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# The impact of non-uniform bifunctional catalyst for the isomerization of n-hexane in fixed bed catalytic reactor

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**Abstract**—Catalytic reforming is a very important process in chemical industry. The aim of this process is to transform treated naphtha (paraffins, olefins, naphthenes, aromatics) into reformates with a better yield in aromatics such as benzene, toluene, and xylenes (BTX) that are very important petrochemical materials and providing a high octane index. In this work, a mathematical model is proposed to investigate the influence of the concentration and the non-uniform distribution of the catalytic sites on the performances of an isothermal fixed bed reactor with axial dispersion and mass transfer resistance. This model is applied to the naphtha catalytic reforming network. The simulation of the model for a particular chemical reaction network showed that the catalyst activity and selectivity depend on the balance between the number, per unit volume, of the active sites and the way they are distributed throughout the pellet.

**Keywords**— *bifunctional catalyst, non-uniform distribution, activity, selectivity*

## I. INTRODUCTION

It is well established that the presence of poisoning and deactivation phenomena by coke deposit on the external lateral surface of the catalytic pellet reduces activity and selectivity and stability of the bi-functional catalytic pellet. The performance of this latter is conditioned by the way the catalytic sites are distributed inside the pellet. It is here that lies the importance of studying the active site distribution inside the catalytic pellet. It has long been known that a uniform distribution is not always the adequate choice for an optimal functioning. This is particular important when using noble and costly materials as catalysts. An optimal use of these materials is thus necessary.

## II. LITERATURE REVIEW

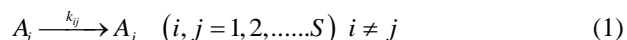
Dario et al. [1, 2] studied theoretically the influence of the distribution profiles of the active sites on both activity and selectivity of a bi-functional non uniformly distributed catalyst, in a catalytic cylindrical particle and in the fixed bed reactor without axial dispersion. They established that

catalytic activity and selectivity of the different species were largely influenced by the active site concentration and distribution when searching optimal performances of the catalyst. Morbidelli et al. [3-5], showed analytically that for a given amount of active metal, the Dirac distribution, in which the catalyst was concentrated at a specified position, leads to an optimal efficiency. Gavriilidis and Varma [6] analyzed numerically the problem of practically positioning the active material. The active sites were distributed in a narrow zone (thin layer) around the optimal position, with a thickness less than 5% of the catalytic particle diameter. This optimal position, which depends on the Thiele modulus, corresponds to a maximum reaction rate.

## III. MATHEMATICAL FORMULATION OF THE PROBLEM

### A. Kinetic model

Let us consider a complex reaction scheme involving 'S' species which can be represented by R reaction series.



In the case of a bifunctional catalytic particle, with two types of active sites (site I and site II) existing simultaneously, the reaction rate is supposed to be written as the sum of the two contributions, that is:

$$r_{ij} = [k_{ij} \Phi_I(x) + k_{ij} \Phi_{II}(x)] c_i \quad (2)$$

The active sites distribution is represented by the function  $\Phi(x)$ .

### B. Dimensionless equations

Before solving these equations, they need to be converted into a dimensionless form. Let us introduce the following dimensionless variables:

$$\rho = \frac{x}{a}, \xi = \frac{z}{L}, \Psi_i = \frac{C_i}{u_{i0}}, U_i = \frac{u_i}{u_{i0}} \quad (3)$$

1) Mass balance in catalyst phase

$$\frac{d^2\Psi_i}{d\rho^2} + \frac{p}{\rho} \frac{d\Psi_i}{d\rho} - \frac{a^2}{D_i} \beta_{ij} \Psi_i = -\frac{a^2}{D_i} \sum_{j=1, j \neq i}^S \beta_{ji} \Psi_j \quad (4)$$

$$\left. \frac{d\Psi_i}{d\rho} \right|_{\rho=0} = 0 \quad (5)$$

$$\left. \frac{d\Psi_i}{d\rho} \right|_{\rho=1} = Bio(U_i - \Psi_{i,s})$$

$$\beta_{ij} = \sum_{\substack{j=1 \\ i \neq j}}^S \{ [k_{ij} \Phi_I(\rho)] + [k_{ij} \Phi_{II}(\rho)] \} \quad (6)$$

$$\beta_{ji} = \{ [k_{ji} \Phi_I(\rho)] + [k_{ji} \Phi_{II}(\rho)] \} \quad (7)$$

