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Distribution for Maximum Activity of a Composite Catalyst

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For a catalyst composed of a more active component embedded in a less active (but not inert) and more diffuse matrix, an optimum distribution of the active component in the catalyst pellet may lead to significantly higher reaction rates per unit volume of pellet, compared with reaction rates using pellets with a uniformly distributed active component or with an active component concentrated on the outside or the inside of the pellet. The optimum distribution changes qualitatively with the physical parameters of the pellet and with changes in the rate constants and diffusion coefficients of the catalytic components. This is relevant to the performance of coking zeolite/silica-alumina catalysts in hydrocarbon cracking reactions.

SCOPE

Catalysts used for the cracking of petroleum fractions consist of particles of rare-earth exchanged zeolite (crystalline aluminosilicate) embedded in a matrix of amorphous silica-alumina. The activity of the zeolite component towards cracking is greater than that of the matrix, but the resistance to diffusion is significantly lower in the matrix than in the zeolite. Such composite catalysts appear to have a higher activity and improved resistance to coking than either constituent used separately.

Ruckenstein (1970) showed that embedding an active catalyst uniformly in a more porous but inactive solid could significantly increase the reaction rate over that if the catalyst only was present. Varghese and Wolf (1980) showed that a uniformly distributed composite catalyst had significant advantages over an undiluted catalyst under conditions of pore mouth poisoning.

It is of interest to consider whether a nonuniform distribution of active component in a porous matrix offers any advantages over a uniform distribution, particularly where the matrix itself is also catalytically active, albeit to a small extent. Further, if the catalyst is coked while it is on stream, the reaction rate constants and diffusion resistance of both components are altered. Hence the optimum distribution is different from that of a fresh catalyst. The objectives of the present paper are to obtain the overall reaction rates for a composite catalyst containing a reactive matrix with different distributions of the more active component, and to obtain optimum distributions for a number of changes in reaction constants, diffusion coefficients, and sizes, of the constituents.

CONCLUSIONS AND SIGNIFICANCE

The overall reaction rate is obtained for a composite catalyst pellet of infinite flat plate geometry, with the more active component also present as flat plates (strata) but of lesser thickness. This geometry leads to a significant ease in analysis with little loss of rigor. Nominal values of parameters used are of the order of those expected in catalytic cracking using zeolite/silica-alumina catalysts.

For the simple case of a uniform distribution of the more active component, increasing the size of the composite catalyst decreases the reaction rate per unit volume of composite, as expected. Two special cases of nonuniform distribution are considered, where the more active component is isolated either at the external surface or at the center of the composite catalyst. The conformation with the more active component in the center is found to be more reactive than the conformation where the more active component is at the surface. This is shown to be a consequence of the non-zero catalytic activity of the matrix. The uniformly distributed catalyst possesses a higher activity than either of the two extreme distributions, except when the size is sufficiently small that diffusional limitations can be ignored. There all three cases tend to the same asymptotic value.

An attempt is made to simulate the effect of coking by decreasing the rate constant of the more active component and the diffusion coefficient of the matrix. As the properties of the matrix and the more active component decrease, so does the

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reaction rate per unit volume. The activity, however, remains in the order: uniform > active center > active surface.

The variational problem of obtaining a distribution function for the more active component to maximize the overall reaction rate is set up, and a simpler version is solved numerically. For the nominal values chosen for this sytem, the optimum distribution has a maximum at the center and decreases to zero at the surface. The shape of the optimum distribution changes qualitatively as the size or the reaction parameters are changed. Increasing the size results in an optimum distribution with no active component at the center, a maximum between the center and the surface, and a finite amount of active material at the surface. For a catalyst at some state of "coking," the optimum distribution may consist of no active material at the surface, a maximum between the surface and the center, and a local minimum at the center.

The reaction rate corresponding to an optimum distribution under a given set of circumstances is of course greater than that for any of the three special cases considered earlier, under the same circumstances. The difference is especially significant for intermediate-sized and "fresh" catalysts. For the larger or "coked" catalysts, the corresponding rate approaches that for the uniformly distributed case.

The significance of the present work lies in the existence of an optimum distribution of a more active component in a less active matrix to maximize the overall reaction rate for a catalyst. However, since the optimum distribution changes as the catalyst is "coked", a global optimum distribution for a catalyst on stream will differ from that of a fresh catalyst. Furthermore, it is expected that the effect of distribution on selectivity may be even greater than its effect on activity. Work in this direction is currently underway.

BACKGROUND

Ruckenstein (1970) first considered the advantages of placing small particles of a catalyst uniformly in an inert porous matrix, *vis-a-vis* using a homogeneous pellet of the same size as the matrix but containing only the active catalyst. If the diffusion coefficient of the active component is sufficiently small, and the size of the homogeneous pellet is sufficiently large, then the concentration inside the homogeneous pellet is low enough that the overall reaction rate for the pellet is very small. In other words, the effectiveness of the catalyst pellet is very small. A way to increase the effectiveness factor is of course to use a smaller-sized pellet, but there may be physical constraints that require a minimum size. Embedding sufficiently small sized particles of the catalyst uniformly in a matrix which is inert but very porous, may be an acceptable compromise. Ruckenstein's analysis shows a maximum in overall reaction rate with the fraction of active component in the non-homogeneous pellet, balancing the overall rate constant with the overall diffusion coefficient. Depending upon the ratio of the diffusion coefficients of the catalyst and the inert, and the Thiele modulus of the active particles, the overall reaction rate for the non-homogeneous pellet can be several times greater than the overall reaction rate for the homogeneous pellet having the dimensions of the matrix.

Noble metal catalyst particles, which are placed on supports that are either inert or contain a different catalytic function, are often poisoned starting from the external surface of the support and working toward the center (pore-mouth poisoning). Becker and Wei (1977) showed that where poisoning (and selectivity) considerations are unimportant, the active metal is optimally placed at the outside of the pellet (the so-called "egg shell" distribution). A poisoned catalyst operates best when the active catalyst is placed at the center ("egg yolk"), beyond the reach of the pore-mouth poison. For fresh catalyst subject to poisoning, an intermediate position for the active material ("egg white" distribution) may be better than either of the two extremes.

Varghese and Wolf (1980) noted that placing small particles of active but diffusion limited catalysts uniformly in a porous inert matrix has advantages for a pore mouth poisoned pellet as well as for a fresh pellet. The homogeneous pellet, when fresh, uses only a small fraction of its volume to catalyze the reaction, since the concentration of reactant towards the center of the pellet is negligible due to the diffusional limitation of the catalyst. Under pore mouth poisoning conditions, even that small amount of activity is lost, since the catalyst near the inside surface is the first to be poisoned. For a fresh non-homogeneous pellet, the concentration of reactant inside the pellet does not tend to zero as sharply as for the homogeneous pellet, and a greater fraction of the pellet volume plays a catalytic role. Hence losing the external surface to a poison is not as catastrophic for a non-homogeneous pellet as it is for the homogeneous pellet.

