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Selectivity Enhancement in Ethylene Oxidation Employing Partially Impregnated Catalysts

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The effects of radially nonuniform distributions of catalytic activity on the performance of spherical catalyst pellets under ethylene oxidation conditions are investigated. It is shown that partially impregnated catalysts exhibit higher effectiveness factors than uniformly activated ones, in a large range of values of the Thiele modulus. The opposite is observed for Thiele modulus values close to zero. Significantly enhanced selectivity to ethylene oxide formation is also shown to result from nonuniform activity distributions for all values of the Thiele modulus. Multiple steady states in effectiveness and selectivity are observed under sufficiently high values of the heat-of-reaction parameter. This phenomenon occurs in a narrow range of Thiele modulus values which is a strong function of the activity distribution within the catalyst pellet.

NOTATION

$A = C_A/C_{As}$	dimensionless concentration of ethylene
$B = C_B/C_{Bs}$	dimensionless concentration of oxygen
C_A, C_B	concentration of ethylene and oxygen, respectively
D_e	effective mass diffusivity within catalyst pellet
E	activation energy
F	denominator in rate expression, defined by Eqs. (4) and (5)
K	activity distribution function defined by Eq. (1)
k_e	effective thermal conductivity of catalyst pellet
r	radius of catalyst pellet
R	rate of reaction
S	selectivity toward ethylene oxide formation
T	temperature
$X = r/r_s$	dimensionless pellet radius
$Y = T/T_s$	dimensionless temperature

Greek Letters

α	parameter defining activity profile according to Eq. (1)
β	heat-of-reaction parameter defined by Eq. (15)
$\gamma = E/RT_s$	dimensionless activation energy
ΔH	standard enthalpy change of reaction
η	effectiveness factor
θ	constant defined by Eq. (20)
σ	constant defined by Eq. (13)
ϕ_A	modified Thiele modulus defined by Eq. (10)
ψ	dimensionless surface rate constant

Subscripts

1, 2	refer to epoxidation and combustion reactions, respectively
s	refers to surface conditions

INTRODUCTION

Numerous quantitative assessments of the influence of mass and heat intrapellet diffusion upon catalytic activity and selec-

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tivity have been reported (*1–3*). The implications of nonuniform distributions of active sites within the porous structure of the support have also received considerable attention (*4–9*) after it was realized that increased yield and selectivity, as well as decreased thermal sensitivity, result in certain cases of industrial importance. Partially impregnated catalysts have been shown to offer significant yield advantage over uniformly activated pellets under SO_2 oxidation (*4*), increased selectivity to phthalic anhydride from naphthalene (*5*), and increased activity for carbon monoxide oxidation (*6–8*).

Catalysts with nonuniform activity distributions can arise either intentionally or unintentionally. Partial impregnation of a porous support with a salt solution of active metal will result in activity profiles decreasing toward the pellet center. On the other hand, catalysts partially poisoned from impurities in chemical feedstocks will exhibit oppositely shaped activity distributions.

The distribution of activity within catalyst pellets influences concentration and temperature gradients which result from mass and heat diffusional resistances. In parallel reaction networks of similar kinetic rate expressions, intraparticle concentration gradients are not expected to influence the selectivity of the catalyst. However, intraparticle temperature gradients, which develop under sufficiently exothermic reactions, can alter significantly the local selectivity if the reaction paths are of different activation energy requirements.

In the present study, the epoxidation of ethylene, which proceeds in parallel with the combustion reaction over supported silver catalysts, is simulated on nonuniformly activated catalysts under conditions closely resembling those of industrial practice. Both reactions are highly exothermic, while the activation energy of the desired reaction (epoxidation) is lower than the activation energy of the undesired reaction. The effects of nonuniform distributions of catalytic activity on effectiveness and selectivity are investigated. It is shown that temperature gradients within the catalyst particle have a detrimental effect on local and overall selectivity and that these gradients are strongly influenced by the distribution of the catalytically active ingredient within the pellet.

THEORY

The performance of spherical catalyst pellets with activity distributions of the form

$$K(r) = K_s(r/r_s)^{\alpha}, \qquad \alpha > 0, \tag{1}$$

under ethylene oxidation conditions is investigated. The distribution function defined by Eq. (1) was first introduced by Shadman-Yazdi and Petersen (*9*). It incorporates the reaction rate constant with the activity of the catalyst in terms of the amount of active ingredient which is assumed to be a function of the radius of the pellet. The parameter α defines the steepness of the activity profile.

