfer function $H_i(s)$ takes the form

$$H_i(S) = \left[1 + \tau S + 2\tau_1 \epsilon_1 \frac{D_1}{r_1^2} (\alpha(S) \coth \alpha(S) - 1) \right]^{-1} \quad (6)$$

with

$$H_i(S) = \tilde{Y}(S)/\tilde{X}(S), \\ \tau = V/F, \\ \tau_1 = \frac{v_1}{F} = n \frac{4\pi R_1^3}{3F}.$$

BASIC EQUATIONS FOR SPHERICAL PELLETS WITH A BIPORE DISTRIBUTION (MICROPORES AND MACROPORES)

A schematic diagram of a pellet containing both micropores and macropores is shown in Fig. 2. In addition to the assumptions made previously for single-pore pellets, the following assumptions are made:

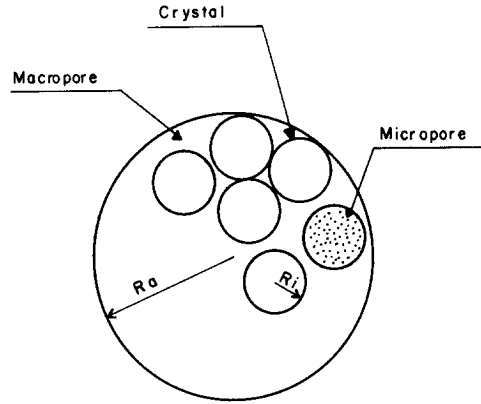


FIG. 2. Schematic diagram of the cross section of the pellet.

1. The spherical catalyst pellets are assemblies of small microporous spherical crystals of uniform size.

2. Both intercrystalline and intracrystalline diffusion processes can be described by Fick's equation with constant diffusion coefficients.

3. The first-order, irreversible chemical reaction occurs only in the micropore region.

With these assumptions, in addition to Eqs. (1) and (2) describing the concentration changes within the microporous region, the differential equation describing the concentration changes within the macroporous region is

$$\frac{D_a}{r_a^2} \left[\frac{\partial}{\partial r_a} \left(r_a^2 \frac{\partial C_a}{\partial r_a} \right) \right] = \frac{\partial C_a}{\partial t} + \frac{3\epsilon_1 (1 - \epsilon_a) D_1}{\epsilon_a R_1} \left. \frac{\partial C_1}{\partial r_1} \right|_{r_1=R_1} \quad (8)$$

with $D_a = D_{\text{eff},a}/\epsilon_a$.

The differential equation for the fluid phase in the well-mixed reactor is

$$V \frac{dY}{dt} = F(X - Y) - N 4\pi R_a^2 \epsilon_a D_a \left. \frac{\partial C_a}{\partial r_a} \right|_{r_a=R_a} \quad (9)$$

The boundary and initial conditions for Eqs. (1), (2), (8), and (9) are

$$\begin{aligned}
C_{si}(r_i, r_a, 0) &= 0, \\
\frac{\partial C_i}{\partial r_i}(0, r_a, t) &= 0, \\
C_i(R_i, r_a, t) &= C_a(r_a, t), \\
C_i(r_i, r_a, 0) &= 0,
\end{aligned} \tag{10}$$

and

$$\begin{aligned}
\frac{\partial C_a}{\partial r_a}(0, t) &= 0, \\
C_a(R_a, t) &= Y(t), \\
C_a(r_a, 0) &= 0, \\
Y(0) &= 0.
\end{aligned} \tag{11}$$

After defining new variables

$$\begin{aligned}
\rho_i &= \frac{r_i}{R_i}, \\
\xi_i &= \xi_i(\rho_i, \rho_a, t) = C_i(r_i, r_a, t) r_i, \\
\rho_a &= \frac{r_a}{R_a}, \\
\xi_a &= \xi_a(\rho_a, t) = C_a(r_a, t) r_a
\end{aligned}$$

and applying the Laplace transform technique, the solution to Eqs. (1), (2), (8), and (9), subjected to boundary conditions (10) and (11), is

$$\tilde{\xi}_e(\rho_i, \rho_a, S) = \frac{R_i \tilde{C}_a(r_a, S) \sinh \alpha(S) \rho_i}{\sinh \alpha(S)} \tag{12}$$

with

$$\alpha(S) = \frac{R_i}{(D_i)^{1/2}} \left(S + k_a - \frac{k_a^2}{K_a S + K_a k_s + k_a} \right)^{1/2}$$