In the present work, the physical situation is based on hydrocarbon cracking by zeolite/silica-alumina catalysts. A single reactant proceeding to a single product is considered, i.e. the selectivity problem is ignored. Both the zeolite (crystalline aluminosilicate) and the amorphous silica-alumina catalyze the reaction; however the rate constants and diffusion coefficients of the two components are different. The composite catalyst is vulnerable to deactivation by coking, which is expected to change both the rate constants and the diffusion coefficients. Since the exact nature of the coking phenomenon is not clearly known, a simple model is used. The changes in a coking catalyst are assumed to be the same throughout the pellet (i.e., uniform, as opposed to pore-mouth, coking). A coking reaction in conjunction with the main reaction is not written; instead, instantaneous rates of the main reaction are evaluated corresponding to snapshots of a coking catalyst.

The analysis is presented in the following section. Since a different pellet geometry is used here than was used by Ruckenstein (1970) or Varghese and Wolf (1980), it is of interest first to consider the case of a fresh, uniformly distributed, composite catalyst. Then the two extreme cases of more active component (zeolite) distribution are discussed. Finally the problem of defining an optimum distribution is set up, and a less general case is solved.

ANALYSIS

Uniform Distribution

Figure 1a illustrates a spherical composite catalyst containing spherical particles of more active material in a less active (but not catalytically inert) matrix. It is implicitly assumed henceforth that the distribution of the smaller particles in the matrix is random, and that the overall volume fraction $\bar{\epsilon}$ of the more active material is sufficiently low that the smaller particles act independently of one another. [Experimental data on cracking as reported by Magee (1977) seem to validate the latter assumption, at least for less than 7 percent of zeolite in the matrix.] For the present, a uniform distribution is also assumed. A considerably more amenable geometry for the pellet is given in Figure 1b, which represents a flat plate doubly infinite in two dimensions. The equivalent thickness of the plate is related to the diameter of the composite in Figure 1a by (Aris, 1957)

$$2L_C = d_C/3$$

All spheres of diameter d_z a distance r_C from the center of the spherical matrix of Figure 1a are then replaced by an infinitely

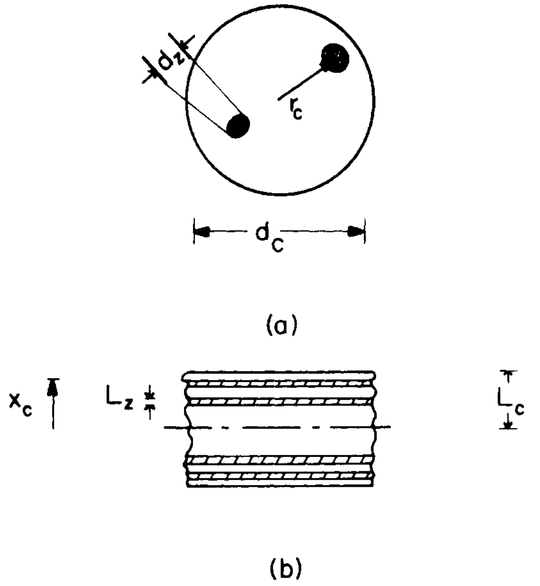

Figure 1. (a) Spherical composite catalyst pellet of diameter d_C containing more diffuse matrix in which are randomly placed spheres diameter d_z of more active component. (b) Infinite flat plate composite pellet of half-width L_C. Strata of more active material, half width L_z, are embedded in the matrix.

large flat plate of thickness L_z a distance x_C from the center of the plate in Figure 1b. Relations similar to the one above relate these parameters.

As is customary in such cases, two scales of length are employed to analyze the situation. The dimension of the strata of more active component is considered large with respect to the small scale, but is considered smaller than a differential element in the large scale.

Consider one stratum of more active material, a distance x_C from the center of the plate. A material balance for reactant A in this stratum yields

$$D_{Az}\frac{d^2A_{zu}}{dx_z^2} + r_{Azu} = 0 \tag{1a}$$

at steady state. If the reaction rate is first order in A, i.e.

$$r_{Azu} = -k_{Az}A_{zu} \tag{1b}$$

then Eqs. 1a,b together with boundary conditions

$$A_{zu} = A_{Cu} \quad \text{at} \quad x_z = L_z \tag{1c}$$

and

$$\frac{dA_{zu}}{dx_z} = 0 \quad \text{at} \quad x_z = 0 \tag{1d}$$

yield the concentration profile for A in the stratum

$$A_{zu} = A_{Cu}\,\text{Cosh}[\phi_{Azu}x_z/L_z]/\text{Cosh}[\phi_{Azu}] \tag{2a}$$

Here A_{Cu} is the concentration of A in the matrix at the location of the stratum. Note that the boundary condition of Eq. 1c assumes $L_z \ll L_C$. In Eq. 2a ϕ_{Azu} is the Thiele modulus of the stratum and is defined by

$$\phi_{Azu} \equiv L_z\sqrt{k_{Az}/D_{Az}} \tag{2b}$$

The overall rate of reaction in the stratum per unit volume of stratum is then

$$\bar{r}_{Azu} = -\bar{k}_{Azu}A_{Cu} \tag{3a}$$

where

$$\bar{k}_{Azu} \equiv k_{Az}\,\text{Tan}h[\phi_{Azu}]/\phi_{Azu} \tag{3b}$$

In the composite catalyst, note that the reaction occurs in both the matrix and the more active component. A material balance for a differential element in the uniformly distributed composite yields

$$D_{ACu}\frac{d^2A_{Cu}}{dx_C^2} + r_{Amu}(1-\bar{\epsilon}) + \bar{\epsilon}\,\bar{r}_{Azu} = 0 \tag{4a}$$

again assuming that $L_z \ll L_C$. The rate of reaction in the matrix is given by

$$r_{Amu} = -k_{Am}A_{Cu}. \tag{4b}$$

The boundary conditions for Eq. 4a are

$$A_{Cu} = A_S \quad \text{at} \quad x_C = L_C \tag{4c}$$

and

$$\frac{dA_{Cu}}{dx_C} = 0 \quad \text{at} \quad x_C = 0 \tag{4d}$$

Here A_S is the concentration of A at the external surface of the composite catalyst. The solution of Eqs. 4 with $\bar{r}_{Azu}$ defined by Eq. 3a yields the concentration profile of A in the composite catalyst

$$A_{Cu} = A_S\,\text{Cos}h[\phi_{ACu}x_{xC}/L_C]/\text{Cos}h[\phi_{ACu}] \tag{5a}$$