The reaction scheme considered is the epoxidation of ethylene to form ethylene oxide which occurs in parallel with the combustion to carbon dioxide and water over supported silver catalysts. Both reactions are assumed to be irreversible and the further oxidation of ethylene oxide is not accounted for in the model (*10*). Reaction rate expressions were obtained from the work of Klugherz and Harriott (*10*) who developed Langmuir–Hinshelwood-type rate expressions at 220°C and atmospheric pressure. If the activity distribution function is incorporated into these rate expressions they can be written in terms of dimensionless variables as:

$$R_1 = \frac{C_{As}C_{Bs}^2AB^2K_{10}\exp(\gamma_1(1 - 1/Y))}{F_1^2}, \tag{2}$$

$$R_2 = \frac{C_{As}C_{Bs}^2AB^2K_{20}\exp(\gamma_2(1 - 1/Y))}{F_2^2}, \tag{3}$$

where

$$F_1 = (0.0106 + 2144\,C_{As}A + 805\,C_{Bs}B)(1 + 1271\sqrt{C_{Bs}B}), \tag{4}$$

$$F_2 = (0.008 + 4166 C_{As}A + 1578 C_{Bs}B)(1 + 718\sqrt{C_{Bs}B}). \quad (5)$$

K_{10} and K_{20} are reaction rate constants for the epoxidation and combustion reactions, respectively, evaluated under surface conditions:

$$K_{10} = k_{1s}\exp(-E_1/RT_s),, \quad (6)$$

$$K_{20} = k_{2s}\exp(-E_2/RT_s). \quad (7)$$

A steady-state differential material balance on ethylene inside the spherical catalyst pellet yields

$$\frac{d}{dX}\left(X^2\frac{dA}{dX}\right) = \phi_A{}^2X^{2+\alpha}AB^2 \left\{\frac{\exp(\gamma_1(1 - 1/Y))}{F_1{}^2} + \psi\,\frac{\exp(\gamma_2(1 - 1/Y))}{F_2{}^2}\right\} \quad (8)$$

with boundary and symmetry conditions

$$\text{at } X = 1,\ A = 1,$$

$$\text{at } X = 0,\ \frac{dA}{dX} = 0. \quad (9)$$

ϕ_A is a modified Thiele modulus defined by

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

and

$$\psi = K_{20}/K_{10}. \quad (11)$$

An expression relating the local concentration of oxygen to that of ethylene can be developed from steady-state material balances on ethylene and oxygen and from stoichiometric considerations:

$$dB = \sigma(3 - 2.5S)\,dA, \quad (12)$$

where σ is a starvation parameter defined by

$$\sigma = D_{Ae}C_{As}/D_{Be}C_{Bs}. \quad (13)$$

A relationship between the dimensionless concentration of ethylene and the dimensionless temperature inside the catalyst pellet can be obtained following the analysis of Prater (*11*) by a combined mass and energy balance:

$$dA = -\,dY/\beta(Y), \quad (14)$$

where

$$\beta(Y) = -\Delta H(Y)C_{As}D_{Ae}/k_eT_s. \quad (15)$$

The overall heat of reaction is a function of the local selectivity; thus

$$\Delta H(Y) = \Delta H_1\cdot S + \Delta H_2(1 - S). \quad (16)$$

Then Eq. (14) becomes

$$dY = \frac{-\beta_s(S(\Delta H_1 - \Delta H_2) + \Delta H_2)}{S_s(\Delta H_1 - \Delta H_2) + \Delta H_2}\,dA \quad (17)$$

with boundary condition: at $A = 1$, $Y = 1$.

