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## ACTIVITY AND SELECTIVITY OF NON-UNIFORM BIFUNCTIONAL CATALYSTS

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The activity and selectivity of non-uniform bifunctional catalysts are treated in this paper. For a bifunctional reacting network similar to pure hydrocarbons reforming, the effect of different radial distribution profiles of both catalytic functions in the catalytic particle on the activity and selectivity were theoretically predicted using an arbitrary set of kinetic parameters.

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Bifunctional catalysts have a wide application in industry. Naphtha reforming catalysts have a metallic and an acidic function, and are good examples of bifunctional catalysts. Their performance depends not only on the characteristics of each function but also on the distribution profile of each of the supported catalytic species. The latter factor is critical in processes kinetically controlled by internal mass transfer. Hence, it is very important to study the influence of the distribution profiles of both functions on the activity and selectivity. Furthermore, the metallic content and its distribution profile must be optimized in catalysts containing expensive noble metals.

Many papers have been published about the incidence of nonuniform distribution profiles on the activity and selectivity. The first studies were performed by Kasaoka and Sakata<sup>1</sup>. They considered a slab of a monofunctional catalyst with nonuniform distribution and obtained the effectiveness factor for a single reaction with a first order kinetic. Wang and Varma<sup>2,3</sup> and Nyström<sup>4</sup> worked years later on a similar problem and normalized the Thiele's modulus for different geometries of the catalytic particles. More complex reacting schemes were studied by other authors<sup>5,6</sup>. Mobidelli and coworkers<sup>7</sup> proposed a mathematical treatment to obtain the optimum activity distribution for bimolecular Langmuir-Hinshelwood kinetic. The performance of non-uniform bifunctional catalysts was studied by Rutkin and Petersen<sup>8</sup>. They considered three catalysts with a step distribution of both catalytic functions along the cylindrical pore. The reacting scheme involved successive reactions and each reaction required only one catalytic function.

The present paper studies a bifunctional reacting network similar to pure hydrocarbons reforming. The mathematical treatment considers cylindrical geometry for the catalyst particles and different radial distribution profiles for each catalytic function. The effect of the different radial profiles of both catalytic functions on the activity and selectivity is analyzed by using arbitrary values of the kinetic parameters.

## THEORETICAL

For the single reaction:



which takes place on a monofunctional catalyst with non-uniform distribution of the active sites, the first order reaction rate can be written as follows<sup>6</sup>:

$$r_{i1} = k_{i1} \phi(\varrho) C_i, \quad (2)$$

where  $\varrho$  indicates the dimensionless position,  $\phi(\varrho)$  represents the active sites distribution and fulfils the condition:

$$\frac{1}{V_p} \int_{V_p} \phi(\varrho) dV_p = 2 \int_0^1 \phi(\varrho) \varrho d\varrho = C_s \quad (3)$$

being  $V_p$  the particle volume and  $C_s$  the mean concentration of active sites.

A bifunctional reaction network (like Fig. 1 shows) involving  $L$  reacting species can be represented as a group of  $R$  single reactions:

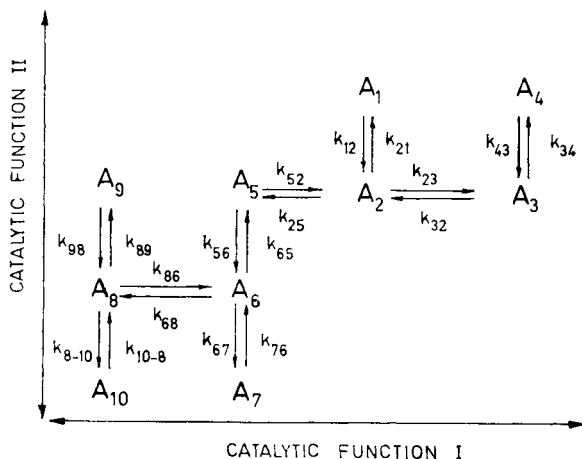
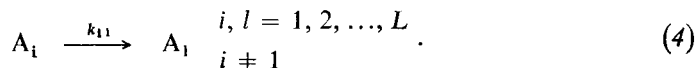


FIG. 1  
Scheme of the reacting system

Assuming that reaction (4) takes place on two types of active sites or catalytic functions (I and II) with nonuniform distributions, the reaction rate for first-order kinetic can be written as:

$$r_{i1} = [[k_{i1} \phi(\varrho)]_I + [k_{i1} \phi(\varrho)]_{II}] C_i, \quad (5)$$

where  $C_i$  is the  $A_i$  concentration.

