ρ_g = gas density, kg/m^3
ρ_l = liquid density, kg/m^3
σ = surface tension, N/m
ω = radial velocity, rad/s
μ = viscosity, Pa·s

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Effects of Radially Nonuniform Distributions of Catalytic Activity on Performance of Spherical Catalyst Pellets

The performance of spherical catalyst pellets with radially nonuniform distributions of activity is simulated under parallel reaction networks closely resembling hydrocarbon oxidation reactions. Both reaction paths are assumed to be exothermic with the desired path exhibiting lower activation energy requirements than the undesired one. It is shown that nonuniform activity distributions enhance effectiveness and selectivity over a large range of values of the Thiele modulus. Multiple steady states in effectiveness and selectivity are observed for certain values of the heat of reaction parameter.

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SCOPE

It is well known that significant concentration gradients develop within industrial catalyst particles due to increased diffusional resistances offered by the tortuous pore structure of the catalyst. Furthermore, if the reactions are sufficiently exothermic, significant intraparticle temperature gradients can also develop. These gradients alter not only the effectiveness of the catalyst in terms of its global rate, but also the selectivity in cases where multiple reactions of different order and/or activation energy occur. It has been shown (Becker and Wei, 1974, 1977a,b; Shadman Yazdi and Petersen, 1972; Corbett and Luss, 1974; Villadsen, 1976) that the distribution of catalytic activity within the catalyst particle can alter intrapellet concentration and temperature gradients which, in turn, can significantly influence the effectiveness and selectivity of the catalyst.

In the present study, the performance of spherical catalyst pellets with nonuniform activity distributions of the form: $K(r) = K_s(r/r_s)^\alpha$, $\alpha > 0$, is simulated under a parallel reaction network of the form: $A + B \rightarrow C + D$; $A + B \rightarrow E + F$. Reactions are assumed to exhibit second-order kinetics and to be exothermic. The desired reaction is of lower activation energy requirements than the undesired reaction. This reaction scheme, with the stated assumptions, very closely resembles catalytic hydrocarbon oxidation reactions. Intraparticle concentration and temperature profiles are obtained for various activity distributions by numerically solving the mass and energy diffusion equations. Effectiveness factors and overall pellet selectivities for various values of the dimensionless activation energies and heat of reaction parameters are then computed as a function of the Thiele modulus.

CONCLUSIONS AND SIGNIFICANCE

A mathematical simulation of the performance of spherical catalyst particles with radially nonuniform distribution of catalytic activity under parallel, exothermic reaction networks is presented. It is demonstrated that significant reduction of intraparticle concentration and temperature profiles results from nonuniform activity distributions. Effectiveness factors

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per unit weight of active ingredient are shown to increase with increasing nonuniformity in the activity distribution for large values of the Thiele modulus. The opposite is observed in a narrow range of ϕ_A. The range of ϕ_A for which nonuniform activations are more effective depends on the heat of reaction parameter as well as on the activation energies of the reactions.

The overall pellets selectivity towards the reaction with the lower activation energy is found to be a strong function of the activity distribution within the catalyst pellet. Nonuniform activity distributions are shown to enhance selectivity for all values of the Thiele modulus with more dramatic enhancement at intermediate values of ϕ_A. Selectivity is found to increase with increasing nonuniformity in activity distribution.

The oxidation of ethylene was simulated on nonuniformly activated catalysts under conditions closely resembling those of industrial practice. It is shown that significant benefits in selectivity towards ethylene oxide formation can be realized if such catalysts are employed.

For high values of the heat of reaction parameter, multiple steady states in effectiveness and selectivity are observed. These are associated with particle stability and parametric sensitivity.

The results of the present investigation can be utilized to design more effective and more selective catalysts for exothermic parallel reactions if the desired reaction is of lower activation energy requirements than the undesired one. Hydrocarbon oxidation is a representative class of reactions which fits this scheme.

INTRODUCTION

The effects of heat and mass intrapellet diffusional resistances on the activity and selectivity of porous heterogeneous catalysts has been extensively studied (Satterfield, 1970; Aris, 1975). In most investigations it has been assumed that the catalytically active ingredient is uniformly distributed throughout the porous structure of the support. Interest in the implications of nonuniform activity distributions within catalyst pellets has heightened in recent years. It has now been realized that increased yield and selectivity as well as decreased thermal sensitivity can be obtained in certain cases of industrial importance when nonuniformly activated catalysts are employed. Such catalysts can be intentionally produced by partial impregnation of porous supports resulting in activity distributions decreasing towards the pellet center. Oppositely shaped activity distributions are unintentionally obtained in cases where slow poisoning or deactivation is taking place by impurities in chemical feedstocks.