The local selectivity, defined as the rate of ethylene oxide produced divided by the rate of ethylene consumed at any point along the radius of the pellet, can be obtained as a function of temperature and concentrations by

$$S = \frac{1}{1 + \dfrac{(F_1/F_2)^2\,\psi}{\exp[(\gamma_2 - \gamma_1)(1 - 1/Y)]}}. \quad (18)$$

Equations (8), (12), and (17) describe the diffusion of mass and heat in a spherical pellet under steady-state conditions. They can be numerically solved to obtain the concentration and temperature profiles within the catalyst pellet. Furthermore, the selectivity, at any point along the radius, can be determined by Eq. (18). Once the concentration and temperature profiles are known, the pellet effectiveness factor and overall selectivity can be computed by their defining relationships. The expression for the effectiveness factor reduces to

$$\eta = \frac{3}{\theta}\int_0^1 AB^2X^{2+\alpha}\left\{\frac{\exp(\gamma_2(1 - 1/Y))}{F_1{}^2} + \psi\,\frac{\exp(\gamma_1(1 - 1/Y))}{F_2{}^2}\right\}dX, \quad (19)$$

while the expression for the overall selectivity reduces to

$$\bar{S} = \frac{3}{\eta\theta} \int_0^1 AB^2X^{2+\alpha} \frac{\exp(\gamma_1(1 - 1/Y))}{F_1^2}\, dX, \quad (20)$$

where

$$\theta = ((0.0106 + 2144\, C_{\mathrm{As}} + 805\, C_{\mathrm{Bs}})(1 + 1271\sqrt{C_{\mathrm{Bs}}}))^2 + ((0.008 + 4166\, C_{\mathrm{As}} + 1578\, C_{\mathrm{Bs}})(1 + 718\sqrt{C_{\mathrm{Bs}}}))^2. \quad (21)$$

Equations (12) and (17) were numerically integrated using a fourth-order Runge–Kutta algorithm with 500 intervals. The resulting temperature and oxygen concentration profiles were substituted into the material balance equations. To avoid a trial-and-error solution of Eq. (8), the equation was converted to an initial value problem by a variable transformation technique developed by Wei (*16*). Effectiveness factors and overall selectivities were then computed employing Eqs. (19) and (20), respectively.

In order to compare the performance of catalyst particles with different activity distributions, it is useful to define a normalized effectiveness factor, η', which places each activity profile on the same basis of total amount of active material. Since each of the distributions studied is assumed to have the same surface activity but differing amounts of total catalytic activity, η' is obtained by multiplying the usual effectiveness factor by the ratio of the volume-averaged activity of a uniformly activated pellet to that of the nonuniformly activated one. Thus,

$$\eta' = \frac{(\frac{4}{3})\pi r_s^3 \eta}{\iiint_V (r/r_s)^\alpha\, dV}. \quad (22)$$

Such a normalization places all activity distributions on the same basis of total amount of active metal.

Similarly the overall pellet selectivities are normalized by dividing the volume-averaged selectivity with the selectivity at the surface of the catalyst pellet. The surface selectivity is the same for all catalyst particles since they are all exposed to the same conditions of temperature and concentrations.

RESULTS AND DISCUSSION

The global activity of porous heterogeneous catalysts under industrial applications is frequently altered by diffusional resistances of mass and heat within the catalyst pellet. The effectiveness factor, a measure of the utilization of catalytic activity, provides a quantitative assessment of this phenomenon. The distribution of active catalytic sites within the pellet affects both the concentration and temperature profiles, which, in turn affect the effectiveness factor and frequently the selectivity of the catalyst.

The effects of nonuniform distributions of catalytic sites on the activity and selectivity of the catalyst pellet under ethylene oxidation conditions are shown as plots of a normalized effectiveness factor and normalized selectivity versus a Thiele-type modulus. In these computations the surface temperature of the catalyst was assumed to be 220°C, the temperature at which the kinetic rate expressions were derived (*10*). The dimensionless activation energies, γ_1 and γ_2, were computed from reported values of the activation energies of the epoxidation and combustion reactions of 21.4 and 29.0 kcal/mole, respectively (*12*). Thus γ_1 assumes the value of 21.9 and γ_2 of 29.7. Surface concentrations of ethylene and oxygen were computed for a typical feed stream consisting of 4–6 mole% ethylene, 12–18 mole% oxygen, the balance being nitrogen, assuming negligible external diffusional resistances. Temperature and concentration gradients external to the catalyst pellet were not accounted for so as to reduce the complexity of the model. Such gradients are best accounted for in an inte-