and

$$\tilde{\xi}_a(\rho_a, S) = \frac{\tilde{Y}(S) R_a \sinh \beta(S) \rho_a}{\sinh \beta(S)} \tag{13}$$

with

$$\beta(S) = \frac{R_a}{(D_a)^{1/2}} \left(S + \frac{3\epsilon_i(1-\epsilon_a)D_i}{\epsilon_a} \frac{D_i}{R_i^2} (\alpha(S) \coth \alpha(S) - 1) \right)^{1/2},$$

$$\alpha(S) = \frac{R_i}{(D_i)^{1/2}} \left(S + k_a - \frac{k_a^2}{K_a S + K_a k_s + k_a} \right)^{1/2}$$

and the transfer function $H_a(S)$ takes the form

$$H_a(S) = \left[1 + \tau S + 3\tau_a \epsilon_a \frac{D_a}{R_a^2} (\beta(S) \coth \beta(S) - 1) \right]^{-1} \tag{14}$$

with

$$\begin{aligned}
H_a(S) &= \tilde{Y}(S)/\tilde{X}(S), \\
\tau_a &= \frac{v_a}{F} = N \frac{4\pi R_a^3}{3F}.
\end{aligned} \tag{15}$$

If reactant is injected into the reactor as a unit impulse $\delta(t)$, the solution for $\tilde{Y}(S)$ is obtained by replacing $\tilde{X}(S)$ by 1 in Eqs. (7) and (15). Since the transfer functions are too complex to be inverted, the moments of the response curve to a unit impulse are obtained.

MOMENTS OF THE RESPONSE CURVE

The n th moment of a function $y(t)$ is given by

$$\mu_n = \int_0^\infty t^n y(t) dt. \tag{16}$$

The n th normalized moment is

$$\hat{\mu}_n = \frac{\mu_n}{\mu_0} = \frac{\int_0^\infty t^n y(t) dt}{\int_0^\infty y(t) dt} \tag{17}$$

and the n th normalized central moment is

$$\hat{\mu}_n = \frac{\int_0^\infty (t - \mu_1)^n y(t) dt}{\int_0^\infty y(t) dt}. \tag{18}$$

The moments of the functions $y(t)$ are related to their Laplace transform $\tilde{Y}(S)$ by

$$\mu_n = (-1)^n \lim_{S \rightarrow 0} \frac{d^n Y(S)}{dS^n}.$$

For a unit impulse

$$\tilde{X}(S) = 1.$$

Therefore, when the reactor contains particles with micropores only, Eq. (7) becomes

$$\bar{Y}(S) = H_i(S). \quad (19)$$

If one defines

$$I(S) = \frac{1}{H_i(S)}$$

and

$$\begin{aligned} I &= I(0), \\ I' &= \left. \frac{dI(S)}{dS} \right|_{S=0}, \\ I'' &= \left. \frac{d^2I(S)}{dS^2} \right|_{S=0} \end{aligned}$$

then

$$\bar{Y}(S) = \frac{1}{I(S)}$$

and the zeroth, normalized first, and second central moments take the forms

$$\begin{aligned} \mu_0 &= I^{-1}, \\ \bar{\mu}_1 &= I'/I, \\ \bar{\mu}_2 &= \left(\frac{I'}{I} \right)^2 - \frac{I''}{I}. \end{aligned} \quad (20)$$

When the reactor contains pellets with both micropores and macropores, Eq. (15) becomes

$$\bar{Y}(S) = H_a(S). \quad (21)$$

If one defines

$$\begin{aligned} J(S) &= \frac{1}{H_a(S)} \\ J &= J(0), \\ J' &= \left. \frac{dJ(S)}{dS} \right|_{S=0}, \\ J'' &= \left. \frac{d^2J(S)}{dS^2} \right|_{S=0} \end{aligned}$$

then

$$\bar{Y}(S) = \frac{1}{J(S)} \quad (22)$$

and the zeroth-, first-, and second-order moments take the same form as in Eqs. (20) with I , I' , and I'' replaced by J , J' , and J'' , respectively.

It should be noted that I and J may be regarded as the characteristic functions for microporous and biporous pellets, respectively. Instead of impulse perturbation, it is also possible to employ a square-wave input. The derivation for a square-wave input is given in (26) but the expressions for the moments are quite complex and depend on the duration of the square wave.