On the other hand, the steady-state mass balance for the species  $A_i$  in a infinite cylindrical pellet is given by:

$$\frac{D_i}{r} \frac{d}{dr} \left[ r \frac{dC_i}{dr} \right] = \sum_{\substack{l=1 \\ l \neq i}}^L r_{il} - \sum_{\substack{l=1 \\ l \neq i}}^L r_{li}, \quad (6)$$

where monomolecular reactions were assumed.

The boundary conditions are:

$$dC_i/dr = 0 \quad \text{at} \quad r = 0 \quad (7a)$$

$$C_i = C_{is} \quad \text{at} \quad r = a \quad (7b)$$

being  $C_{is}$  the concentration of  $A_i$  at the external surface of the particle and  $a$  the particle radius.

Combining Eqs (5) and (6) and introducing the following dimensionless variables:

$$\varrho = r/a \quad (8)$$

$$\psi_i = C_i/C_{is} \quad (9)$$

it results:

$$\begin{aligned} \frac{d^2\psi_i}{d\varrho^2} + \frac{1}{\varrho} \frac{d\psi_i}{d\varrho} = \frac{a^2}{D_i} \left( \sum_{\substack{l=1 \\ l \neq i}}^L ([k_{il} \phi(\varrho)]_I + [k_{il} \phi(\varrho)]_{II}) \psi_i - \right. \\ \left. - \sum_{\substack{l=1 \\ l \neq i}}^L ([k_{li} \phi(\varrho)]_I + [k_{li} \phi(\varrho)]_{II}) \psi_l \right). \end{aligned} \quad (10)$$

Defining:

$$\beta_i = \sum_{\substack{l=1 \\ l \neq i}}^L [k_{il} \phi(\varrho)]_I + [k_{il} \phi(\varrho)]_{II} \quad (11)$$

$$\beta_{li} = [k_{li} \phi(\varrho)]_I + [k_{li} \phi(\varrho)]_{II} \quad (12)$$

Eq. (10) can be written as:

$$\frac{d^2\psi_i}{d\varrho^2} + \frac{1}{\varrho} \frac{d\psi_i}{d\varrho} - \frac{a^2}{D_i} \beta_i \psi_i = - \frac{a^2}{D_i} \sum_{\substack{l=1 \\ l \neq i}}^L \beta_{li} \psi_l. \quad (13)$$

The boundary conditions in dimensionless form are given by:

$$\frac{d\psi_i}{d\varrho} = 0 \quad \text{at} \quad \varrho = 0 \quad (14a)$$

$$\psi_i = \psi_{is} \quad \text{at} \quad \varrho = 1. \quad (14b)$$

The boundary value problem was solved by a finite differences method. Consequently, the radial position was discretized according to:

$$\varrho = n \Delta\varrho \quad (15)$$

$$n = 0, 1, 2, \dots, N,$$

where  $N$  is the total number of radial increments. Hence:

$$\psi_{i,n} = \psi_i|_{\varrho=n\Delta\varrho} \quad (16)$$

$$\beta_{i,n} = \beta_i|_{\varrho=n\Delta\varrho} \quad (17)$$

$$\beta_{li,n} = \beta_{li}|_{\varrho=n\Delta\varrho}, \quad (18)$$

In this way for each reacting species the following tridiagonal system was obtained

$$\psi_{i,0} - \frac{1}{1 + \beta_{i,0} a^2 \Delta\varrho^2 / 4D_i} \psi_{i,1} = \frac{(a^2/D_i) \left( \sum_{\substack{l=1 \\ l \neq i}}^L \beta_{li,0} \psi_{l,0} \right) \Delta\varrho^2}{4 + \beta_{i,0} a^2 \Delta\varrho^2 / D_i}$$