Minhas and Carberry (1969) have shown partially impregnated catalysts to offer significant yield advantage over uniformly activated pellets under SO_2 oxidation conditions. Increased selectivity of phthalic anhydride from naphthalene was demonstrated by Smith and Carberry (1975) when the catalytic activity is distributed in a thin shell at the outer periphery of the catalyst. Similarly, Becker and Wei (1974, 1977a,b) have shown that certain nonuniform distributions enhance the activity of automotive catalysts for carbon monoxide conversion. Similar results have been reported by other investigators (Kasaoka and Sakata, 1968; Horvath and Engrasser, 1973; Villadsen, 1976; Cervello et al., 1977) who modeled the performance of catalyst particles of various geometries and with various forms of uniform activity distributions under simple reaction schemes.

In catalytic systems where more than one reaction is taking place, nonuniform distributions of catalytic activity would be expected to influence not only the effectiveness but also the selectivity of the catalyst. Indeed, this has been demonstrated to be the case by Shadman-Yazdi and Petersen (1972) and by Corbett and Luss (1974) who modeled the performance of spherical catalyst particles under isothermal conditions for the series reactions: $A \rightarrow B \rightarrow C$. They showed that selectivity is a strong function of the distribution of activity within the catalyst particle. Similar conclusions were reached by Ernst and Dougherty (1978) who modeled the reaction of deuterium exchange with neopentane over nonuniformly activated catalyst pellets.

In the case of parallel reactions of similar kinetic rate expressions intrapellet mass diffusional resistances are not expected to influence the selectivity of the catalyst. Nevertheless, when the reactions are exothermic, considerable temperature gradients can exist within the catalyst particle. Since selectivity depends on temperature according to:

$$S = \frac{1}{1 + (\text{const.}) \exp((E_1 - E_2)/RT)} \tag{1}$$

such temperature gradients can alter significantly the local selectivity when the reaction paths are of different activation energy requirements. The constant in Eq. 1 is the ratio of the frequency factors of the undesired and the desired reactions.

The present study demonstrates the effects of nonuniform activity distributions on effectiveness and selectivity in parallel exothermic reaction networks in which the reaction paths have different activation energies. It is shown that temperature gradients within the catalyst particle have a detrimental effect on local and overall selectivity and that these gradients are a strong function of the distribution of catalytically active material within the pellet.

THEORY

Spherical catalyst particles with activity distribution of the form:

$$K(r) = K_s(r/r_s)^{\alpha}, \quad (\alpha > 0) \tag{2}$$

are examined in this study. This distribution function was first introduced by Shadman-Yazdi and Petersen (1972). The function $K(r)$ incorporates the reaction rate constant and the activity of the catalyst in terms of the amount of active ingredient which is a function of the radius of the pellet. K_s is the activity at the surface of the pellet, r_s is the pellet radius and α is an adjustable parameter which defines the shape of the activity profile. Figure 1 shows activity profiles in terms of the relative activity $(K(r)/K_s)$ as a function of the dimensionless radius (r/r_s) for various values of α.

The following parallel reaction scheme is analyzed:

$$A + B \xrightarrow{1} C + D$$

$$A + B \xrightarrow{2} E + F$$

with Reaction 1 being the desired reaction. Kinetics are assumed to be second order and to follow the Arrhenius law of temperature dependence. Furthermore, both reactions are assumed to be exothermic and of different activation energy requirements with the desired reaction exhibiting lower activation energy. This reaction scheme with the stated assumptions is a good representation of heterogeneously catalyzed hydrocarbon oxidation reactions. In such a scheme, Reaction 1 would represent the partial oxidation while Reaction 2 would represent the combustion reaction.

The reaction rates can be written as:

$$\begin{aligned} R_1 &= K_{1s}(r/r_s)^{\alpha} C_A C_B \exp(-E_1/RT) \\ R_2 &= K_{2s}(r/r_s)^{\alpha} C_A C_B \exp(-E_2/RT) \end{aligned} \tag{3}$$

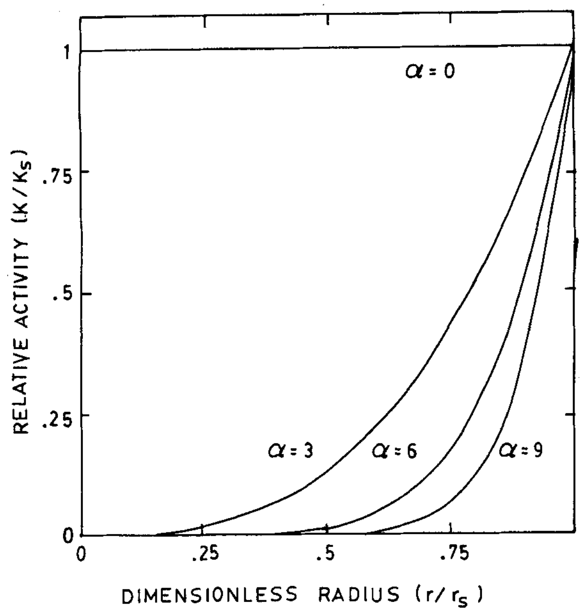

Figure 1. Activity profiles for various values of parameter α.