2) Mass balance in fluid phase

$$\frac{1}{Pe} \frac{d^2 U_i}{d\xi^2} - \frac{dU_i}{d\xi} - K_L^* (U_i - \Psi_{i,s}) = 0 \quad (8)$$

$$\left. \frac{dU_i}{d\xi} \right|_{\xi=1} = 0 \quad (9)$$

$$\left. \frac{1}{Pe} \frac{dU_i}{d\xi} \right|_{\xi=0} = \begin{cases} U_i(0) - 1 & \text{for } i = 1 \\ U_i(0) & \text{for } i \neq 1 \end{cases}$$

$$\text{Where } Pe = \frac{vL}{D_{ea}}, K_L^* = (1-\varepsilon)(p+1)Bio \frac{D_i}{a^2} \tau, Bio = \frac{K_c a}{D_i}$$

$K_L^*$ : is a dimension less transfer coefficient (fluid-solid)

C. Choice of the distribution function

The mathematical expressions of the different distribution functions used are summarized in the following table:

TABLE I. CONTINUOUS DISTRIBUTION FUNCTIONS [4]

Nature of $\Phi(\rho)$	$\mu$	Mathematical expression	Variation
Parabolic	-2	$\Phi(\rho) = 6C_s(1-\rho)^2$	decreasing
	+2	$\Phi(\rho) = 2C_s\rho^2$	increasing
Linear	-1	$\Phi(\rho) = 3C_s(1-\rho)$	decreasing
	+1	$\Phi(\rho) = 1.5C_s\rho$	increasing
Uniform	0	$\Phi(\rho) = C_s$	Constant

The  $\mu$  parameter is used to identify the nature of the distribution profile.

#### IV. APPLICATION

In order to simulate our mathematical model, it was tested on a reaction scheme involving the catalytic isomerization of hexane (see fig.1).

Two kinds of reactions appear in this reaction network:

- The reactions taking place on acid sites are represented horizontally (Site I).
- The reactions taking place on metallic sites are represented vertically (Site II).

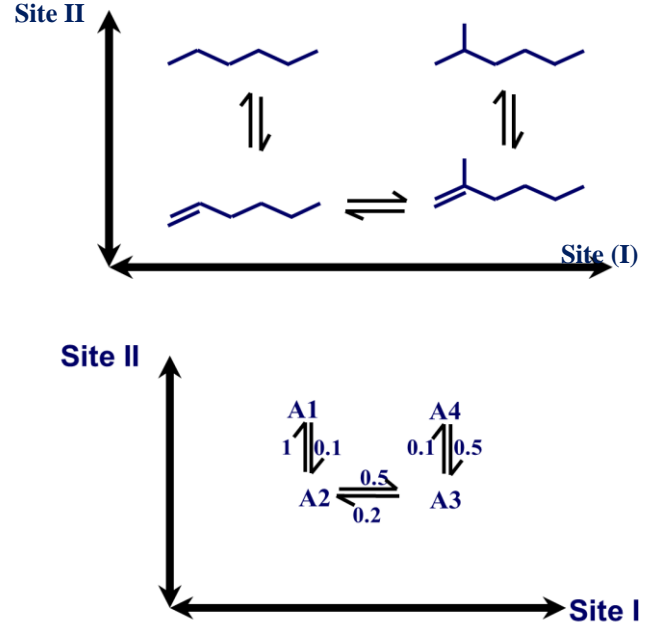


Fig. 1. Catalytic isomerization of hexane.