$$\psi_{i,n} - \frac{2 + \beta_{i,n} a^2 \Delta\varrho^2 / D_i}{(1 - 1/2n)} \psi_{i,n} + \frac{2n + 1}{2n - 1} \psi_{i,n+1} = \frac{a^2 \left( \sum_{\substack{l=1 \\ l \neq i}}^L \beta_{li,n} \psi_{l,n} \right) \Delta\varrho^2}{D_i (1 - 1/2n)}$$

$$\psi_{i,N} = \psi_{is} \quad (19)$$

The solution involves three steps: a) Tearing of the system (19), i.e. the selection

of the iterative variables which for this case have been taken as the concentration of a group of reacting species. This group will be named "group of key species".  
 b) Inversion of the system through Thomas' method<sup>9</sup> by using the previously estimated values of the iterative variables. c) Application of a successive substitution method with acceleration of convergence according to Wegstein<sup>10</sup>.

The convergence criterion was:

$$\sum_{i \in V} \sum_{n=0}^N \Delta \psi_{i,n}^2 < \varepsilon, \quad (20)$$

where  $V$  denotes the "group of key species",  $\Delta \psi_{i,p}$  is the difference between  $\psi_{i,n}$  values calculated for two successive iterations and  $\varepsilon$  a error bound.

After obtaining the concentrations of each reacting species at different radial positions, the mean reaction rate ( $\bar{r}_{i1}$ ) was calculated as follows:

$$\bar{r}_{i1} = 2 \int_0^1 r_{i1} \varrho \, d\varrho. \quad (21)$$

In order to obtain activity and selectivity of catalysts with different distribution radial profiles mean reaction rates given by Eq. (18) are required.

#### APPLICATION

The mathematical model was applied to a bifunctional reacting system similar to reforming of pure hydrocarbons (n-hexane or n-heptane). Fig. 1 shows the reacting system, where the horizontal reaction paths require the catalytic function named I (acidic sites in reforming) and the vertical ones require the catalytic function named II (metallic function in reforming). Each reaction involves only one catalytic function.

In agreement with the hypothesis proposed by Rutkin and Petersen<sup>8</sup> a constant  $H_2$  concentration was assumed. In other words, a very high  $H_2$ /hydrocarbons molar ratio was considered. Moreover, as the hydrocarbons mixture is highly diluted in  $H_2$ , the hydrocarbon diffusivities can be taken as independent of the concentration. Furthermore, as the reacting scheme does not take into account polymerization and cracking reactions, the molecular weights of the different reactants are similar. Hence, a same diffusivity values for all of them can be adopted.

The radial profiles, for both catalytic functions, shown in Fig. 2 were used for the analysis. Fifteen different distribution cases, or catalysts were selected for the study. They correspond to different combinations of the above mentioned radial profiles. The activity and selectivity to intermediary and final products were calculated for each catalyst. A parameter  $\mu$  was defined to identify the radial profiles

for each catalytic function. The  $\mu$  absolute value was equal to the exponent  $\gamma$  in the profile function (see Fig. 2). The  $\mu$  sign was arbitrarily adopted. For positive  $\mu$  values the active sites concentration increases with dimensionless radial position  $\rho$  from the particle center meanwhile for negative  $\mu$  values it decreases. Uniform profiles are indicated by  $\mu = 0$ . We have also studied three different cases in which the mean concentration of the catalytic function II was fixed at 0.01, 0.1 and 1 site/cm<sup>3</sup>, holding constant the mean concentration of the catalytic function I at 1 site/cm<sup>3</sup>.

For this case, the activity was defined as the  $A_1$  net disappearance rate and selectivity of the species  $i$  ( $S_i$ ) was calculated as the ratio between the net formation rate of  $A_i$  and the net disappearance rate of  $A_1$ . The kinetic parameter values of the reaction network were arbitrarily adopted and they are shown in Table I. In the same Table details concerning the numerical procedure ( $N$ ,  $\varepsilon$  and the "group of key species") are also displayed.