In Eq. 5a, ϕ_{ACu} is the Thiele modulus of the composite catalyst, given by

$$\phi_{ACu} \equiv L_C\sqrt{k_{ACu}/D_{ACu}} \tag{5b}$$

Here D_{ACu} is the diffusion coefficient for the composite. An expression for this can be given by

$$D_{ACu} = \bar{\epsilon}D_{Az} + (1-\bar{\epsilon})D_{Am} \tag{5c}$$

Further, k_{ACu} is short form notation for

$$k_{ACu} \equiv \bar{\epsilon}\,\bar{k}_{Azu} + (1-\bar{\epsilon})k_{Am} \tag{5d}$$

Finally the overall rate of reaction in the composite catalyst with a uniform distribution of active component is given by

$$\bar{r}_{ACu} = -\bar{k}_{ACu}A_S \tag{6a}$$

where $\bar{k}_{ACu}$ is the overall rate constant for a uniformly distributed composite

$$\bar{k}_{ACu} \equiv k_{ACu}\,\text{Tan}h[\phi_{ACu}]/\phi_{ACu} \tag{6b}$$

Equations 5 and 6 are used in the Results section when the performance of uniform composite catalysts is to be considered. Recall that both components of this catalyst are active, albeit to different extents. Hence the evaluation of an effectiveness factor with respect to one or the other component would lead to ambiguity. The overall rate constant is therefore a good measure of the performance of the composite catalyst. As defined in Eq. 6b for the uniform distribution case, it can be compared to analogous expressions for other types of distributions to determine their effect on performance, and to k_{AC} to determine the diffusional limitations of the given distribution.

Active Surface Distribution

The two special cases of non-uniform distribution of the more active component are now separately considered. The case where all of the more active material is placed as a layer at the external surface of the infinite flat plate is analogous to the "egg shell" distribution of Becker and Wei (1977) in spherical geometry, and is illustrated in Figure 2a. The active surface layer coordinate x_z now ranges from $(1-\bar{\epsilon})L_C$ to L_C, and the matrix center layer coordinate x_m ranges from 0 to $(1-\bar{\epsilon})L_C$. In the active surface layer, then, the concentration profile is

$$A_{zs} = M_1\,\text{Cos}h\left[\phi_{Azs}\frac{x_z}{L_C}\right] + M_2\,\text{Sin}h\left[\phi_{Azs}\frac{x_z}{L_C}\right] \tag{7a}$$

Note that the Thiele modulus for the active component in the active surface distribution

$$\phi_{Azs} \equiv L_C\sqrt{k_{Az}/D_{Az}} \tag{7b}$$

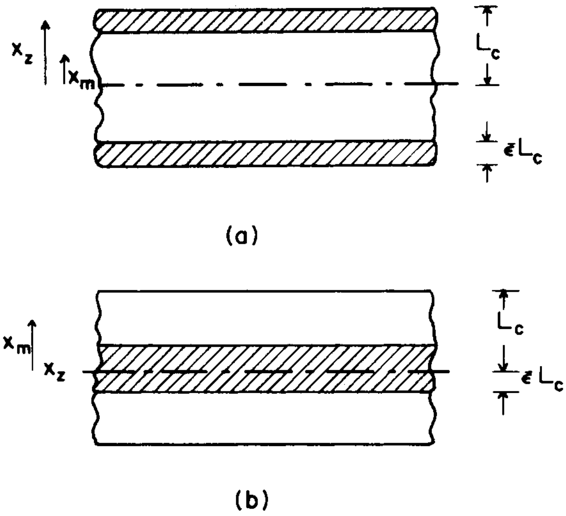

Figure 2. (a) Active surface distribution in the flat plate geometry. A layer of more active component comprising a fraction $\bar{\epsilon}$ of the total catalyst volume is placed at the surface of the pellet. (b) Active center distribution. The same amount of more active component is now placed at the center of the flat plate.

is defined differently from that in the uniform distribution, ϕ_{Azu}. Similarly in the matrix

$$A_{ms} = N_1 \operatorname{Cos}h\left[\phi_{Ams}\frac{x_m}{L_C}\right] + N_2 \operatorname{Sin}h\left[\phi_{Ams}\frac{x_m}{L_C}\right] \tag{8a}$$

where

$$\phi_{Ams} \equiv L_C\sqrt{k_{Am}/D_{Am}} \tag{8b}$$

The constants of integration M_1, M_2, N_1 and N_2 are eliminated by the two boundary conditions

$$A_{zs} = A_S \quad \text{at} \quad x_z = L_C \tag{9a}$$

$$\frac{dA_{ms}}{dx_m} = 0 \quad \text{at} \quad x_m = 0 \tag{9b}$$

and two matching relations at $x_z = x_m = (1 - \bar{\epsilon})L_C$

$$A_{zs} = A_{ms} \tag{9c}$$

$$D_{Az}\left(\frac{dA_{zs}}{dx_z}\right) = D_{Am}\left(\frac{dA_{ms}}{dx_m}\right) \tag{9d}$$

Equations 7 to 9 lead to

$$M_1 = A_S\{1 - \psi_s \operatorname{Tan}h[\phi_{Ams}(1 - \bar{\epsilon})] \operatorname{Tan}h[\phi_{Azs}(1 - \bar{\epsilon})]\}/\text{dens} \tag{10a}$$

$$M_2 = A_S\{\psi_s \operatorname{Tan}h[\phi_{Ams}(1 - \bar{\epsilon})] - \operatorname{Tan}h[\phi_{Azs}(1 - \bar{\epsilon})]\}/\text{dens} \tag{10b}$$

$$N_1 = \{M_1 \operatorname{Cos}h[\phi_{Azs}(1 - \bar{\epsilon})] + M_2 \operatorname{Sin}h[\phi_{Azs}(1 - \bar{\epsilon})]\}/ \operatorname{Cosh}[\phi_{Ams}(1 - \bar{\epsilon})] \tag{10c}$$

$$N_2 = 0 \tag{10d}$$

where

$$\text{dens} \equiv \operatorname{Cos}h[\phi_{Azs}]\{1 - \operatorname{Tan}h[\phi_{Azs}] \operatorname{Tan}h[\phi_{Azs}(1 - \bar{\epsilon})] + \psi_s \operatorname{Tan}h[\phi_{Ams}(1 - \bar{\epsilon})](\operatorname{Tan}h[\phi_{Azs}] - \operatorname{Tan}h[\phi_{Azs}(1 - \bar{\epsilon})])\} \tag{10e}$$

and

$$\psi_s \equiv (\phi_{Ams}D_{Am})/(\phi_{Azs}D_{Az}) \tag{10f}$$

Finally, the overall rate of reaction per unit volume of the composite flat plate for the active surface distribution is given by

$$\bar{r}_{ACs} = -\bar{k}_{ACs}A_S \tag{11a}$$

where

$$\bar{k}_{ACs} = \frac{k_{Az}}{\phi_{Azs}} \frac{\{\psi_s \operatorname{Tan}h[\phi_{Ams}(1 - \bar{\epsilon})] + \operatorname{Tan}h[\phi_{Azs}\bar{\epsilon}]\}}{\{\psi_s \operatorname{Tan}h[\phi_{Ams}(1 - \bar{\epsilon})] \operatorname{Tan}h[\phi_{Azs}] + 1\}} \tag{11b}$$

Equations 10 and 11 with the active surface distribution can be compared with Eqs. 5 and 6 previously obtained for the concentration profile and overall reaction rate with the uniform distribution.