The numerical results presented here are the concentration profiles of all the species in the fluid phase. The influence of the following parameters: the average concentration ( $C_{sII}$ ) of the metallic sites and the nature of their distribution  $\mu_{II}$  on the concentrations profiles is investigated. It should be noted that the parameter  $\mu_I$  and the average concentration ( $C_{sI}$ ) are supposed to be equal to 0 and 1 site/cm<sup>3</sup> respectively.

#### V. EFFECT OF ( $C_{sII}$ ) ON THE CONCENTRATION PROFILE OF ALL SPECIES ALONG THE CATALYTIC REACTOR.

Fig. 2 shows that the concentration profiles of all species, along the catalytic reactor, are very affected by  $C_{sII}$ . It should be noted that the concentration of species  $A_1$  decreases rapidly with higher values of  $C_{sII}$ . This is probably due to the fact that most active metallic sites are concentrated at the inner peripheral surface of the particle. The concentration of the

desired species  $A_4$  also seems to increase with higher values of  $C_{sII}$ .

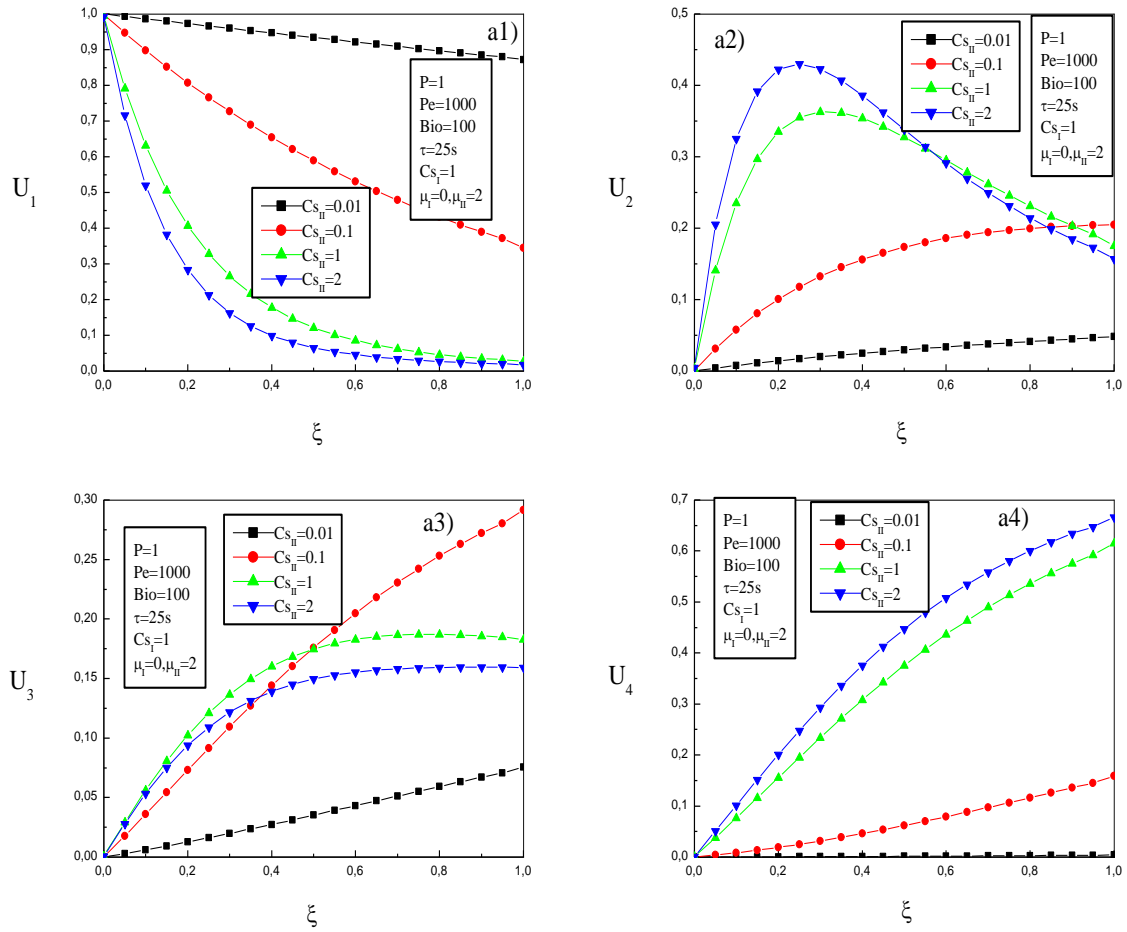


Fig. 2. Effect of ( $C_{sII}$ ) on the concentration profile of all species along the catalytic reactor a1)  $C_{sII} = 0.01 \text{ site} / \text{cm}^3$  a2)  $C_{sII} = 0.1 \text{ site} / \text{cm}^3$  a3)  $C_{sII} = 1 \text{ site} / \text{cm}^3$  a4)  $C_{sII} = 2 \text{ site} / \text{cm}^3$