## RESULTS AND DISCUSSION

The activity of the different catalysts is shown in Fig. 3. It can be observed that activity is not affected by the acidic sites distribution but is strongly dependent on the metallic sites distribution profile. For a given  $C_{sII}$  value, the activity decreases. Then the metallic function is deposited in the central zone of the particle. When  $C_{sII}$  values decrease a smaller influence of the metallic sites distribution is observed. Besides, then  $C_{sII}$  changes from 1 to 0.1 site/cm<sup>3</sup> the maximum of the activity decreases about twenty six times. It must be noted that a one hundred times reduction in the metallic sites does not produce a proportional activity reduction. This behavior can be explained in terms of the effectiveness factor ( $\eta$ ) for the  $A_1$  disap-

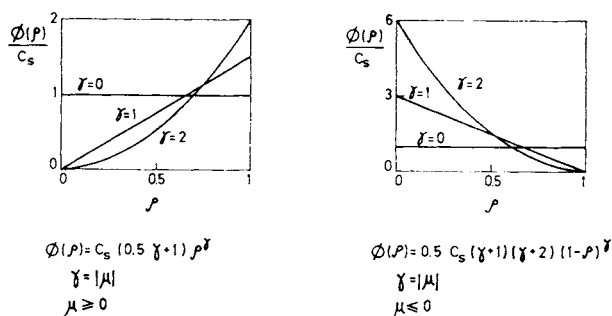


FIG. 2

Radial profiles adopted for the analysis.  $\rho$  is dimensionless radius.  $\rho = 0$  corresponds to particle center

TABLE I  
Values of the parameters

$k_{12}$ (cm <sup>3</sup> /site . s)	10.00	$k_{86}$ (cm <sup>3</sup> /site . s)	1.00
$k_{21}$ (cm <sup>3</sup> /site . s)	20.00	$k_{89}$ , mc <sup>3</sup> /site . s)	10.00
$k_{23}$ (cm <sup>3</sup> /site . s)	0.01	$k_{98}$ , cm <sup>3</sup> /site . s)	0.50
$k_{32}$ (cm <sup>3</sup> /site . s)	1.00	$k_{8-10}$ (cm <sup>3</sup> /site . s)	10.00
$k_{34}$ (cm <sup>3</sup> /site . s)	10.00	$k_{10-8}$ (cm <sup>3</sup> /sit <sup>o</sup> . s)	0.00
$k_{43}$ (cm <sup>3</sup> /site . s)	0.50	$a$ (cm)	0.15
$k_{25}$ (cm <sup>3</sup> /site . s)	0.10	$\psi_{1s}$	1
$k_{52}$ (cm <sup>3</sup> /site . s)	10.00	$\psi_{is}$ ( $i \neq 1$ )	0
$k_{56}$ (cm <sup>3</sup> /site . s)	10.00	$D_i$ (cm <sup>2</sup> /s)	$5 \cdot 10^{-3}$
$k_{65}$ (cm <sup>3</sup> /site . s)	20.00	$N$	20
$k_{67}$ (cm <sup>3</sup> /site . s)	10.00	$\varepsilon$	$10^{-10}$
$k_{76}$ (cm <sup>3</sup> /site . s)	10.00	Group of the key species	{A <sub>2</sub> , A <sub>4</sub> , A <sub>6</sub> , A <sub>8</sub> }
$k_{68}$ (cm <sup>3</sup> /site . s)	0.10		