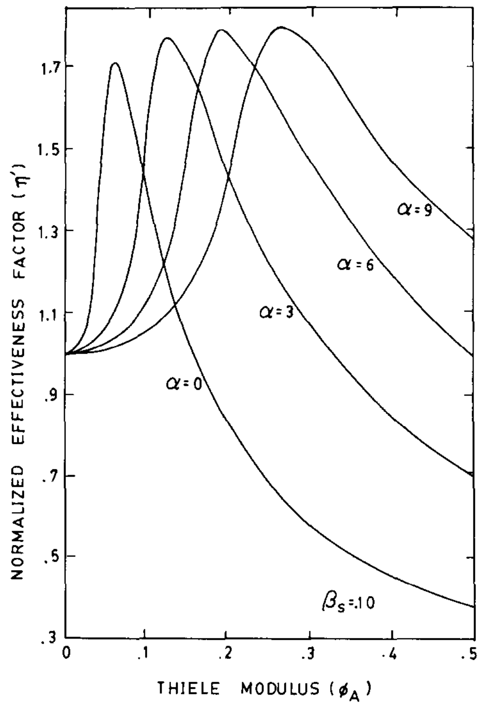

FIG. 1. Effects of nonuniform activity distributions on effectiveness factor. $\beta_s = 0.10$.

gral reactor model. Since dimensionless temperature and concentration parameters were employed in the present work, this omission does not, in any way, reduce the accuracy of the results. Effective diffusivities of ethylene and oxygen inside the catalyst particle were estimated from bulk diffusivities assuming porosity and tortuosity of typical low-surface-area α-aluminas which are common supports for ethylene oxidation silver catalysts. Under these conditions the starvation parameter, σ, is computed to be 0.263.

The normalized effectiveness factor is shown in Figs. 1 and 2 as a function of the Thiele modulus for uniform and nonuniform activity distributions. Catalysts with nonuniform activity profiles exhibit higher effectiveness factors at high values of the Thiele modulus due to the reduced mass diffusional resistance afforded by the nonuniform distributions. Uniform activity distributions, however, result in higher effectiveness factors at low values of ϕ_A. The reaction rates in this case are enhanced due to large temperature gradients developing within the particles.

The parameter varied between Figs. 1 and 2 is β_s which gives a measure of the resistance to heat transfer relative to that of mass transfer. As β_s increases, η' increases because of the larger temperature gradients associated with high resistance to heat transfer. Larger temperature gradients, in turn, result in greater enhancement of reaction rates.

Figure 2 reveals that for a value of β_s of 0.15, up to three steady-state solutions are possible for a narrow range of values of the Thiele modulus. Multiple steady-state solutions have been observed by many investigators for both uniformly (*3*, *13*, *14*) and nonuniformly (*6*, *8*, *15*) activated catalysts when internal heat transfer effects are severe. According to Wei (*16*), when three steady-state solutions exist, at least one will be unstable. The particular solution converged upon in a fixed-bed reactor depends on the initial conditions of temperature and reactant concentration.

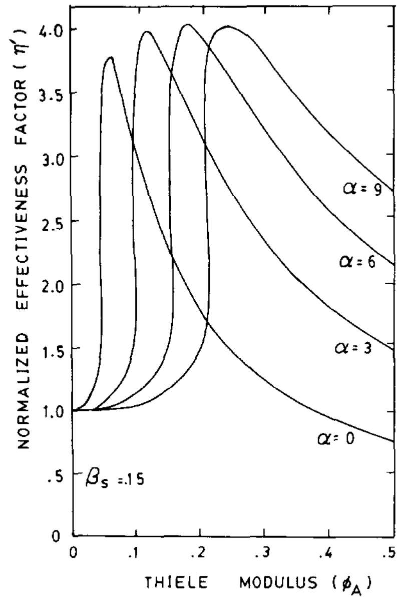

FIG. 2. Effects of nonuniform activity distributions on effectiveness factor. $\beta_s = 0.15$.

