
**ACTIVITY AND SELECTIVITY OF NON-UNIFORM
BIFUNCTIONAL CATALYSTS.
ANALYSIS OF THE FIXED-BED REACTOR PERFORMANCE**

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This paper reports a study about the effect of activity distributions of a bifunctional catalyst on the conversion and product distribution in a fixed-bed reactor. Uniform as well as increasing and decreasing activity profiles of both catalytic functions are considered. The analysis is performed assuming three different reaction schemes. Results show that reactor performance is greatly affected by the use of catalysts with non-uniform activity distributions.

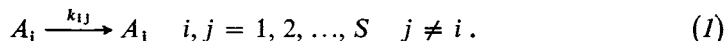
First studies about reaction-diffusion problems in bifunctional catalysts were carried out by Gunn and Thomas¹. They considered three different reaction networks and determined the optimum catalyst composition in order to obtain the maximum exit concentration of the desired product. Gunn² investigated the existence of an optimum profile of catalyst composition along the reactor for the same kind of reactions. However, only the relative amounts of active components were taken as variables for the analysis of reactor performance. The use of non-uniform distributions of catalytic sites in the particle as a tool to modify the activity and selectivity of bifunctional catalysts was introduced by Rutkin and Petersen³, who considered that the two kinds of catalytic sites are separated along the support pores and distributed according to a step function. In this way, the effect of the fraction of metal catalyst as well as the position of each function (metal-pore mouth or acid-pore mouth) on the conversion and product distribution was analyzed.

In a previous paper⁴, we have discussed some features of the diffusion-reaction problem in non-uniform bifunctional catalysts for a reaction scheme similar to that of pure hydrocarbons reforming. It was shown that activity and selectivity of individual catalyst particles can be greatly improved through the use of non-uniform activity profiles.

The purpose of this work is to extend the above analysis to the case of a whole fixed-bed reactor. In order to study the influence of activity distributions of both catalytic functions on the conversion and product distribution, three reaction schemes, which represent the isomerization of paraffins or aromatization of naphthenes were considered.

PROBLEM FORMULATION

A complex reaction scheme, involving S species, can be represented as a set of R single reactions:



Assuming first-order kinetics, reaction rates on a bifunctional catalyst can be expressed as:

$$R_{ij}(c_i) = \{[k_{ij}\varphi(\varrho)]_I + [k_{ij}\varphi(\varrho)]_{II}\} c_i, \quad (2)$$

where I and II denote the types of catalytic sites.

The formulation of the diffusion-reaction problem for the catalyst particle will assume: a) cylindrical geometry; b) isothermicity; c) negligible resistance to external mass transfer. Continuity equation for the species A_i is therefore:

$$\frac{D_i}{r} \frac{d}{dr} \left[r \frac{dc_i}{dr} \right] = \sum_{\substack{j=1 \\ j \neq i}}^S [R_{ij}(c_i) - R_{ji}(c_j)]. \quad (3)$$

Boundary conditions of Eq. (3) are:

$$\frac{dc_i}{dr} = 0 \quad \text{at } r = 0, \quad 0 \leq z \leq L \quad (4a)$$

$$c_i = u_i \quad \text{at } r = a, \quad 0 \leq z \leq L \quad (4b)$$

being z the distance from reactor inlet and L the length of the reactor.

Introducing the following dimensionless variables:

$$C_i = \frac{c_i}{c_1(a, 0)} = \frac{c_i}{u_1(0)} \quad (5)$$

$$\varrho = \frac{r}{a} \quad (6)$$

$$h_i^2(\varrho) = \frac{a^2}{D_i} \sum_{\substack{j=1 \\ j \neq i}}^S \{[k_{ij}\varphi(\varrho)]_I + [k_{ij}\varphi(\varrho)]_{II}\} \quad (7)$$

$$h_{ij}^2(\varrho) = \frac{a^2}{D_i} \{[k_{ji}\varphi(\varrho)]_I + [k_{ji}\varphi(\varrho)]_{II}\}. \quad (8)$$