In order to utilize the moment technique for the determination of the parameters describing the sorption, diffusion, and reaction rate phenomena, it is necessary to relate the characteristic functions to these parameters. However, this, in general, results in rather complex equations (26). Therefore, only the cases when equilibrium adsorption occurs ($k_a \rightarrow \infty$) are considered. Only the final results are given here and detailed derivations can be found in Schobert (26).

The zeroth moment is obtained using the characteristic functions I and J :

$$I = 1 + \tau_i \epsilon_i K_a k_s \eta_i, \quad (23)$$

$$J = 1 + \tau_a \epsilon_i (1 - \epsilon_a) K_a k_s \eta_i \eta_a, \quad (24)$$

$$\eta_i = \frac{3}{\phi_i^2} (\phi_i \coth \phi_i - 1), \quad (23a)$$

$$\phi_i = \left(\frac{R_i^2 K_a k_s}{D_i} \right)^{1/2}, \quad (23b)$$

$$\eta_a = \frac{3}{\phi_a'^2} (\phi_a' \coth \phi_a' - 1), \quad (24a)$$

$$\phi_a' = \left[\frac{R_a^2 K_a k_s}{D_a} \left(\frac{\epsilon_i (1 - \epsilon_a)}{\epsilon_a} \eta_i \right) \right]^{1/2}. \quad (24b)$$

η_i and η_a can be regarded as microeffectiveness and macroeffectiveness factors, respectively, for a first-order reaction in spherical particles, expressed in terms of modified Thiele's moduli ϕ_i and ϕ_a' .

The zeroth-order moment represents the amount of unreacted reactant leaving the reactor. Therefore, Eqs. (23) and (24) show the effect of adsorption, diffusion, and reaction on the conversion in the reactor. When there is no chemical reaction, I , J , and the

zeroth-order moment are equal to unity as expected for a unit impulse perturbation.

The first-order moment is related to the parameters through I' and J' , where

$$I' = \tau + \frac{3}{2} \tau_i \epsilon_i (1 + K_a) M(\phi_i), \quad (25)$$

$$J' = \tau + \frac{3}{2} \tau_a \epsilon_a \left[1 + \frac{3}{2} \frac{\epsilon_i (1 - \epsilon_a)}{\epsilon_a} (1 + K_a) M(\phi_i) \right] M(\phi'_a). \quad (26)$$

$M(\phi_i)$ and $M(\phi'_a)$ are hyperbolic functions such that

$$M(\phi) = \frac{(\cosh \phi)(\sinh \phi) - \phi}{\phi \sinh^2 \phi}. \quad (27)$$

In the absence of a reaction ($k_s = 0$), the normalized first-order moments become

$$\bar{\mu}_1 = \frac{1}{F} \left[V + v_i \epsilon_i (1 + K_a) \right] = \tau + \tau_i \epsilon_i (1 + K_a) \quad (28)$$

for microporous crystals, and

$$I'' = \frac{3}{4} \frac{v_i}{F} \epsilon_i \frac{R_i^2}{D_i} (1 + K_a)^2 N(\phi_i), \quad (30)$$

$$J'' = \frac{9}{8} \frac{v_a}{F} \epsilon_i (1 - \epsilon_a) (1 + K_a)^2 \frac{R_i^2}{D_i} N(\phi_i) M(\phi'_a) + \frac{3}{4} \frac{v_a}{F} \epsilon_a \frac{R_a^2}{D_a} \left[1 + \frac{3}{2} \frac{\epsilon_i (1 - \epsilon_a) (1 + K_a)}{\epsilon_a} M(\phi_i) \right]^2 N(\phi'_a), \quad (31)$$

where

$$N(\phi) = \frac{2\phi^2 \cosh \phi - \phi \sinh \phi - \cosh \phi \sinh^2 \phi}{\phi^3 \sinh^3 \phi}.$$

As can be seen from Eq. (31) J'' is the sum of two terms T_1 and T_2 . In the presence of a chemical reaction, the diffusional processes are coupled with the reaction. Moreover, effects of the diffusional processes in the micropores and macropores cannot be separated. However, in the absence of a reaction, $M(\phi_i)$, $N(\phi_i)$, $M(\phi'_a)$, and $N(\phi'_a)$ all

$$\bar{\mu}_1 = \frac{1}{F}$$

$$\left[V + v_a \epsilon_a \left(1 + \frac{\epsilon_i (1 - \epsilon_a) (1 + K_a)}{\epsilon_a} \right) \right]$$

$$= \tau + \tau_a \epsilon_a + \tau_a \epsilon_i (1 - \epsilon_a) (1 + K_a) \quad (29)$$

for biporous pellets.