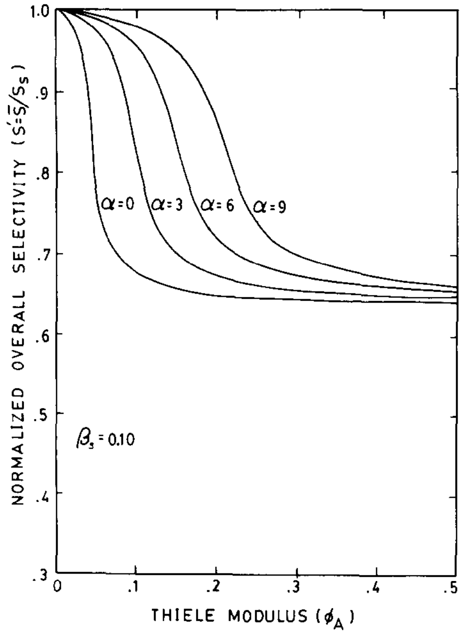

FIG. 3. Selectivity enhancement of nonuniform activity distributions. $\beta_s = 0.10$.

The overall pellet selectivities are normalized by dividing the volume-averaged selectivity with the selectivity at the surface of the catalyst particle. The effects of nonuniform activity distributions on selectivity to ethylene oxide formation are shown in Figs. 3 and 4. Nonuniformly activated catalysts exhibit higher selectivities than uniformly activated pellets for all values of the Thiele modulus. Furthermore, high selectivities are obtained for a considerably larger range of ϕ_A when nonuniformly activated catalysts are employed. A comparison of Figs. 3 and 4 reveals that selectivity decreases with increasing value of β_s. This phenomenon is caused by the larger temperature gradients associated with higher values of β_s, coupled with the greater thermal sensitivity of the combustion reaction as compared to the epoxidation reaction.

Figure 4 also reveals that multiple steady states in selectivity can be obtained at sufficiently high values of β_s, for a narrow range of values of ϕ_A. The range of values of the Thiele modulus at which multiple selectivities occur is dependent on the shape of the activity distribution. The existence of more than one selectivity under a particular set of operating conditions results from the existence of more than one possible temperature profile inside the catalyst pellet. Which of these temperature profiles will be achieved in actual operation depends on the initial temperature profile in the particle.

Figure 5 summarizes the selectivity advantages offered by nonuniform activity distributions for this exothermic parallel reaction system. Up to a 45% increase in selectivity to ethylene oxide over that exhibited by a uniformly activated particle can be obtained with $\alpha = 9$. The magnitude of the selectivity enhancement depends on the intrinsic selectivity of the catalyst under surface conditions, which, in this work is approximately 50%. The relative advantage of concentrating catalytic activity near the periphery of the catalyst pellet reaches a maximum at some intermediate value of the Thiele modulus, approximately 0.10.

The normalized overall reaction rate to ethylene oxide, which is the product of the

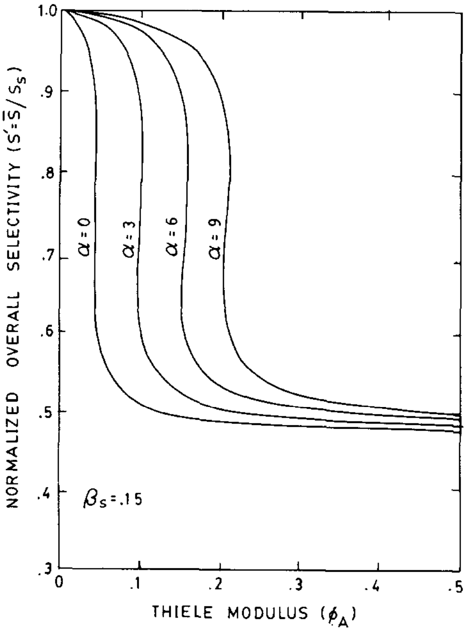

FIG. 4. Selectivity enhancement of nonuniform activity distributions. $\beta_s = 0.15$.

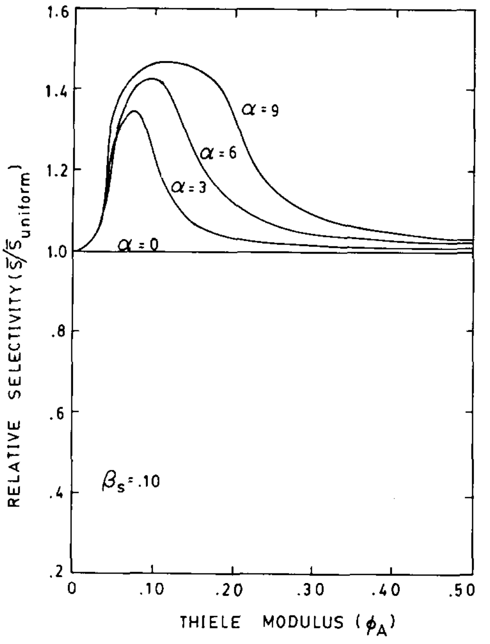

FIG. 5. Effects of nonuniform activity distributions on relative selectivity.