Active Center Distribution

The other special case, where the more active component is placed in the center of the flat plate and is surrounded by the less reactive matrix, is illustrated in Figure 2b. This distribution corresponds to the "egg yolk" distribution of Becker and Wei (1977).

A comparison of Figure (2b) with (2a) shows that a second analysis for this special case is unnecessary. The active center distribution consists of a surface layer of the matrix up to a fractional distance $(1 - \bar{\epsilon})$ from the surface, while the active surface distribution consists of a surface layer of the more active component up to a fractional distance $\bar{\epsilon}$ from the surface. Hence the overall reaction rate for the active center distribution can be obtained by inspection from Eq. 11, by substituting subscript m for z and vice versa, and by substituting $(1 - \bar{\epsilon})$ for $\bar{\epsilon}$. Then, using subscript c for the active center distribution, the overall reaction rate constant is

$$\bar{k}_{ACc} = \frac{k_{Am}}{\phi_{Amc}} \frac{\{\psi_c \operatorname{Tan}h[\phi_{Azc}\bar{\epsilon}] + \operatorname{Tan}h[\phi_{Amc}(1 - \bar{\epsilon})]\}}{\{\psi_c \operatorname{Tan}h[\phi_{Azc}\bar{\epsilon}] \operatorname{Tan}h[\phi_{Amc}] + 1\}} \tag{12}$$

where

$$\psi_c = (\phi_{Azc}D_{Az})/(\phi_{Amc}D_{Am}) \tag{13a}$$

$$\phi_{Azc} = L_C\sqrt{k_{Az}/D_{Az}} \tag{13b}$$

and

$$\phi_{Amc} = L_C\sqrt{k_{Am}/D_{Am}} \tag{13c}$$

From Eqs. 7 through 10 the concentration profile for the active center distribution can be similarly obtained.

Equation 12 with the active center distribution can be compared with the relations previously derived for the uniform and active surface distribution.

Optimum Distribution

Consider a composite catalyst with the more active component distributed in strata. This is similar to the flat plate shown in Figure 1b, except that now the distribution is not required to be uniform throughout the thickness of the plate. Even so, as long as there is no interaction between strata and if $L_z \ll L_C$, the overall rate of reaction in a stratum per unit volume of the stratum is

$$\bar{r}_{Az} = -\bar{k}_{Az}A_C \tag{14a}$$

where

$$\bar{k}_{Az} \equiv k_{Az} \operatorname{Tan}h[\phi_{Az}]/\phi_{Az} \tag{14b}$$

and

$$\phi_{Az} = L_z\sqrt{k_{Az}/D_{Az}} \tag{14c}$$

Note the similiarity with Eqs. 2 and 3, except that the subscript u has been removed for the general, non-uniform distribution. Now in the composite, if at position x_C the volume fraction of the more active material is $\epsilon(x_C)$, then the diffusion coefficient at that position is

$$D_{AC} = \epsilon D_{Az} + (1 - \epsilon)D_{Am} \tag{15a}$$

A material balance in a differential element in the composite then yields

$$\frac{d}{dx}\left(D_{AC}\frac{dA_C}{dx_C}\right) - (1 - \epsilon)k_{Am}A_C - \epsilon\bar{k}_{Az}A_C = 0 \tag{15b}$$

The boundary conditions are

$$A_C = A_S \quad \text{at} \quad x_C = L_C \tag{15c}$$

and

$$\frac{dA_C}{dx_C} = 0 \quad \text{at} \quad x_C = 0 \tag{15d}$$

The optimum distribution of the more active component must be such that the overall reaction rate per volume of composite is a maximum. In other words a function $\epsilon(x_c)$ is required such that

$$(-\bar{r}_{AC}) = \frac{1}{L_C}\left(D_{AC}\frac{dA_C}{dx_C}\right)_{x_C=L_C} \tag{16a}$$

is a maximum. Note that D_{AC} varies with x_C since D_{AC} is a function of ϵ. In the calculus of variations format, it is advantageous to consider maximizing the equivalent expression for $\bar{r}_{AC}$

$$-\bar{r}_{AC} = \int_0^{L_C} \{k_{Am} + (\bar{k}_{Az} - k_{Am})\epsilon\} A_C dx_C \tag{16b}$$

A constraint on $\epsilon(x_C)$ is that

$$\int_0^{L_C} \epsilon dx_C = \bar{\epsilon} L_C \tag{16c}$$

On physical grounds it is required that the range of ϵ be restricted to between 0 and 1, and that A_C is never less than 0. Reducing and rearranging terms, the problem statement is to obtain $\delta(x)$ for

$$\max \int_0^1 \{a_1 + a_2\delta(x)\} y(x) dx \tag{17a}$$

subject to

$$\int_0^1 \delta dx = 1 \tag{17b}$$

where the functions $\delta(x)$ and $y(x)$ are related by

$$\frac{d}{dx}\left[\{b_1 + b_2\delta(x)\}\frac{dy}{dx}\right] - \{a_1 + a_2\delta(x)\} = 0 \tag{18a}$$

with

$$y = 1 \quad \text{at} \quad x = 1 \tag{18b}$$

and

$$\left(\frac{dy}{dx}\right) = 0 \quad \text{at} \quad x = 0 \tag{18c}$$

Furthermore

$$0 \le \delta \le 1/\bar{\epsilon} \quad \text{for} \quad 0 \le x \le 1 \tag{19a}$$

and

$$y \ge 0 \quad \text{for} \quad 0 \le x \le 1 \tag{19b}$$

Since b_2 is expected to be very much less than b_1 in absolute value, the term containing the first derivative of $\delta(x)$ in the expansion of the lefthand side of Eq. 18a can be considered negligible. Now the relationship between δ and y simplifies considerably, to