In this case, the first-order moment is independent of the diffusional process and is only a function of the geometry of the system (V , v_i , v_a , ϵ_i , ϵ_a), the adsorption equilibrium constant K_a , and the flow rate F . This result is similar to that obtained in a chromatographic column (27). $\bar{\mu}_1$ is the total mean residence time of the reactant in the reactor and in the zeolite. τ is the residence time in the gaseous phase of the reactor, while $\tau_i \epsilon_i$ (or $\tau_a \epsilon_i (1 - \epsilon_a)$ for pellets) and $\tau_a \epsilon_a$ are the residence times in micropores and macropores, respectively. For the case of an empty reactor ($v_i = v_a = 0$), the normalized first-order moment is equal to τ which is the response of a continuous stirred reactor of volume V and flow rate F to an impulse input.

The second-order moment is related to the parameters through I'' and J'' , where

approach finite values. As a result, T_1 and T_2 represent diffusional resistances from micropores and macropores, respectively.

EVALUATION OF SORPTION, DIFFUSION,
AND REACTION RATE PARAMETERS

Experiments should be made with micro-

porous crystals and also with biporous pellets. When the intracrystalline diffusion resistance is negligible, only experiments with pellets are necessary. In all cases, experiments should be conducted at different flow rates and particle sizes. The moments of the response curve are then deter-

mined and values, of $I, I', I'', J, J',$ and J'' are calculated according to the above equations. ϕ_i is calculated from Eq. (32) using a combination of Eqs. (23), (25), and (30) in conjunction with the definitions of $\eta_i, M(\phi),$ and $N(\phi)$.

$$\frac{I''(I-1)}{(I'-\tau)^2} = \frac{(\phi_i \cosh \phi_i - \sinh \phi_i)(2\phi_i \cosh \phi_i - \phi_i \sinh \phi_i - \cosh \phi_i \sinh^2 \phi_i)}{\phi_i(\cosh \phi_i \sinh \phi_i - \phi_i^2)} \quad (32)$$

The function $F_1(\phi)$ which is the right-hand side of Eq. (32) is plotted as a function of ϕ in Fig. 3. Once ϕ_i is obtained, η_i is determined from Eq. (23a). The parameter K_a may be obtained from the slope of the straight line by plotting I' versus $1/F$ according to Eq. (25). A similar plot according to Eqs. (23) and (24) will give the values of k_s and η_a . D_i can then be determined from

$$D_i = \frac{R_i^2 k_s K_a}{\phi_i^2}$$

ϕ'_a is determined from Eq. (24a). The func-

tion $F_2(\phi)$ which is the right-hand side of Eq. (24a) is plotted as a function of ϕ in Fig. 4. Once ϕ'_a is obtained, D_a is calculated from

$$D_a = \frac{R_a^2 \epsilon_i(1-\epsilon_a)}{\phi'_a \epsilon_a} K_a k_s \eta_i \quad (33)$$

The procedure is thus quite simple and gives values of four parameters with only two sets of experiments, one with microporous crystals and one with biporous pellets. Since both microeffectiveness and macroeffectiveness factors are determined, the results also provide information on the im-

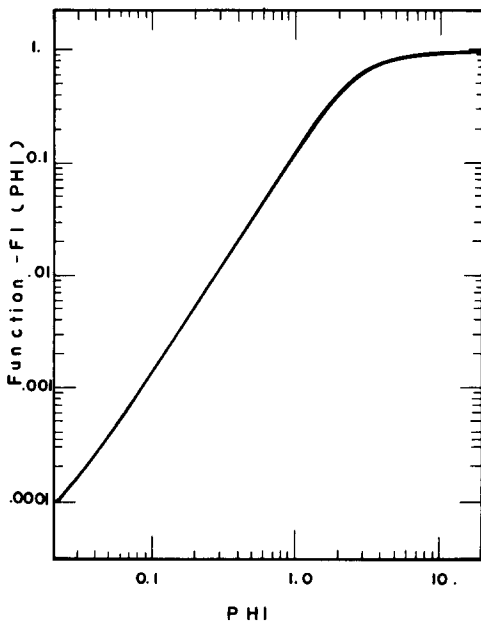


FIG. 3. Log-log plot of function $F_1(\phi)$ versus ϕ .