Eq. (3) can be written as:

$$\frac{d^2 C_i}{d\varrho^2} + \frac{1}{\varrho} \frac{dC_i}{d\varrho} = h_i^2(\varrho) C_i - \sum_{\substack{j=1 \\ j \neq i}}^s h_{ji}^2(\varrho) C_j \quad (9)$$

with the boundary conditions:

$$\left. \frac{dC_i}{d\varrho} \right|_{0, \xi} = 0 \quad (10a)$$

$$C_i(1, \xi) = U_i(\xi), \quad (10b)$$

where the dimensionless variables U_i and ξ are defined as:

$$U_i = \frac{u_i}{u_1(0)} \quad (11)$$

$$\xi = \frac{z}{L}. \quad (12)$$

On the other hand, the fixed-bed reactor is assumed as unidimensional, without axial dispersion. Continuity equation for the species A_i is given by:

$$v \frac{du_i}{dz} = \varrho_B \langle R_i \rangle \quad (13)$$

being $\langle R_i \rangle$ the volume-averaged production rate of A_i per gram of support:

$$\langle R_i \rangle = \frac{1}{\varrho_p V_p} \int_{V_p} \left\{ \sum_{\substack{j=1 \\ j \neq i}}^s [R_{ij}(C_i) - R_{ji}(C_j)] \right\} dV. \quad (14)$$

By using the previously-defined dimensionless variables, Eq. (13) can be written as:

$$\frac{dU_i}{d\xi} = \frac{L\varrho_B}{v} \frac{\langle R_i(c_i) \rangle}{u_1(0)} = \frac{L\varrho_B}{v} \langle R_i(C_i) \rangle \quad (15)$$

with the inlet conditions:

$$\begin{aligned} U_1(0) &= 1 \\ U_i(0) &= 0, \quad i \neq 1. \end{aligned} \quad (16)$$

The solution of boundary-value problem, Eqs (9, 10a, 10b), coupled with the reactor conservation equation (15) often requires a great computational effort.

However, taking into account the linear characteristics of these equations (first-order kinetics), a semianalytical procedure can be used. In fact, if we define:

$$\langle R_i \rangle_j = \langle R_i \rangle \quad (17)$$

with boundary conditions:

$$U_j = 1, \quad U_i = 0, \quad i \neq j$$

the volume-averaged reaction rate of A_i at a given reactor position can be expressed as a linear combination:

$$\langle R_i \rangle = \sum_{j=1}^S \langle R_i \rangle_j U_j. \quad (18)$$

So, Eq. (15) is reduced to:

$$\frac{dU_i}{d\xi} = \frac{Lq_B}{v} \sum_{j=1}^S \langle R_i \rangle_j U_j, \quad (19)$$

i.e., a set of linear differential equations, and only the solution of S boundary-value problems is required. This was performed by using a previously-reported technique⁴, whereas a matrix method⁵ was used for the solution of Eq. (19).

APPLICATION

In order to illustrate the effects of particle activity profiles on the conversion and product distribution, three different reaction schemes were considered, being such schemes similar to those found in naphtha reforming. Catalytic sites were supposed to be distributed according to the following functions:

$$\varphi(\varrho) = 1 \quad (\text{uniform}) \quad (20a)$$

$$\varphi(\varrho) = 2\varrho^2 \quad (\text{increasing toward the pellet surface}) \quad (20b)$$

$$\varphi(\varrho) = 6(1 - \varrho)^2 \quad (\text{decreasing toward the pellet surface}) \quad (20c)$$

which are shown in Fig. 1. In this way, a total number of nine different catalysts was used for this study. Distribution functions $\varphi(\varrho)$ are normalized as:

$$\frac{1}{V_p} \int_{V_p} \varphi(\varrho) dV = 2 \int_0^1 \varphi(\varrho) \varrho d\varrho = 1. \quad (21)$$

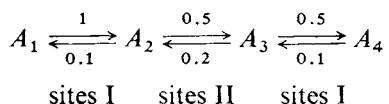
A general comment on reforming reactions is required at this point. In fact, reactions are carried out with a high H_2 /hydrocarbon molar ratio. Therefore, a first-

-order kinetics can be taken as a reasonable assumption. For the same reaction, effective diffusivities were considered independent on concentrations. In addition to this, as the molecular weight of hydrocarbons involved in the reaction network remains nearly constant, the same effective diffusivity was adopted for all the species.

For all the reaction schemes, it was assumed that A_1 is fed to reactor with a great excess of hydrogen.

Numerical values used for the calculations were: $a = 0.5$ cm; $D = 0.005$ cm² s⁻¹ whereas the values of kinetic constants are indicated below, for each reaction system.

Reaction System a



Numerical values indicated in this scheme correspond to kinetic constant (in s⁻¹); the reaction system would represent paraffin isomerization through the following steps: dehydrogenation of paraffins (metallic sites)-isomerization of olefins (acidic sites)-hydrogenation of olefins (metallic sites).