$$\delta = \frac{a_1 y - b_1 y''}{b_2 y'' - a_2 y} \tag{20}$$

Substituting this in Eqs. 17a and 17b results in

$$\max \int_0^1 f(y,y'') dx \tag{21a}$$

subject to

$$\int_0^1 g(y,y'') dx = 1 \tag{21b}$$

where

$$f(y,y'') \equiv \frac{(a_1 b_2 - a_2 b_1) y'' y}{b_2 y'' - a_2 y} \tag{21c}$$

and

$$g(y,y'') \equiv \frac{a_1 y - b_1 y''}{b_2 y'' - a_2 y} \tag{21d}$$

Then the calculus of variations defines the concentration profile corresponding to the optimum distribution to be the solution of

$$\frac{\partial f}{\partial y} + \frac{d^2}{dx^2}\left(\frac{\partial f}{\partial y''}\right) + \lambda\left\{\frac{\partial g}{\partial y} + \frac{d^2}{dx^2}\left(\frac{\partial g}{\partial y''}\right)\right\} = 0 \tag{22a}$$

subject to

$$\frac{d}{dx}\left(\frac{\partial f}{\partial y''}\right) + \lambda \frac{d}{dx}\left(\frac{\partial g}{\partial y''}\right) = 0 \quad \text{at} \quad x = 0 \tag{22b}$$

and

$$\left(\frac{\partial f}{\partial y''}\right) + \lambda\left(\frac{\partial g}{\partial y''}\right) = 0 \quad \text{at} \quad x = 1 \tag{22c}$$

where λ is a Lagrangian multiplier.

An analytic solution to Eqs. 22 together with the boundary conditions of Eqs. 18b,c and inequalities (Eq. 19) appears impractical. An approximate solution can be obtained by assuming y to be a polynomial in x, then using the relations above to obtain the coefficients of the polynomial. If a polynomial form is assumed, however, the advantage of the calculus of variations approach is essentially lost. In that case, the direct extremization of the reaction rate with respect to the polynomial coefficients is a simpler approach, and one which is now no less general.

Consequently the direct approach is used. Assume

$$y = \sum_{i=0}^{\infty} C_i x^i \tag{23}$$

Then the overall reaction rate corresponding to Eq. 16a is to be maximized with respect to the C_i for the optimum distribution. In reduced parameters the overall rate constant can be written

$$\bar{k}_{AC} = (\{b_1 + b_2\delta\} y')_{x=1} \tag{24}$$

Once the optimum values of C_i are known, substitution in Eqs. 23 and 20 yields the optimum distribution of the more active component.

To equalize the numbers of unknowns and equations, Eq. 23 is truncated after four terms, i.e.

$$y = C_0 + C_1 x + C_2 x^2 + C_3 x^3 \tag{25}$$

Then from Eq. 18c

$$C_1 = 0 \tag{26a}$$

Equation 18b yields

$$C_0 + C_2 + C_3 = 1 \tag{26b}$$

and from Eqs. 17b and 20

$$\int_0^1 \frac{(a_1C_0 - 2b_1C_2) - (6b_1C_3)x + (a_1C_2)x^2 + (a_1C_3)x^3}{(2b_2C_2 - a_2C_0) + (6b_2C_3)x - (a_2C_2)x^2 - (a_2C_3)x^3} \times dx = 1 \tag{26c}$$

Further,

$$\bar{k}_{ACo} = \max\left\{\frac{(a_1b_2 - a_2b_1)(2C_2 + 3C_3)}{2b_2(C_2 + 3C_3) - a_2}\right\} \tag{27}$$

Values of C_0, C_1, and C_3 for a given value of C_2 are obtained numerically from Eqs. 26. The optimum set of values of the C_i are then those that yield a maximum value for the quantity in brackets in Eq. 27 without violating the inequalities of Eqs. 19. Finally, substitution of y in Eq. 20 results in the optimum distribution function.

RESULTS AND DISCUSSION

The cracking reaction with zeolite/silica-alumina catalysts is considered as an example of a process using composite catalysts having a non-inert matrix. Nominal values of the parameters of the process and the catalyst components are collected in Table 1.

The reaction rate constants k_{Az} and k_{Am} are calculated from the data of Thomas and Barmby (1968), and the values of the diffusion coefficients D_{Az}, D_{Am} are suggested by the work of Weisz (1973). Overall dimensions of the catalyst range from of the order of 100 μ to 1 cm depending upon the reactor type. The nominal value chosen for L_C lies between these two; the effect on the results of varying L_C is considered below. The nominal value used for L_z corresponds to that given by Venuto and Habib (1979). The overall volume fraction of more active component, $\bar{\epsilon}$, has a nominal value somewhat smaller than the range 0.10–0.15 in use (Magee, 1977). The nominal value was chosen to be small enough to avoid the possibility of zeolite-matrix-zeolite interactions, but larger values are not expected to change the results qualitatively.

Fresh Catalyst

First note that a quick calculation using Table 1 shows that values of k_{Az} and $\bar{k}_{Azu}$ are virtually indistinguishable. Clearly the particle size of the zeolite in the uniformly distributed composite is chosen so that particular component is not in the diffusion limiting regime.

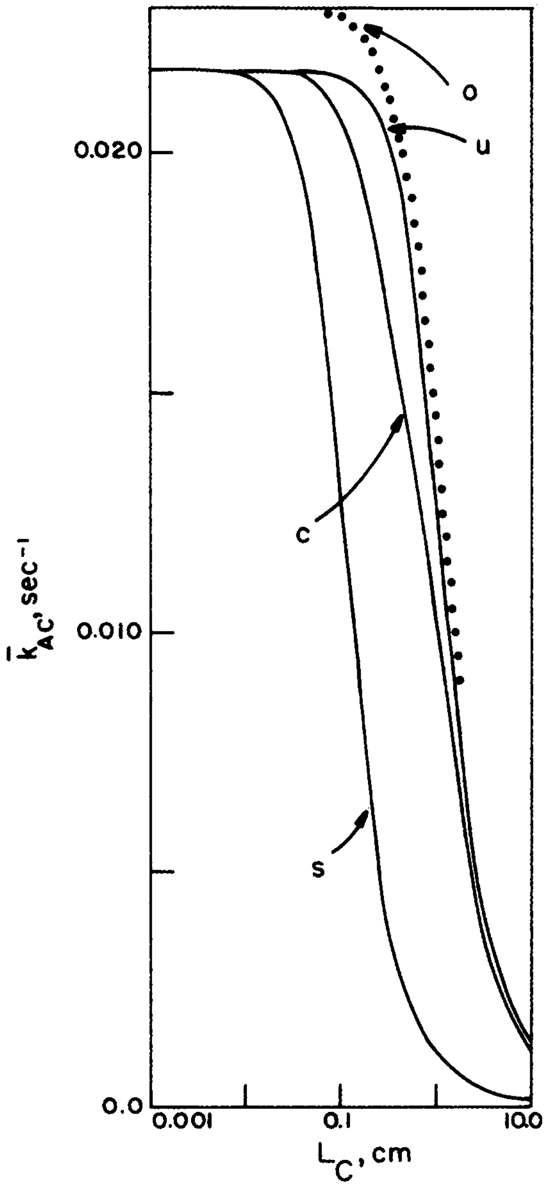

Figure 3. Overall (volume averaged) reaction rate constant $\bar{k}_{AC}$ for various distributions of more active component in the flat plate composite catalyst. The size parameter of the "fresh" catalyst pellet is varied. Other parameters have the values of Table 1. Labels *o*, *u*, *c*, and *s* define curves for optimum, uniform, active center, and active surface distributions respectively.