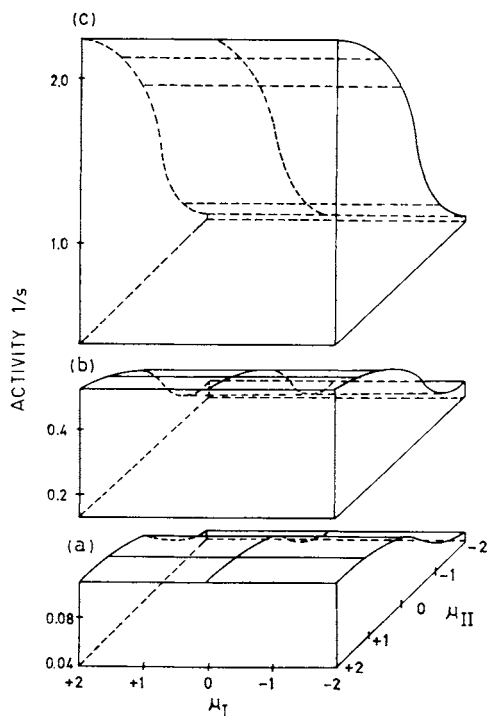


FIG. 3

Activity vs radial profile parameter of both catalytic functions (I and II) for different  $C_{SII}$  values. a)  $C_{SII} = 0.01$  site/cm<sup>3</sup>; b)  $C_{SII} = 0.1$  site/cm<sup>3</sup>; c)  $C_{SII} = 1$  site/cm<sup>3</sup>;  $C_{SI} = 1$  site/cm<sup>3</sup>

pearance reaction.  $\eta$  is given by:

$$\eta = \frac{2 \int_0^1 [k_{12} \phi_{II}(\varrho) \psi_1 - k_{21} \phi_{II}(\varrho) \psi_2] \varrho \, d\varrho}{(k_{12} \psi_{1s} - k_{21} \psi_{2s}) C_{sII}} \quad (22)$$

TABLE II  
Values of  $\eta$  and  $\eta C_{sII}$  as a function of  $C_{sII}$  and for  $\mu_{II} = 2$

$C_{sII}$ , site/cm <sup>3</sup>	$\eta$	$\eta C_{sII}$ , site/cm <sup>3</sup>
0.01	0.925	0.00925
0.1	0.600	0.060
1.0	0.244	0.244

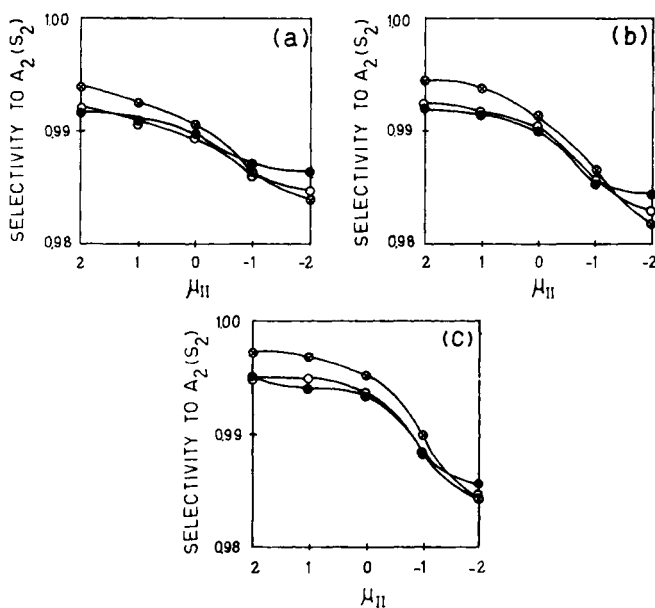


FIG. 4

Selectivity to  $A_2$  vs radial profile parameter of the function II for different radial profile parameters of the function I. a)  $C_{sII} = 0.01$  site/cm<sup>3</sup>; b)  $C_{sII} = 0.1$  site/cm<sup>3</sup>; c)  $C_{sII} = 1$  site/cm<sup>3</sup>;  $\odot$   $\mu_1 = -2$ ;  $\circ$   $\mu_1 = 0$ ;  $\bullet$   $\mu_1 = 2$ ;  $C_{sI} = 1$  site/cm<sup>3</sup>



From Table I,  $\psi_{2s} = 0$  and  $\psi_{1s} = 1$ . Hence, Eq. (22) can be rewritten as:

$$(\bar{r}_{12} - \bar{r}_{21}) = k_{12} C_{sII} \eta. \quad (23)$$

Therefore the activity  $(\bar{r}_{12} - \bar{r}_{21})$  is proportional to  $\eta C_{sII}$  for a given metallic sites distribution.