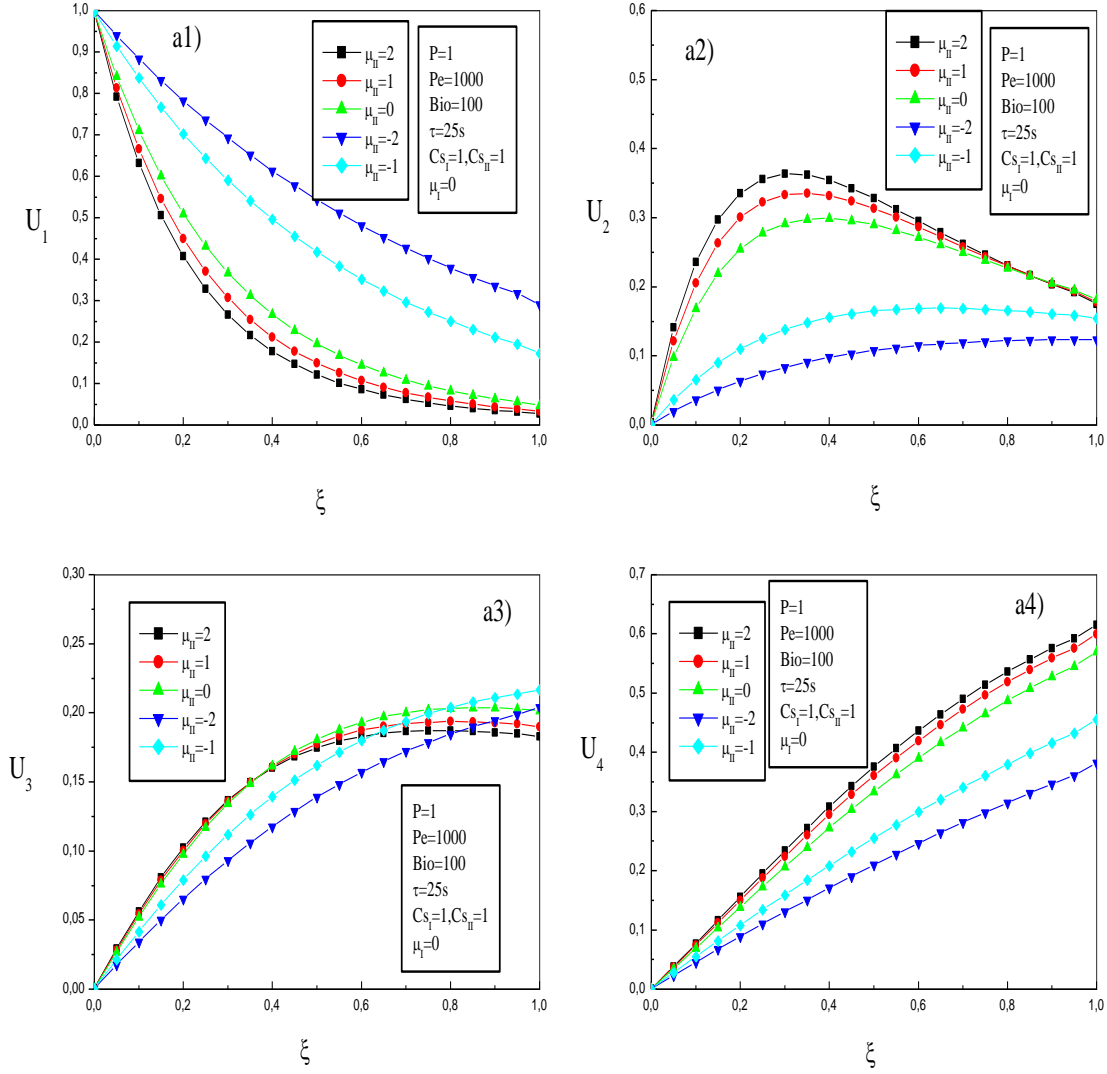


Fig. 3. Effect of the metallic site distribution on the concentration profiles of all species along the reactor

## VI. EFFECT OF THE METALLIC SITE DISTRIBUTION ON THE CONCENTRATION PROFILES OF ALL SPECIES ALONG THE REACTOR

Fig. 3 illustrates the concentration profiles of the all species along the catalytic reactor. It can be seen that higher values  $C_{S_{II}}$  and increasing distributions of metallic sites seem to favor the production of species  $A_4$ .

## VII. CONCLUSION

In order to improve the catalytic performances in terms of efficiency and selectivity with respect to the desired species  $A_4$ , a mathematical model, based on an isothermal fixed bed, reactor hypothesis, was proposed and simulated. The results obtained for the concentration profiles of the active species led to the following; the concentrations of active sites and their distributions. In order to obtain a high conversion rate, the metallic sites involved in the first reaction, i.e.

( $A_1 \xrightarrow{\text{site II}} A_2$ ) must be concentrated at the inner peripheral surface of the catalytic particles.

It was shown in this work that the mathematical model proposed can be applied to any chemical reaction network and an appropriate choice of the different parameters of the problem can led to optimum results.

## NOMENCLATURE

$A_i, A_j$	Active species
$S$	Number of species