A steady-state differential material balance inside the catalyst pellet yields:

$$\frac{D_{Ae}}{r^2}\frac{d}{dr}\left(r^2\frac{dC_A}{dr}\right) = (r/r_s)^{\alpha} C_A C_B[K_{1s}\exp(-E_1/RT) + K_{2s}\exp(-E_2/RT)] \quad (4)$$

It is convenient to define the following dimensionless variables:

$$X = r/r_s;\quad A = C_A/C_{As};\quad B = C_B/C_{Bs}$$
$$\gamma_1 = E_1/RT_s;\quad \gamma_2 = E_2/RT_s;\quad Y = T/T_s \quad (5)$$

In terms of dimensionless variables Eq. 4 becomes:

$$\frac{d}{dX}\left(X^2\frac{dA}{dX}\right) = \phi_A^2 X^{2+\alpha} AB\{\exp[\gamma_1(1-1/Y)] + \psi\exp[\gamma_2(1-1/Y)]\} \quad (6)$$

where ψ is a dimensionless surface rate constant defined by:

$$\psi = \frac{K_{20}}{K_{10}} = \frac{K_{2s}\exp(-E_2/RT_s)}{K_{1s}\exp(-E_1/RT_s)} \quad (7)$$

and ϕ_A is a modified Thiele modulus defined

$$\phi_A = r_s\sqrt{K_{10}C_{Bs}/D_{Ae}} \quad (8)$$

A relationship between the local concentration of reactant A to the local concentration of reactant B can be obtained from stoichiometric considerations:

$$B = 1 - \sigma(1-A) \quad (9)$$

where σ is a starvation parameter defined by:

$$\sigma = D_{Ae}C_{As}/D_{Be}C_{Bs} \quad (10)$$

Thus the final form of the differential material balance is:

$$\frac{d}{dX}\left(X^2\frac{dA}{dX}\right) = \phi_A^2 X^{2+\alpha} A[1-\sigma(1-A)]\{\exp[\gamma_1(1-1/Y)] + \psi\exp[\gamma_2(1-1/Y)]\} \quad (11)$$

with boundary and symmetry conditions:

$$X = 1,\quad A = 1;\quad X = 0,\quad \frac{dA}{dX} = 0 \quad (12)$$

A relationship between the dimensionless concentration, A, and the dimensionless temperature, Y, can be obtained, following the analysis of Prater (1958), by a combined mass and energy balance in the spherical pellet:

$$dA = -dY/\beta(Y) \quad (13)$$

where $$\beta(Y) = -\Delta H(Y) C_{As} D_{Ae}/k_e T_s \quad (14)$$

The overall heat of the reaction is a function of the local selectivity of the catalyst:

$$\Delta H(Y) = \Delta H_1 S + (1-S)\Delta H_2 \quad (15)$$

The local selectivity, defined as the ratio of the rate of the desired reaction to the total rate of reaction, is given by:

$$S = \frac{1}{1+\psi\exp[(\gamma_2-\gamma_1)(1-1/Y)]} \quad (16)$$

Equation 13 then becomes:

$$dY = \frac{-\beta_s\left[\Delta H_2 - \left(\dfrac{\Delta H_2-\Delta H_1}{1+\psi\exp[(\gamma_2-\gamma_1)(1-1/Y)]}\right)\right]dA}{\left(\Delta H_2 - \dfrac{\Delta H_2-\Delta H_1}{1+\psi}\right)} \quad (17)$$

with boundary condition: @ $A = 1$, $Y = 1$. Equations 11 and 17 describe the diffusion of mass and heat in a spherical pellet under steady-state conditions and can be numerically solved to obtain the concentration and temperature profiles within the catalyst pellet. Once the concentration and temperature profiles are known, the effectiveness factor and overall selectivity can be computed from their defining relationships. The expression for the effectiveness factor reduces to:

$$\eta = \frac{3}{1+\psi}\int_0^1 ABX^{2+\alpha}\{\exp[\gamma_1(1-1/Y)] + \psi\exp[\gamma_2(1-1/Y)]\}dX \quad (18)$$

while the expression for the overall pellet selectivity reduces to:

$$\bar{S} = \frac{3}{\eta(1+\psi)}\int_0^1 ABX^{2+\alpha}\exp[\gamma_1(1-1/Y)]dX \quad (19)$$

Equation 17 was solved using a fourth-order Runge-Kutta algorithm with 500 intervals. The numerical approximation to the concentration-temperature function was curve fitted with a fourth-order polynomial which was substituted into the material balance, Eq. 11. To avoid a trial and error solution, the material balance differential equation was converted to an initial value problem by a variable transformation developed by Wei (1965). The variable transformation technique is preferable over finite difference methods in nonisothermal systems because this method establishes all solutions when multiple steady-states exist. In addition, finite difference methods do not converge on unstable solutions, and, the solution found depends on the initial assumption of the concentration profile. Effectiveness factors and overall selectivities were calculated employing Eqs. 18 and 19, respectively.