Fig. 2 shows the concentration profiles of species along the reactor for different particle activity distributions. Though a detailed analysis of these results can be made in a similar way to that described in a previous paper⁴, for the sake of conciseness only the more noticeable characteristics will be considered. So, Table I

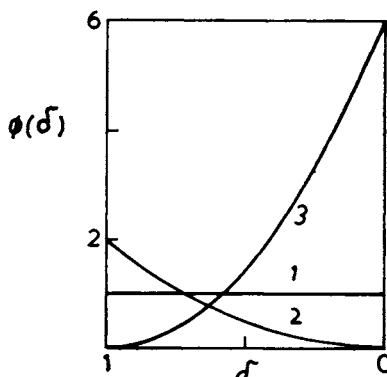


FIG. 1

Distribution functions, φ , adopted for the analysis. 1 $\varphi(\varrho) = 1$; 2 $\varphi(\varrho) = 2\varrho^2$; 3 $\varphi(\varrho) = 6(1 - \varrho)^2$

shows those distributions giving the maximum A_1 conversion and selectivities to different products. A_1 conversion, x_1 , was calculated as:

$$x_1 = 1 - U_1 \quad (22)$$

meanwhile selectivities are given by the expression:

$$s_i = \frac{U_i}{x_1}, \quad (23)$$

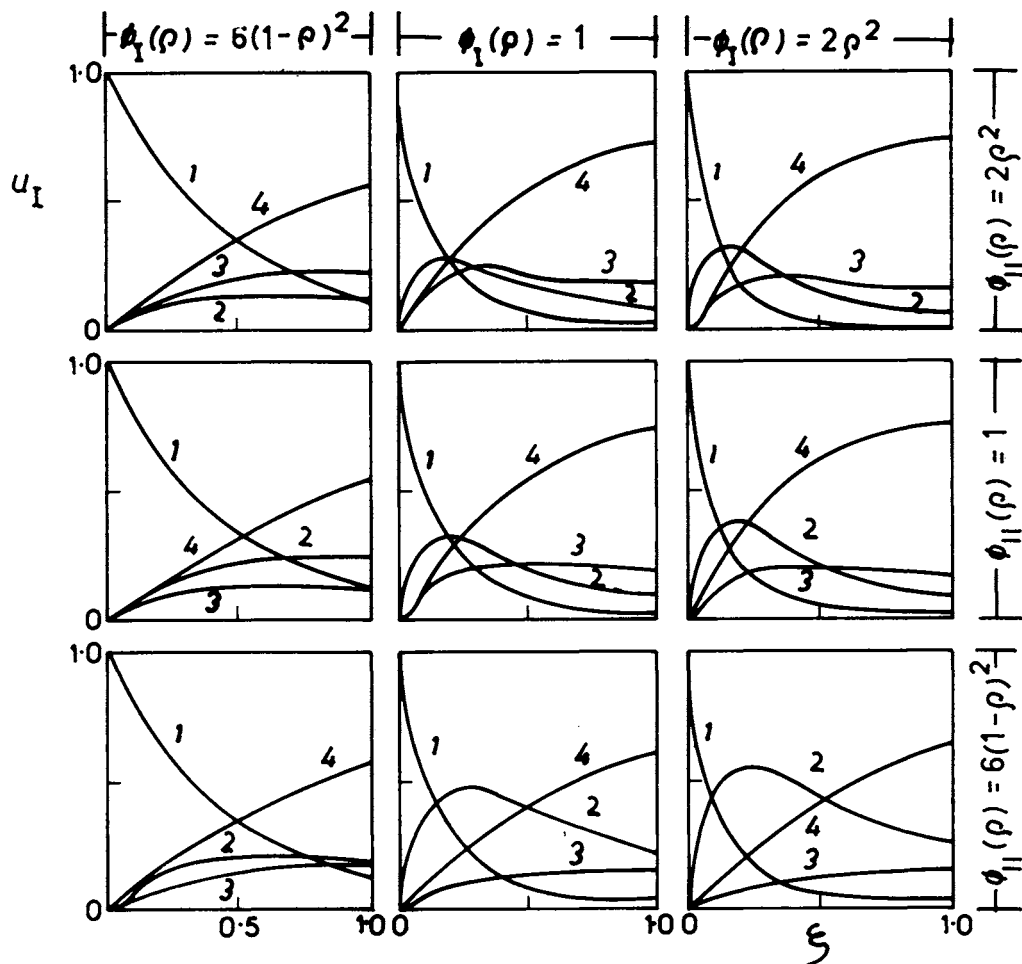
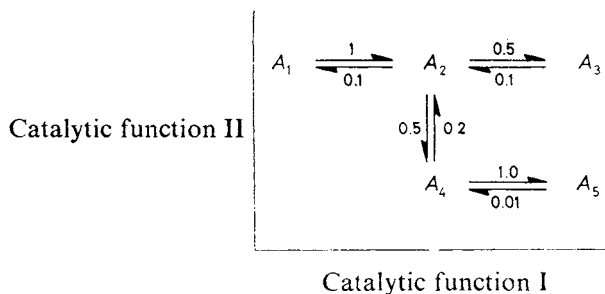