By using Eq. (22)  $\eta$  values for  $\mu_{II} = 2$  and different mean concentrations of the metallic function were calculated. They are shown in Table II. It can be seen that  $\eta C_{sII}$  decreases about twenty six times when  $C_{sII}$  changes from 1 to 0.01 site/cm<sup>3</sup>.

Fig. 4 shows, for different mean metal concentrations ( $C_{sII}$ ) and parametric with the acidic sites distribution, the change of selectivity to  $A_2$  as a function of the metallic sites distribution. The results indicate that selectivity is favoured when the metal is peripherally deposited and the acidic sites are concentrated in the central zone of the particle. This can be explained in a simple way:  $A_2$  is produced on metallic sites and disappears by reaction on acidic sites. Hence, when the metal is peripherally

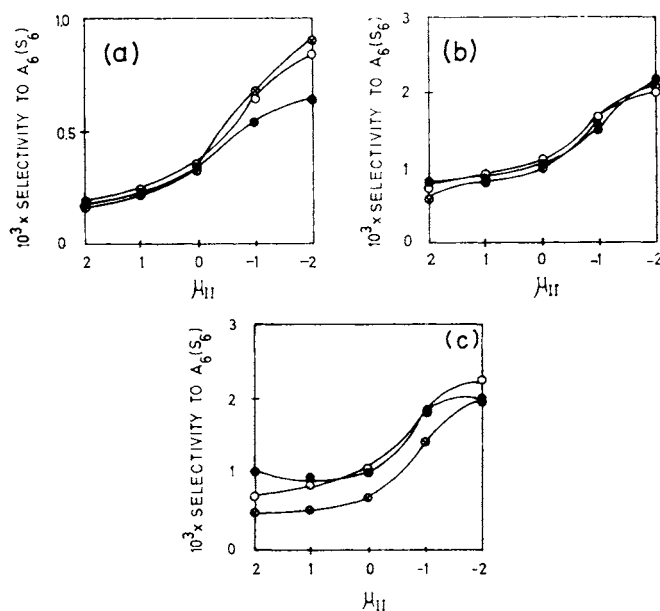


FIG. 5

Selectivity to  $A_6$  vs radial profile parameter of the function II and for different radial profile parameters of the function I. a)  $C_{sII} = 0.01 \text{ site/cm}^3$ ; b)  $C_{sII} = 0.1 \text{ site/cm}^3$ ; c)  $C_{sII} = 1 \text{ site/cm}^3$ ;  $\bullet$   $\mu_I = -2$ ;  $\circ$   $\mu_I = 0$ ;  $\bullet$   $\mu_I = 2$ ;  $C_{sI} = 1 \text{ site/cm}^3$

deposited, the  $A_2$  formation rate is favoured, Whereas when the acidic function is located at the center of the particle the diffusive control will retard the  $A_2$  disappearance reaction. When the metal function is concentrated in the particle center the selectivity to  $A_2$  diminishes. In this case it is convenient to have the acidic sites concentrated in the outer shell of the particle. In brief, the selectivity to  $A_2$  is favoured when both catalytic functions are separated one from the another.

The change of the selectivity to  $A_3, A_4, \dots, A_{10}$  with the metallic and acidic sites distribution can be explained in terms of the selectivity to  $A_2$ . In fact, the distribution radial profiles which increase the  $A_2$  transformation to another products (or decrease the selectivity to  $A_2$ ) will give a high selectivity to  $A_3, A_4, \dots, A_{10}$ . Let us consider  $A_6$  as representative of the intermediary compounds. Fig. 5 shows the change of selectivity to  $A_6$  ( $S_6$ ) with the metallic sites distribution for different acidic sites profiles and diverser mean concentration of the metallic sites. The highest selectivity values were obtained for  $(1 - \rho)^2$  distributions of both catalytic functions. The uniform acidic distribution seems to be more suitable only for  $C_{sII} = 1 \text{ site/cm}^3$ . The selectivity to  $A_6$  is mainly affected by the metallic sites distribution, although