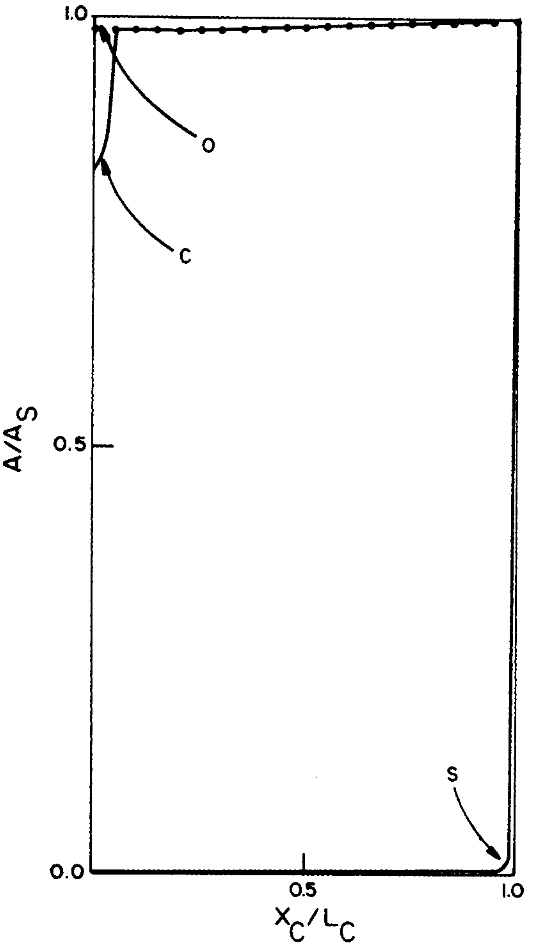

Figure 4. Concentration profiles of reactant for various distributions of more active component in the "fresh" flat plate composite catalyst. The parameters chosen are those Table 1. See Figure 3 for an explanation of the labels used. The profile for the uniform distribution (not shown) is indistinguishable on this scale from curve *o*.

The diffusion limitations of the composite are illustrated in Figure 3 as the overall reaction rate constant is plotted against L_C. Various distributions are shown. Comparing the rate constants for the two special cases with that for the uniform distribution, it is seen that for sufficiently small values of L_C, the overall rate constants tend to the value of the volume-averaged rate constant of Eq. 5d. Note however that a low L_C asymptote may not be meaningful for the uniform distribution case, since we require $L_C \gg L_z$. If L_z is decreased from the value given in Table 1 to meet this condition, the asymptote is expected to lie close to those for the two special cases. For larger values of L_C, placing the more active component on the outside surface results in the lowest value of $\bar{k}_{AC}$. This might seem contrary to intuition until it is recalled that the matrix, while less catalytically active, is not inert. Placing the significantly less diffuse material on the outside surface drops the concentration of the reactant to a considerable extent within a very small distance (Figure 4). Consequently the reaction rate in the major portion of the pellet is insignificant, being the product of the lower rate constant and a small concentration. When the more diffuse component is placed at the outside, Figure 4 shows that the concen-

TABLE 1. NOMINAL PARAMETER VALUES

k_{Am}	0.015 s^{-1}
k_{Az}	0.15 s^{-1}
D_{Am}	1×10^{-2} cm^2/s
D_{Az}	1×10^{-5} cm^2/s
L_C	0.1 cm
L_z	1×10^{-3} cm
$\bar{\epsilon}$	0.05

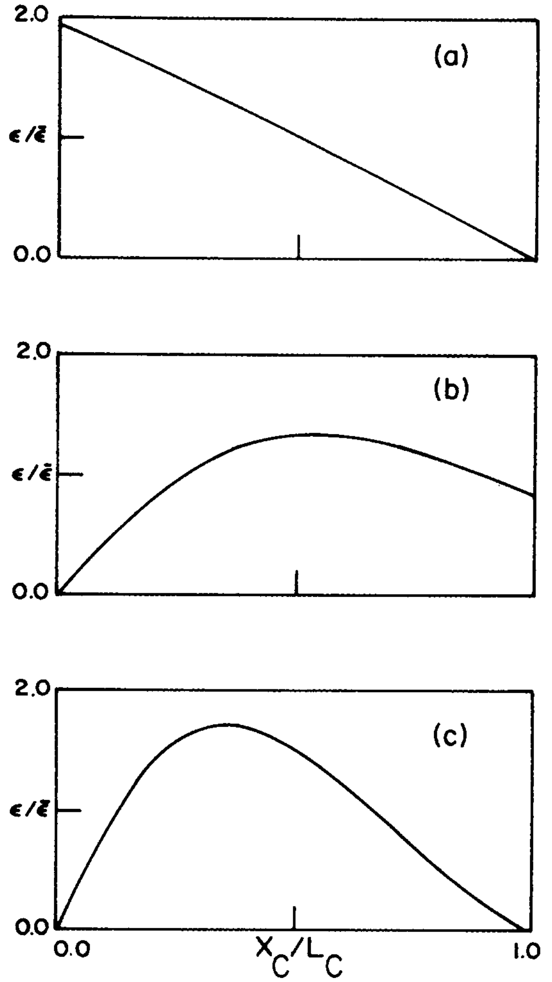

Figure 5. Optimum distribution of more active component for maximum overall reaction rate constant in "fresh" flat plate composite catalyst. (a) L_C = 0.1 cm (b) L_C = 1.0 cm, (c) L_C = 1.58 cm. Other parameters are those of Table 1.