FIG. 2

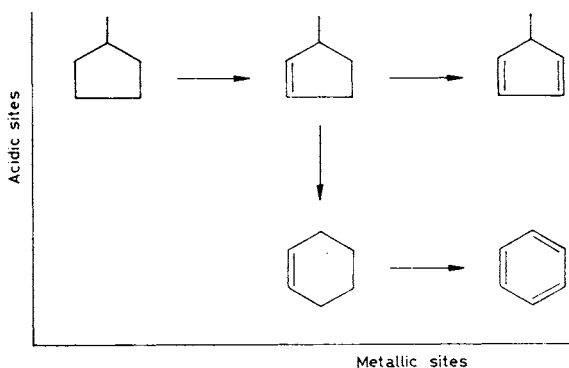
Concentration profiles of reacting species in the reactor for different activity distributions. Reaction system a (numbers in figures denote reacting species)

This case would correspond to isomerization of paraffins (A_1), being A_4 the desired product. A_4 is produced from A_2 isomerization: the step $A_2 \rightarrow A_3$ would represent a further dehydrogenation of the olefin, its polymerization, *etc.* (undesired reaction). Fig. 3 shows the concentration profiles of species for different activity profiles. In Table II, results for distribution giving maximum conversion and selectivities are presented.

Reaction System c



The above scheme would represent the isomerization of paraffins or, for this case, the aromatization of naphthenes (methylcyclopentane).



For the purpose of the analysis, A_5 (benzene) is taken as the desired product whereas A_3 (methylcyclopentadiene) is considered to be a coke precursor⁶, being therefore desirable to keep its concentration as low as possible.

Fig. 4 shows the concentrations of A_1 , A_3 , and A_5 as a function of ξ , for the different activity distributions used for this study. It must be noted that, though

equilibrium concentrations of A_3 and A_5 are 0.0194 and 0.9665, respectively, in the course of reactions high quantities of A_3 will be produced, due to its formation is kinetically favoured with respect to A_4 .

Considering that A_3 is produced on sites I, a distribution $\varphi(\varrho) = 2\varrho^2$ will give the maximum values of A_3 concentration, mainly when sites II are internally distributed. In this way, the competitive reaction $A_2 \xrightarrow{\text{II}} A_4$ would be diffusion-controlled. So, for the catalyst $\{\varphi_{\text{I}}(\varrho) = 2\varrho^2; \varphi_{\text{II}}(\varrho) = 6(1-\varrho)^2\}$ a maximum value of 0.53 for A_3 concentration is obtained, which is considerable higher than the