RESULTS AND DISCUSSION

Very often, in industrial applications, the rate of a heterogeneous chemical reaction is limited by the rate of diffusion of reactants into (or products out of) the porous structure of the catalyst pellets. The effectiveness factor, a measure of the utilization of catalytic activity, provides a quantitative assessment of this phenomenon. When the reactions are exothermic, in addition to concentration gradients, significant temperature gradients also exist within the catalyst pellet. The distribution of catalytic activity within the pellet affects both, the reactant concentration and temperature profiles. These, in turn, affect the effectiveness factor and the selectivity of the catalyst. Figure 2 shows dimensionless concentration and temperature profiles within a spherical catalyst particle for uniform ($\alpha = 0$) and nonuniform ($\alpha = 9$) activity distributions. Less severe temperature and concentration gradients are obtained when nonuniform activity distributions are employed. This is particularly

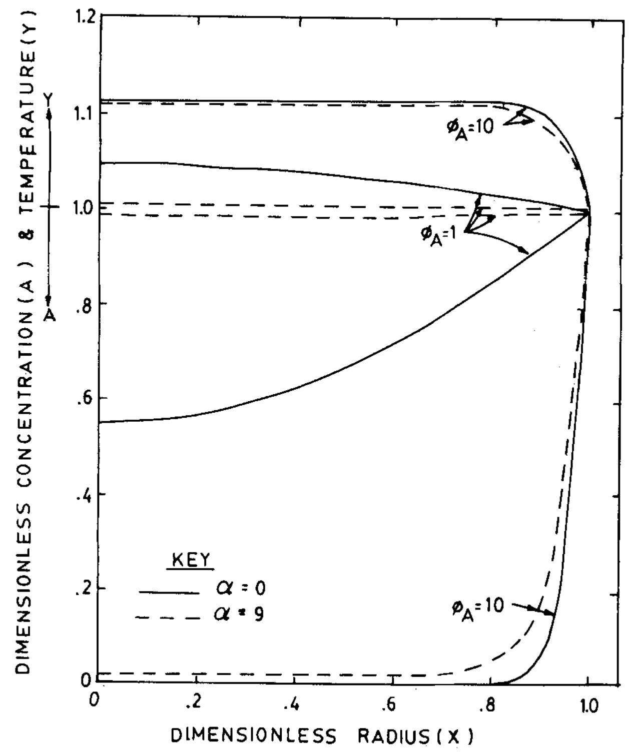

Figure 2. Dimensionless concentration and temperature profiles within spherical catalyst particles.

true at lower values of the Thiele modulus. When the active sites are concentrated near the periphery of the pellet the average diffusional path for the transport of reactants and heat is significantly reduced, resulting in milder concentration and temperature gradients.

A normalized effectiveness factor, η', defined as the usual effectiveness factor divided by the volume-average weight of active ingredient, so as to place all activity distributions on the same basis of total catalytic activity, is shown in Figure 3 as a function of the Thiele modulus after various values of α. The curves are based on values of γ_1, γ_2 and β_s of 20, 30 and 0.10, respectively. The maxima in the normalized effectiveness factors are due to the enhancement of reaction rates by intraparticle temperature gradients. Nonuniform activity distributions are shown to broaden the zone of enhanced effectiveness and shift the maxima in η' to a higher value of the Thiele modulus. A slight increase in maximum η' with increasing α is also observed.

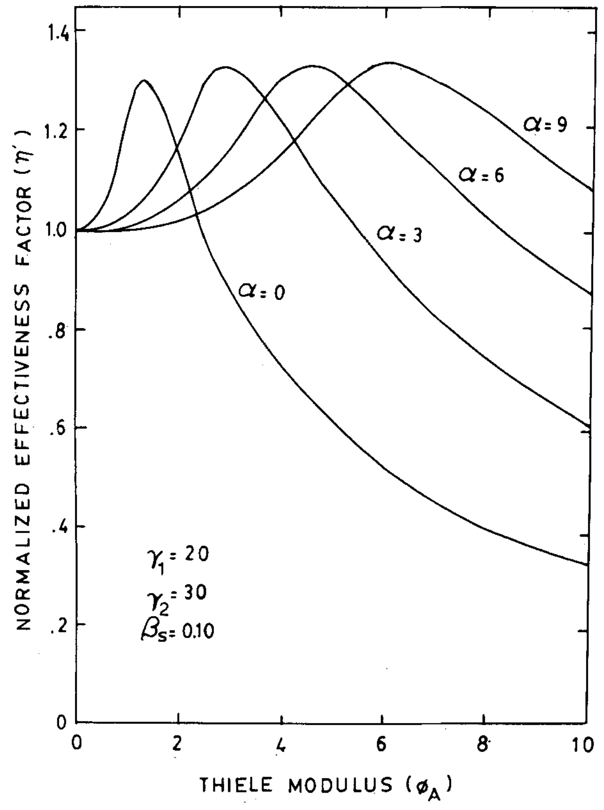

Figure 3. Effects of nonuniform activity distributions on effectiveness factor: β_s = 0.10.