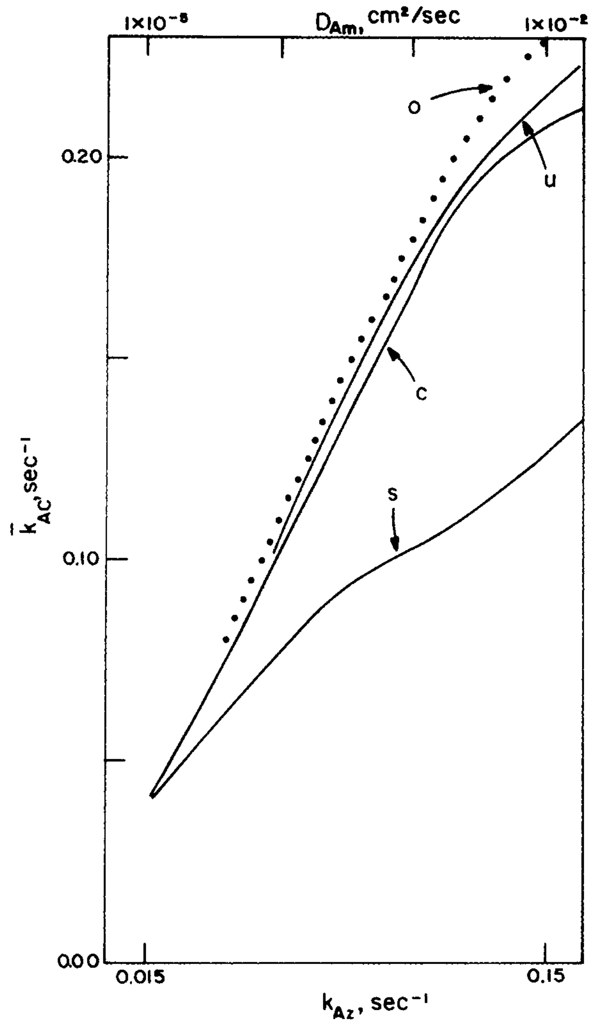

Figure 6. Overall (volume averaged) reaction rate constant $\bar{k}_{AC}$ for various distributions of more active component in the flat plate composite catalyst. The parameters k_{Az} and D_{Am} are decreased to simulate a "coking" catalyst. Other parameters are as in Table 1. See Figure 3 for an explanation of the labels used.

tration is large and the profile is virtually flat throughout the matrix. Hence the matrix can contribute substantially to the overall rate of reaction. Further, the concentration drop through the more active species overwhelms that through the matrix. Consequently, the concentration in the more active species when it is placed at the center is never significantly lower than the concentration at the corresponding point in the layer of the more active species when it is placed at the surface. Hence, the contribution to the overall reaction rate by the more active species in the center active distribution is not significantly lower than its contribution when it is in the active surface distribution.

The maximum overall rate constants for non-uniform distribution of more active material are also shown in Figure 3 with varying L_C. Each point of the dotted line corresponds to a distribution of more active component different from distributions corresponding to the neighboring points. Put differently, the dotted line is an envelope of curves representing overall rate constants for constant (but not uniform) distribution of more active material, and all the curves lie underneath the envelope. Again, a low L_C asymptote may not be meaningful, but is expected to lie near the asymptotes for the other distributions. At intermediate L_C values, the dotted line is significantly higher than the others. This is due to the interplay between rate constant and diffusion coefficient with position for a nonuniformly distributed composite, analogous perhaps to the interplay between rate constant and concentration for a non-isothermal single component catalyst. At larger values of L_C, the maximum overall rate constant decreases but it is still greater than the values for the other distributions.

Some represenative profiles are shown in Figure 5. For sufficiently small catalysts, it is advantageous to have more than the average value of the more active component in the center of the pellet. Recall that neither curve c nor curve s in Figure 3 does as well as the uniform distribution curve, but curve c is better than curve s. The optimum profile will of course depend upon the relative values of the rate constants and diffusion coefficients of the two components. For the present case, a monotonically decreasing concentration from about twice the average value at the center to zero at the surface does the best job (Figure 5a). As the pellet size is increased, two qualitative changes are noted in the optimum profile. Initially there is required a net shift of material from near the center to near the surface of the pellet, as shown in Figure 5b. At this stage the higher rate constant of the more active species overshadows the lower diffusion coefficient involved. At still larger values of L_C, however, this trend needs to be partially reversed with some of the active material returning to nearer the center for the maximum overall reaction rate in Fig. 5c. The maximum in the profile, which had moved towards the surface in Fig. 5b, now moves back towards the center. At this stage it is more important for the matrix to allow reactant to diffuse towards the center of the pellet than for the more active component to convert as much of the reactant as possible near the surface.

Deactivating Catalyst

The changes occurring in a catalyst pellet during the coking phenomenon are not known in general. In fact there is reason to believe that no general behavior exists. The information collected by Butt (1972) appears to indicate that the existence of any change

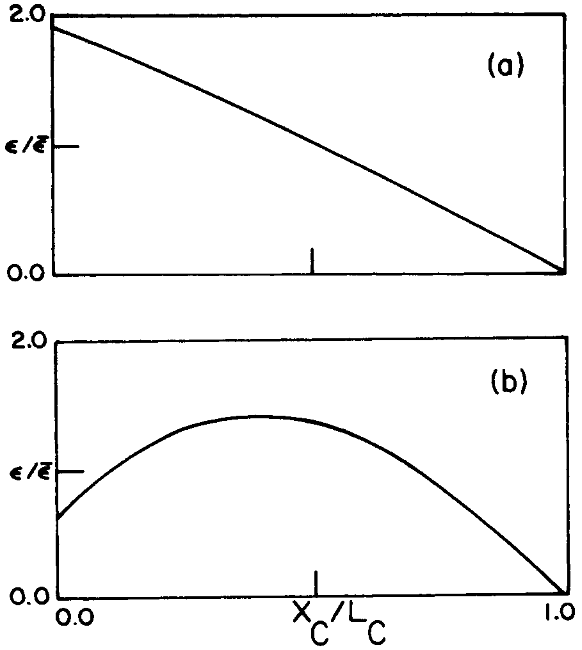

Figure 7. Optimum distribution of more active component for maximum overall reaction rate constant in "coking" flat plate composite catalyst. (a) k_{Az} = 0.0946 s^{-1}, D_{Am} = 0.251 × 10^{-2} cm^2/s (b) k_{Az} = 0.0377 s^{-1}, D_{Am} = 0.158 × 10^{-3} cm^2/s. Other parameters have the values shown in Table 1.

in the diffusion coefficient, for example, depends upon the nature of the catalyst pellet and the feed. Hence a simple model is used here for illustrative purposes. It is reasonable to believe that the value of k_{Az} will suffer a greater absolute decline than that of k_{Am}, since the latter is so much smaller than the former. Similarly D_{Am} will decrease in an absolute sense to a greater extent during coking than will D_{Az}. Consequently below is considered the effect of distribution of the more active component on the overall activity of a composite catalyst as k_{Az} and D_{Am} are simultaneously decreased.