$r_{ij}$	Kinetic rate
$k_{ij}$	Kinetic constant
$D_e$	Effective diffusion coefficient
$D_{ea}$	Effective axial dispersion coefficient
$a$	Indicates the half thickness the catalytic pellet

$c_i$	Concentration of $A_i$ species inside the pellet
$c_{i,s}$	Concentration of $A_i$ species at the surface of pellet
$u_i$	Concentration of $A_i$ species in the fluid phase
$u_{i0}$	Concentration of $A_i$ species just before the entrance of the reactor
$u_i(0)$	Concentration of $A_i$ species at the entrance of the reactor
$U_i$	Dimensionless concentration of $A_i$ species in the fluid phase
$\Psi_i$	Dimensionless concentration of $A_i$ species in the solid phase
$x$	Position in relation with the particle center
$L$	Reactor length
$p$	parameter relative to the catalytic particle shape ( $p = 0$ : slab, $p = 1$ : cylinder, $p = 2$ : sphere)
$\varepsilon$	Porosity of the catalytic bed
$V_p$	volume of the catalytic particle pellet
$\tau$	Residence time
$\rho$	Dimensionless radial position in the catalytic particle
$\xi$	Dimensionless axial coordinate of the reactor
$\Phi$	Distribution function of the active sites
$\mu$	Parameter denoting the type of the distribution
$C_{st}$	Average concentration of the acid sites
$C_{sII}$	Average concentration of the metallic sites

$Pe$	Pellet number
$Bio$	Biot number
$K_L^*$	Dimensionless mass transfer coefficient

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