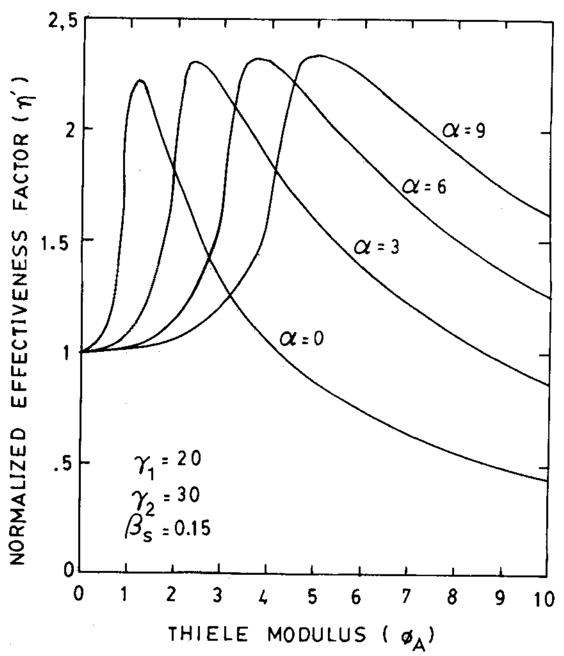

Figure 4. Effects of nonuniform activity distributions on effectiveness factor: β_s = 0.15.

Qualitatively similar results are observed when the value of β_s is increased to 0.15 and 0.20 as shown in Figures 4 and 5 respectively. The maxima in the normalized effectiveness factor increase with increasing values of β_s because of the more dramatic intraparticle temperature gradients associated with higher values of β_s.

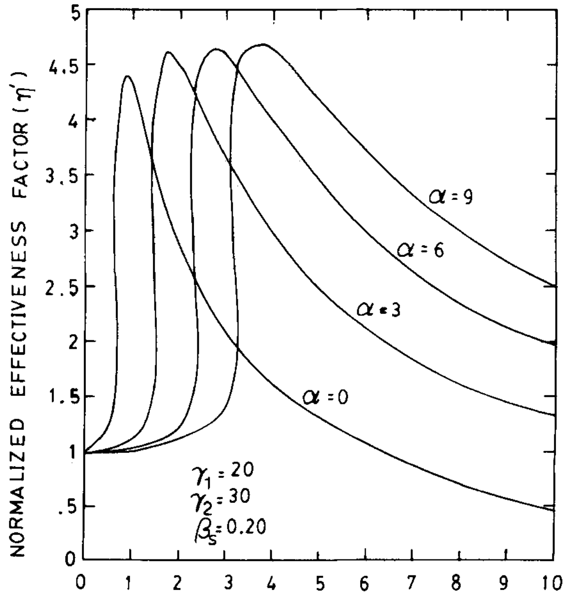

Figure 5. Effects of nonuniform activity distributions on effectiveness factor: β_s = 0.20.

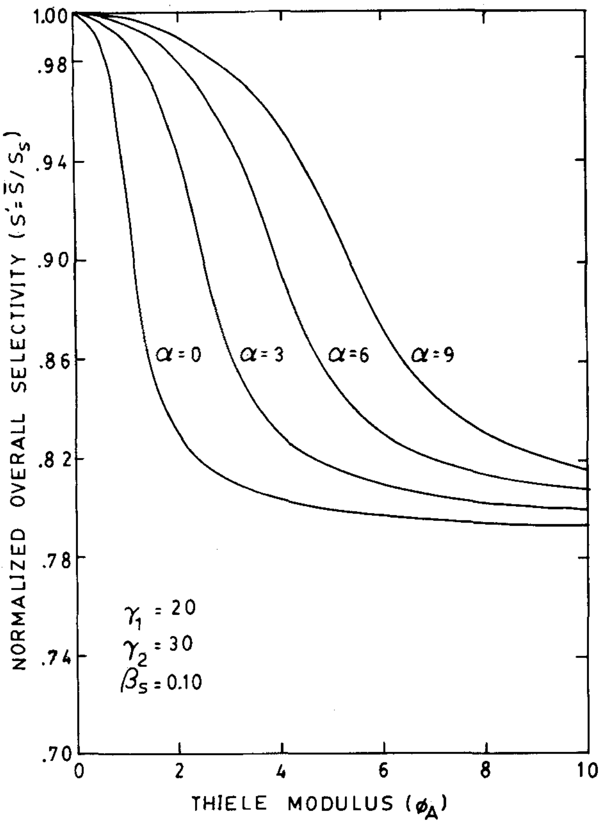

Figure 6. Selectivity enhancement of nonuniform activity distributions: $\gamma_1 = 20$, $\gamma_2 = 30$, $\beta_s = 0.10$.