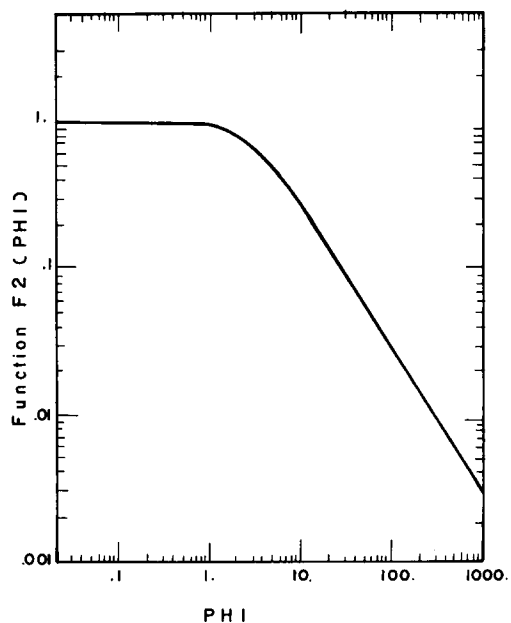


FIG. 4. Log-log plot of function $F_2(\phi)$ versus ϕ .

portance of intercrystalline or intracrystalline diffusion relative to the other rate processes. The method is especially useful since it provides a means for the determination of diffusion coefficients in the presence of a chemical reaction. The method can also be used for cases where one or more of the processes are absent. These limiting cases are presented in (26).

CONCLUSIONS

A mathematical model was developed to describe the transient behavior of a continuous stirred tank reactor. The model included a linear sorption equilibrium constant K_a , a first-order reaction rate constant k_s , an intracrystalline diffusion coefficient D_i , and an intercrystalline diffusion coefficient D_a .

Expressions for the zeroth-, first-, and second-order moments of the response curve to a unit impulse perturbation were given in terms of the parameters K_a , k_s , D_i , and D_a . It was shown that these parameters can be calculated from the experimental data. The general case is quite complicated but microeffectiveness and macroeffectiveness factors can be obtained. This allows one then to determine the relative importance of intercrystalline and intracrystalline diffusion. Furthermore, the method can be used to measure intercrystalline and intracrystalline diffusion under reacting conditions.

A_v surface area, m^2 pore surface area/ m^3 pellet volume
 C concentration of sorbate in gas-phase, mol/m^3
 C_s concentration of sorbed phase, mol/m^2 pore surface area
 C_0 concentration of sorbate in gas-phase at time 0, mol/m^3
 D diffusion coefficient, m^2/s
 D_{eff} effective diffusion coefficient, m^2/s
 F flow rate, m^3/s

$H(S)$ transfer function, dimensionless
 $I(S)$ characteristic function for crystals, dimensionless
 I characteristic function for crystals, evaluated at $S = 0$, dimensionless
 I' first derivative of characteristic function for crystals evaluated at $S = 0$, s
 I'' second derivative of characteristic function for crystals evaluated at $S = 0$, s^2
 J characteristic function for pellets evaluated at $S = 0$, dimensionless
 J' first derivative of characteristic function for pellets evaluated at $S = 0$, s
 J'' second derivative of characteristic function for pellets evaluated at $S = 0$, s^2
 k_a sorption rate constant, s^{-1}
 K_a equilibrium constant for adsorption, dimensionless
 k_s first-order surface reaction rate constant, s^{-1}
 K_p $K_a \epsilon_i / A_v$, equilibrium constant for adsorption, m^3 pellet void/ m^2 pore surface area
 n number of crystals in CSTR
 N number of pellets in CSTR
 r_a radial distance in pellet, m
 r_i radial distance in crystal, m
 R_a radius of pellet, m
 R_i radius of crystal, m
 t time, s
 v volume of catalyst, m^3
 V volume of reactor, m^3
 $X(t)$ concentration of reactant at inlet at time t , mol/m^3
 $Y(t)$ concentration of reactant at outlet at time t , mol/m^3

Greek Letters
 $\alpha(S)$ parameter for crystals
 $\beta(S)$ parameter for pellets
 ϵ void volume = porosity, m^3 pore volume/ m^3 pellet volume
 μ moment

ξ	concentration of reactant, mol/m ²
ϕ	modified Thiele modulus, dimensionless
ϕ'	modified Thiele modulus for pellet, dimensionless
η	effectiveness factor
$\rho = r/R$	dimensionless radial distance
$\tau = V/f$	residence time, s

Subscripts

i	intracrystalline or micropore or powder
a	intercrystalline or macropore or pellet
s	surface

Superscripts

-	Laplace transform of function
-	normalized (moment)
^	central normalized (moment)

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