normalized effectiveness factor and selectivity, is shown in Fig. 6 for uniformly and nonuniformly activated catalyst particles. Uniformly impregnated supports are shown to be superior, in this respect, in a range of small values of the Thiele modulus ($\phi_A < 0.08$). The opposite is true at higher values of the Thiele modulus. Although selectivity is higher in nonuniformly activated pellets, the effectiveness factor is lower in the lower range of values of ϕ_A resulting in lower reaction rates.

Hlavacek *et al.* (*17*) report that a typical value of the Thiele modulus for the industrial epoxidation of ethylene is 0.08. A typical value for the heat-of-reaction parameter, β_S, is computed to be 0.10. Under these conditions, the use of a catalyst with nonuniform activity distribution of the form defined by Eq. (1) with $\alpha = 3$, results in a 34% increase in selectivity over that of a uniformly activated catalyst. The normalized effectiveness factor for $\alpha = 3$ is about 22% less than that for $\alpha = 0$, with the overall rate of ethylene oxide formation per unit weight of active metal remaining about the same. Considering the large benefits in selectivity, the use of nonuniform activity distributions of the type discussed in this study would certainly have a very favorable impact on the economics of the operation.

Although the results presented in this paper are quantitatively based on the ethylene oxidation system, qualitatively similar results are expected from any exothermic parallel reaction network in which the desired reaction is of lower activaion energy requirements than the undesired reaction. The mathematical model presented here can be applied to any such system if appropriate changes in the reaction rate expressions are made, irregardless of whether the rate expressions are of the power law or of the Langmuir–Hinshelwood type. Furthermore, numerical values of the transport parameters must be estimated for each system.

SUMMARY AND CONCLUSIONS

The performance of spherical catalyst particles with nonuniform activity distributions of the form defined by Eq. (1) was

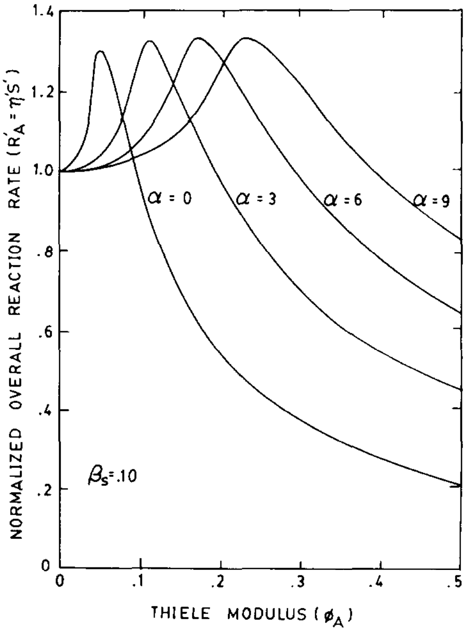

FIG. 6. Effects of nonuniform activity distributions on reaction rate to ethylene oxide formation.

analyzed under ethylene oxidation conditions. Kinetic and physical parameters were estimated under conditions of industrial practice. Partially impregnated catalysts were shown to offer significant selectivity enhancement to ethylene oxide formation for all values of the Thiele modulus. The selectivity advantage was found to be more pronounced at intermediate values of ϕ_A of approximately 0.10.

Rates of ethylene oxide formation were also found to be a function of the distribution of active ingredient within the support. The rates were shown to increase with increasing α for large values of ϕ_A. For a narrow range of values of ϕ_A close to zero, however, the opposite was found to be true.

Multiple steady states in effectiveness and selectivity were shown to exist in the ethylene oxidation scheme at sufficiently large values of the heat-of-reaction parameter, β_s. The phenomenon occurs in a very narrow range of values of ϕ_A while this range depends on the distribution of catalytic activity within the pellet. The more nonuniform the distribution (higher α), the higher the range of values of ϕ_A at which multiple steady states occur.

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