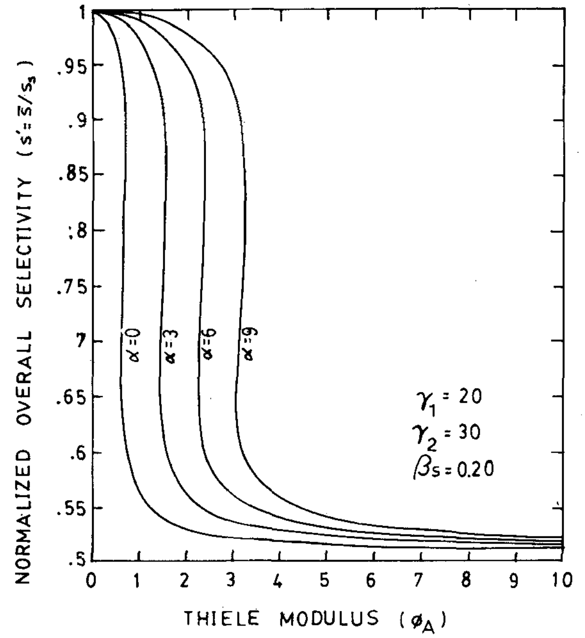

Figure 7. Selectivity enhancement of nonuniform activity distributions: $\gamma_1 = 20$, $\gamma_2 = 30$, $\beta_s = 0.20$.

A closer inspection of Figure 5 reveals that for a narrow range of the Thiele modulus three possible values of the effectiveness factor can be obtained. The instability associated with this phenomenon is due to the fact that the heat generation term in the energy balance equation is a highly nonlinear function of T_s leading to multiple solutions (Froment and Bischoff, 1979). It would be reasonable to assume that only the two extreme values of η' are realizable in practice while the middle value represents an unstable

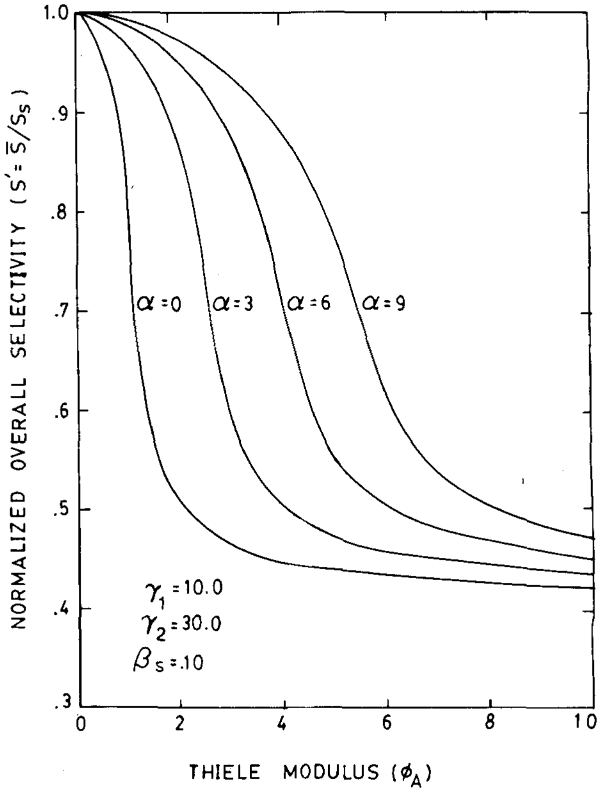

Figure 8. Selectivity enhancement of nonuniform activity distributions: $\gamma_1 = 10$, $\gamma_2 = 30$, $\beta_s = 0.10$.

state. The value of η' which will be obtained in a particular situation would depend on the direction of approach and, thus, on the initial temperature profile of the catalyst pellet. If the uniqueness criterion of Luss (1968).

$$\beta\gamma < 4(1 + \beta) \qquad (20)$$

is applied in this situation, stability is predicted when the desired reaction is considered alone ($4 < 4.8$) but instability is predicted when the undesired reaction is considered ($6 > 4.8$). Finally it should be noted that the range of values of the Thiele modulus for which multiple steady-states exist is a strong function of the activity distribution inside the catalyst particle. Steeper activity profiles (higher α) exhibit multiple steady-states at higher values of the Thiele modulus.