Figure 6 illustrates the change in the value of the overall rate constant during this simple coking process. As in the case for the fresh catalyst, the value of $\bar{k}_{AC}$ for various distributions decreases in the order: optimum > uniform > active center > active surface distribution at any value of k_{Az} and D_{Am}. As the values of k_{Az} and D_{Am} tend to those of k_{Am} and D_{Az} respectively, the overall rate constants for all distributions decrease and tend towards a common value, as expected.

Again, the optimum distribution for a maximum reaction rate changes as "coking" proceeds. Some of these profiles are shown in Figure 7. As in Figure 5, for a fresh catalyst the optimum distribution monotonically decreases from the center to the outside surface. As diffusional limitations progressively increase, a shift in the distribution profile is required. This is analogous to the profiles in Figure 5, where however diffusional limitations were introduced by increasing L_C rather than by decreasing D_{Am}. For the "coking" catalyst, since the diffusional limitation imposed by decreasing D_{Am} is at least somewhat compensated by decreasing k_{Az}, the change in the optimum profile is expected to be less drastic than that noted in Figure 5. This is indeed shown to be so in Figure 7b, where there is a greater amount of material required to be closer to the center of the pellet than in either Figures 5b or 5c. For the "coking" catalyst, the second qualitative change in the optimum profile, as noted in Figure 5c above, is not observed.

CONCLUDING REMARKS

The significance of Figure 7 is not so much to affirm that the concentration profiles shown are in fact optimal ones for a coking catalyst. The present model for coking used is too simple for such an assertion to be valid. However Figure 7 does indicate that an optimal distribution for a fresh catalyst may be qualitatively different from the optimal distribution for a coking catalyst. Clearly the distribution cannot be changed while the catalyst is on stream; hence a global optimal distribution is required. The corresponding objective function will require information on how the overall reaction rate, the rate of coke formation, the component rate constants and diffusion coefficients all influence one another.

Finally it should be noted that selectivity to one of several products may be even more greatly affected than overall reaction rate by the distribution of the more active species. This is particularly true when the multiple reactions have different orders or when products have different mass transfer characteristics. The selectivity problem will be considered later.

NOTATION

a_1 = reduced parameter in optimum distribution, $\equiv k_{Am}$
a_2 = reduced parameter in optimum distribution, $\equiv (k_{Az} - k_{Am})\bar{\epsilon}$
A = reactant concentration: A_C, in composite pellet at coordinate x_C; A_m, in matrix at coordinate x_m; A_S, at outside surface of pellet; A_z, in zeolite at coordinate x_z
b_1 = reduced parameter in optimum distribution, $\equiv D_{Am}/L_C{}^2$
b_2 = reduced parameter in optimum distribution, $\equiv (D_{Az} - D_{Am})\bar{\epsilon}/L_C{}^2$
C_0, C_1, C_2, C_3, C_i = coefficients of polynomial in reduced concentration of reactant as a function of reduced position, Eq. 23
d_C, d_z = diameter in spherical geometry of composite catalyst, zeolite pellet, Figure 1a
dens = grouping of terms in denominator of Eq. 10
D_A = diffusion coefficient of reactant: D_{AC}, in composite catalyst; D_{Am}, in matrix; D_{Az}, in zeolite
f,g = functionals defined in Eqs. 21
k_A = reaction rate constant based on unit volume of catalyst; k_{AC}, in composite catalyst; k_{Am}, in matrix; k_{Az}, in zeolite
L_C = thickness of composite catalyst in flat plate geometry
L_z = thickness of zeolite stratum distributed in composite catalyst in flat plate geometry
M_1, M_2 = constants of integration, Eqs. 7 and 10
N_1, N_2 = constants of integration, Eqs. 8 and 10
r_A = rate of formation of reactant per unit volume catalyst: r_{AC}, in composite catalyst; r_{Am}, in matrix; r_{Az}, in zeolite
x = reduced coordinate in optimum distribution, $\equiv x_C/L_C$
x_C, x_m, x_z = coordinate for composite catalyst, matrix, zeolite
y = reduced concentration in optimum distribution, $\equiv A_{Co}/A_S$

Greek Letters

δ = reduced volume fraction of more active material in optimum distribution, $\equiv \epsilon(x_C)/\bar{\epsilon}$
ϵ = volume fraction of more active material in composite catalyst at position x_C
λ = Lagrangian multiplier, Eqs. 22
$\phi_{AC}, \phi_{Am}, \phi_{Az}$ = Thiele modulus of reactant in composite catalyst, in matrix, in zeolite
ψ_c = non-dimensional grouping for active center distribution, $\equiv (\phi_{Azc} D_{Az})/(\phi_{Amc} D_{Am})$
ψ_s = non-dimensional grouping for active surface distribution, $\equiv (\phi_{Amc} D_{Am})/(\phi_{Azc} D_{Az})$

Superscripts

$(\bar{\ })$ = value averaged over volume
$(\ )', (\ )''$ = first, second derivative

Subscripts

c = active center distribution
o = optimum distribution
s = active surface distribution
u = uniform distribution

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Factors Affecting Secondary Nucleation Rate of Sodium Chloride in an Evaporative Crystallizer

Crystallization kinetics of sodium chloride have been studied in a Continuous Mixed Suspension Mixed Product Removal evaporative crystallizer at 50°C. A marine propeller was found to give a substantially lower nucleation rate than a pitched blade impeller under identical conditions. The crystal turnover time did not affect the effective nucleation rate.

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SCOPE

It has been well established, that one of the main factors, which determine the crystal size distribution (CSD) in an industrial crystallizer is the crystallization kinetics. Controlling the CSD of the product from a crystallizer often implies control over nucleation and growth rate.

From the numerous studies, reported in literature over the past decade, it can generally be concluded that secondary nucleation is the major source of nuclei in industrial crystallizers.

Many authors have studied the phenomenon of secondary nucleation and used their observations to model nucleation kinetics as a function of the operating conditions in an attempt to derive scale-up rules for industrial applications. In spite of these studies, little is known about the mechanism by which secondary nuclei are produced in an industrial crystallizer. So far, this lack of knowledge has hampered attempts to scale up the secondary nucleation process with satisfactory confidence.

The primary objective of this work is to study chemical engineering factors, which affect the performance and scale-up of crystallizer equipment. The experimental work, reported in this paper, is devoted to obtaining the relation between operating conditions, impeller design and crystallizer scale and the salt nucleation rate in an evaporative crystallizer. This study is, moreover, aimed at getting better insight into the intrinsic mechanism of nucleation in order to derive those data, which may have significance for scale-up purposes.

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