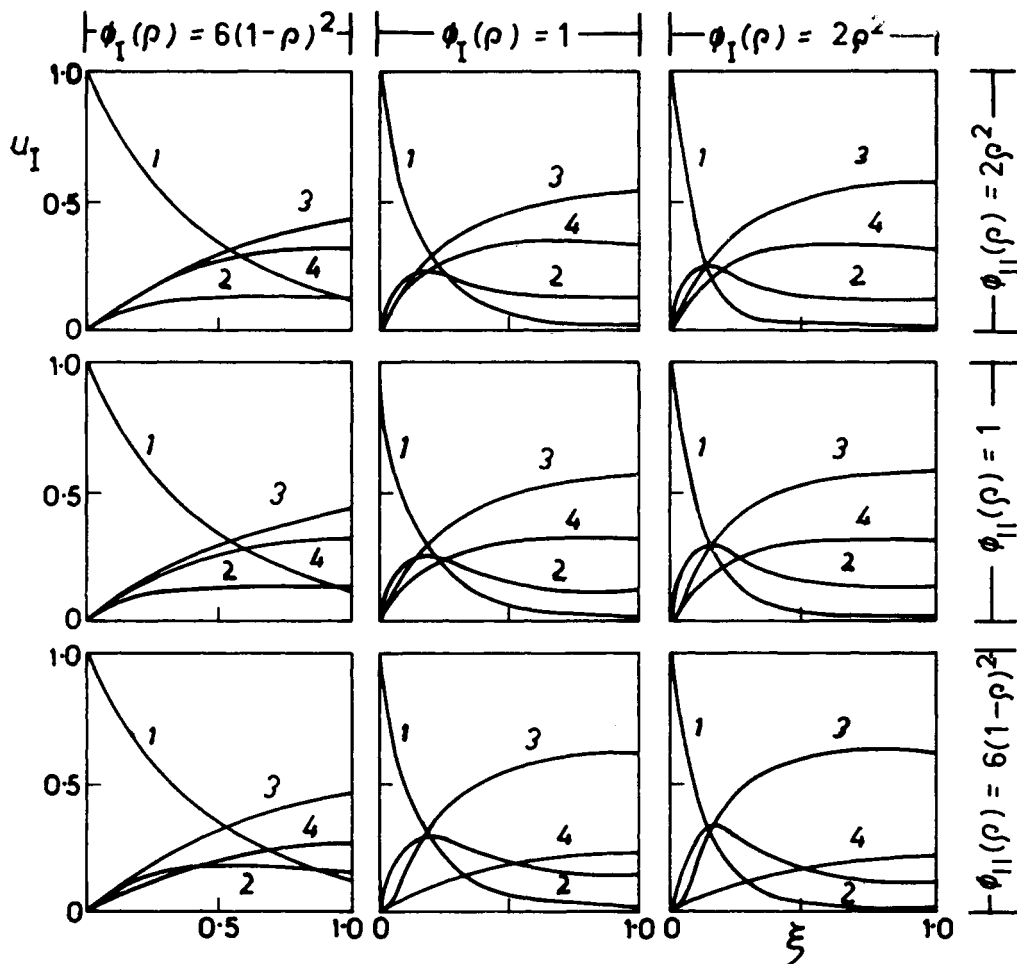


FIG. 3

Concentration profiles of reacting species in the reactor for different activity distributions. Reaction system b (numbers in figures denote reacting species)

equilibrium one (0.0194). Under these conditions, the concentration of A_5 at the reactor exit is only 0.42.

If catalytic function II is concentrated in the external zone of the particle, $\phi_{II}(\rho) = 2\rho^2$, maintaining the sites I distribution, both competitive reactions, $A_2 \xrightarrow{I} A_3$ and $A_2 \xrightarrow{II} A_4$ have similar diffusive restrictions. Then, the maximum value of A_3 concentration is decreased (0.32) and, consequently, A_5 concentration at reactor exit increases (0.72).