The overall pellet selectivities are normalized by dividing the volume-averaged selectivity of the catalyst particle by the local selectivity at the particle surface. Normalized overall selectivities are shown as functions of the Thiele modulus in Figures 6 and 7 for various values of the activity distribution parameter α. Selectivity is shown to decrease monotonically with increasing values of ϕ_A for all activity distributions. This phenomenon is due to the fact that temperature gradients, which are detrimental to selectivity, increase with increasing ϕ_A. Nonuniform activity distributions are shown to offer higher selectivities for all values of the Thiele modulus. Selectivity enhancement increases with increasing values of the parameter α or with the steepness of the activity profile, as a result of decreased temperature gradients inside the catalyst particle. For the same reasons, a reduction in selectivity is observed with increasing values of β_s as a comparison of Figures 6 and 7 reveals. The concept of stability, associated with the existence of multiple steady-states also appears in Figure 7. It is observed that, for narrow ranges of the Thiele modulus, three steady-state selectivities can be obtained. Multiple values of the effectiveness factor for a given value of ϕ_A have been observed by many investigators. The existence of multiple solutions to the differential equations which describe mass and heat transfer within catalyst pellets depends on the parameters β and γ which control

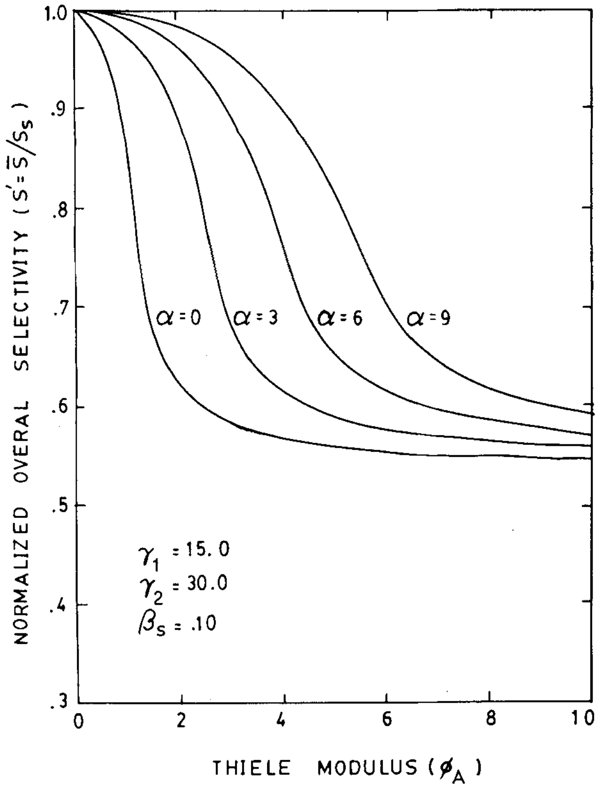

Figure 9. Selectivity enhancement of nonuniform activity distributions: γ_1 - 15, γ_2 = 10, β_s = 0.10.

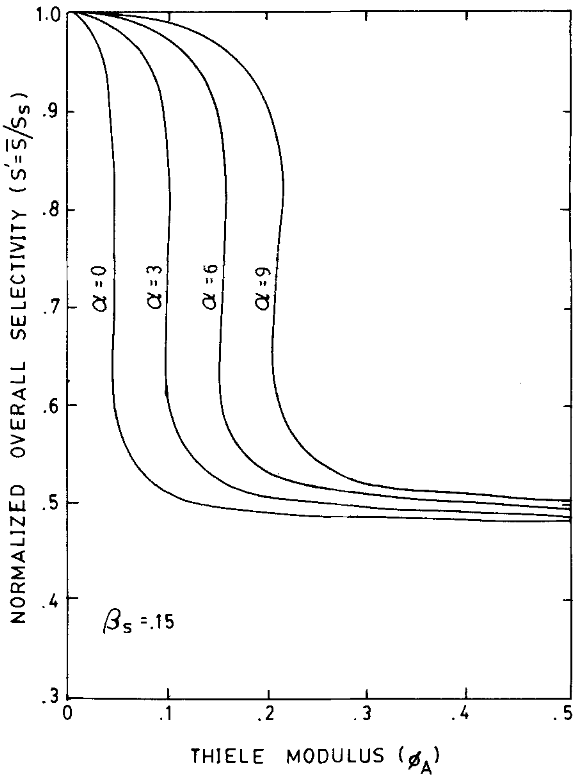

Figure 10. Selectivity enhancement of nonuniform activity distributions under ethylene oxidation conditions.

the nonlinearity of the reaction rate term. Although, to the best of our knowledge, this is the first time that multiple steady-states in selectivity have been observed, this phenomenon is not surprising. Different temperature profiles within the catalyst particle would be expected to result in different selectivities due to the difference in activation energy of the two reactions. Thus, in certain cases, widely different selectivities can be obtained depending upon the initial temperature profile in the catalyst particle, under otherwise identical conditions. This phenomenon occurs at a narrow range of the Thiele modulus and this range is a function of the activity distribution within the catalyst particle. Although not shown, it was also found that, as expected, increasing the values of the parameters β or γ results in much more profound multiplicities in effectiveness factor and selectivity, occuring over a wider range of values of ϕ_A.