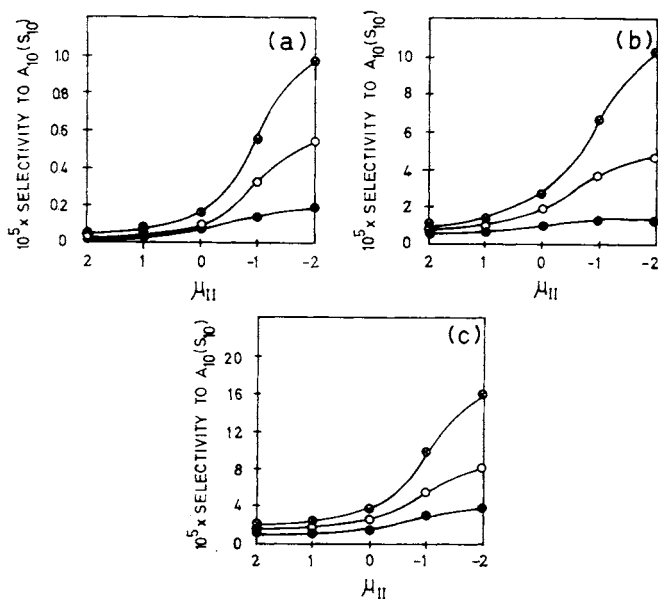


FIG. 6

Selectivity to  $A_{10}$  vs radial profile parameter of the function II and for different radial profile parameters of the function I. a)  $C_{sII} = 0.01 \text{ site/cm}^3$ ; b)  $C_{sII} = 0.1 \text{ site/cm}^3$ ; c)  $C_{sII} = 1 \text{ site/cm}^3$ ;  $\circ \mu_I = -2$ ;  $\circ \mu_I = 0$ ;  $\bullet \mu_I = 2$ ;  $C_{sI} = 1 \text{ site/cm}^3$

the  $S_6$  sensitivity to acidic sites distribution increases for higher  $C_{sII}$  values. The analysis performed on the intermediary products is also valid for the final products. However, Fig. 6, where the behaviour of selectivity to  $A_{10}$  is represented, shows that  $S_{10}$  is clearly more sensitive to changes of the acidic function distribution than  $S_6$ .

### CONCLUSIONS

A mathematical treatment to predict the activity and selectivity of non-uniform bifunctional catalysts with different distribution radial profiles in a reacting system similar to reforming of pure hydrocarbons is presented in this paper. The results show that the activity and selectivity are very strongly influenced by the radial distribution of the two catalytic functions and their mean concentration in the catalysts.

In addition, knowing the kinetic parameter set for a given reacting system, this mathematical treatment allows to determine the appropriate distribution radial profiles of both catalytic functions to obtain the optimal performance of the catalyst. Hence, this can be seen as an important tool in the catalyst design.

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### LIST OF SYMBOLS

$A_i, A_1$	reactants
$a$	particle radius
$C_i$	concentration of $A_i$
$C_s$	mean concentration of active sites
$C_{is}$	concentration of $A_i$ at the external surface of the particle
$D_i$	effective diffusivity of $A_i$
$i, l$	index related to reactants
$k$	reaction rate constant
$L$	total number of reactants
$n, N$	index related to radial positions
$r$	radial position
$r_{i1}$	rate of the $A_i \rightarrow A_1$ reaction
$\bar{r}_{i1}$	average of the reaction $A_i \rightarrow A_1$
$R$	total number of reactions
$S_i$	selectivity defined in the text
$V_p$	particle volume
$V^p$	group of iterative variables
$\beta_i$	function defined in Eq. (11)
$\beta_{li}$	function defined in Eq. (12)
$\gamma$	exponent in the distribution function of the active sites
$\epsilon$	error bound
$\phi$	distribution of the active sites (site/cm <sup>3</sup> )
$\rho$	dimensionless radial position

$\psi_i$	dimensionless concentration of $A_i$
$\psi_{is}$	dimensionless concentration of $A_i$ at the external surface of the particle
$\mu$	parameter which indicates the type of radial profile

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