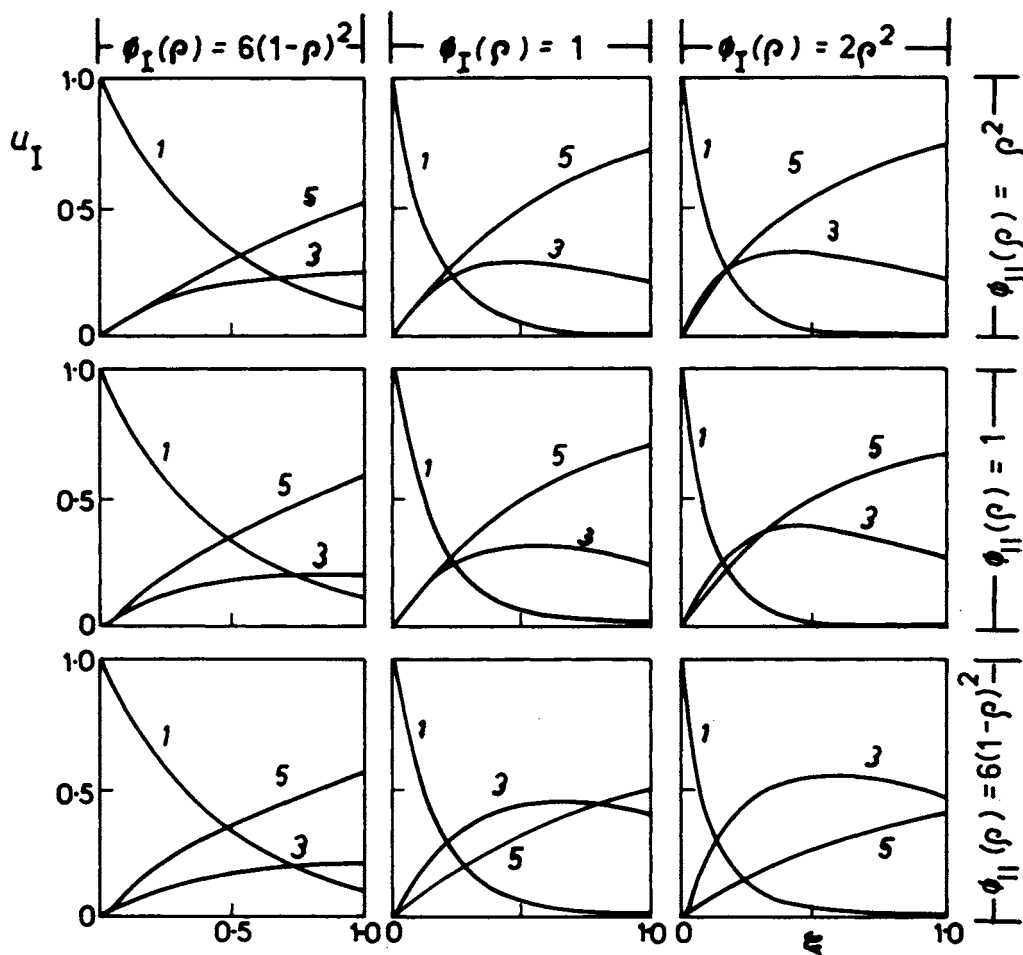


FIG. 4

Concentration profiles of reacting species in the reactor for different activity distributions. Reaction system c (numbers in figures denote reacting species)

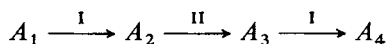
When sites I are distributed according to a function $\varphi_I(\varrho) = 6(1 - \varrho)^2$, the production of A_3 is retarded by diffusive control. This fact leads to a further reduction in the maximum A_3 concentration, being this value only 0.20 for the catalyst $\{\varphi_I(\varrho) = 6(1 - \varrho)^2; \varphi_{II}(\varrho) = 2\varrho^2\}$. However, for this case the first reaction $A_1 \xrightarrow{I} A_2$ is diffusion-controlled and higher reactor sizes (amounts of catalyst) are required to obtain a given conversion.

CONCLUSIONS

From the above study, it can be concluded that particle activity distributions have a strong influence on the conversion and selectivities to different products. Some remarks about the features of the three reaction schemes considered in this work can be made:

(i) If the main objective is to obtain the highest conversion of reactant for a given reactor volume (or, conversely, to minimize the reactor size at constant conversion) then the catalytic function involved in the first reaction ($A_1 \xrightarrow{I} A_2$) must be concentrated in the external zone of the particle.

(ii) If the goal is to achieve the maximum conversion to a given product, for example, A_3 in the following reaction network:



then sites II must be distributed according to functions increasing towards pellet surface, meanwhile sites I must be more concentrated at the core of the particle.

(iii) The above rules of thumb agree reasonably well with the analysis performed on the different reaction systems and they appear to be good initial guesses for activity distributions. A detailed study requires, however, the knowledge of kinetics and diffusive parameters involved in each particular case.

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LIST OF SYMBOLS

A_i	reacting species
a	particle radius
C_i	dimensionless concentration of A_i
c_i	concentration of A_i in the pores of the particle
D_i	effective diffusivity of A_i
i, j	indices related to reacting species
$h_i(\varrho), h_{ij}(\varrho)$	dimensionless variables defined in Eqs (7-8)
k_{ij}	reaction rate constant of $A_i A_j$
L	length of the reactor
R	number of reactions

R_{ij}	reaction rate of A_i A_j
$\langle R_i \rangle$	volume-averaged production rate of A_i
r	radial position
S	number of reacting species
s_i	selectivity to A_i defined in Eq. (23)
U_i	dimensionless concentration of A_i
u_i	concentration of A_i in the gas phase
V_p	particle volume
v	fluid velocity through the reactor
x_1	A_1 conversion defined in Eq. (22)
z	axial position in the reactor
$\xi = z/L$	dimensionless position in the reactor
$\rho = r/a$	dimensionless radial position
ρ_B	bed density
ρ_p	apparent density of the particle
φ	distribution function of catalytic sites

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