A comparison of Figures 6, 8 and 9 reveals the effects of the relative magnitudes of the activation energies of the desired and undesired reactions on the normalized overall pellet selectivities. The curves in these Figures were computed with the same value of β_s. Since γ_1 is assumed to be less than γ_2, selectivity enhancement is observed with increasing values of α in all cases. Furthermore, overall selectivities increase with increasing value of the activation energy of the desired reaction or with decreasing difference in activation energies, $\gamma_2 - \gamma_1$.

Selectivities approach a common asymptotic value at high and at low magnitudes of ϕ_A for all values of α. This phenomenon is due to the fact that, when the Thiele modulus is large, the high reaction rates relative to diffusional rates result in substantially all reaction occurring near the periphery of the catalyst particle. Since the surface activities in all activity distributions are assumed equal, the normalized selectivities would also be equal for all values of α. The asymptotic limit in selectivity varies with the values of γ_1 and γ_2, decreasing as the difference between γ_1 and γ_2 increases due to the greater enhancement of the undesired reaction relative to the desired one for larger differences in activation energies. It should be emphasized that the stated limits of the Thiele modulus at which identical selectivities are obtained for all values of α ($\phi_A \rightarrow 0$ and $\phi_A \rightarrow \infty$) are both unrealistic. To achieve a Thiele modulus close to zero the catalyst particle must be very small, resulting in prohibitively high pressure drops across a fixed bed reactor. On the other hand, when large catalyst particles are employed exhibiting high values of the Thiele modulus, only a small fraction of catalytic activity will be utilized, resulting in excessive capital costs.

The analysis which was presented earlier was applied to a parallel reaction system of high industrial importance, the epoxidation of ethylene over supported silver catalysts which proceeds in parallel with the combustion reaction. Both reaction paths are highly exothermic while the activation energy of the epoxidation reaction is lower than that of the combustion reaction. For a typical reaction temperature of 220°C γ_1 and γ_2 were computed to be 21.7 and 29.7. Typical values of the parameter β_s range between 0.10 and 0.15. The reaction kinetics which were employed in the analysis were those obtained by Klugherz and Harriott (1971) which are of the Langmuir-Hinshelwood type. The effects of nonuniform distribution of catalytic activity on the normalized pellet selectivity are shown on Figure 10 as a function of the Thiele modulus for the extreme value of β_s of 0.15. Nonuniform activity profiles result in higher selectivities for all values of ϕ_A. A typical value of the Thiele modulus under industrial operating conditions is reported by Hlavacek et al. (1969) to be 0.08. Figure 10 then shows that a considerable enhancement in selectivity can be achieved when nonuniformly activated catalyst pellets are employed in industrial reactors. The question of stability associated with the existence of multiple steady-states is also revealed in Figure 10. For very narrow ranges of the Thiele modulus three steady-state selectivities can be achieved. This phenomenon was discussed earlier.

NOTATION

A,B = dimensionless concentrations of reactants A and B
C_A,C_B = concentrations of reactants A and B
D_e = effective diffusivity within catalyst pellet
E = activation energy

K = activity distribution function defined by Eq. 2
k_e = effective thermal conductivity of catalyst pellet
r = radius of catalyst pellet
R = rate of reaction
S = selectivity towards the desired reaction
T = temperature
X = dimensionless pellet radius
Y = dimensionless temperature

Greek Letters

α = parameter defining activity profile according to Eq. 2
β = heat of reaction parameter defined by Eq. 14
γ = dimensionless activation energy
ΔH = standard enthalpy change of reaction
η = effectiveness factor
σ = starvation parameter defined by Eq. 10
ϕ_A = modified Thiele modulus defined by Eq. 8
ψ = dimensionless surface rate constant defined by Eq. 7

Subscripts

1,2 = designate desired and undesired reactions
s = designates surface conditions

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Kinetics of Pyrolysis of Some Fire Retardants and Treated Fabrics

Intermediate phases and reactions occurring on decomposing diammonium hydrogen phosphate, ammonium para molybdate, sodium tungstate dihydrate and ammonium meta vanadate were established by thermal analysis and X-ray examination.

These salts promote fabric degradation at low temperatures but are effective at high temperatures. Diammonium hydrogen phosphate produced maximum amount of gases, absorbed the highest amount of heat and gave the highest fire retardation above 350°C.

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SCOPE

Some soluble salts can be easily applied for the protection of fabrics against incendiary agents and can be easily removed by washing. Conflicting data exist in the literature regarding their decomposition and the mechanism of fire retardation. The objective of this paper is to understand the reactions taking place on heating these salts and the behavior of treated cotton fabrics.

Combined thermal analysis in which DTA, TG and DTG can

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