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Modeling of a gas catalytic chemical reaction, taking into account the diffusion in the adsorbed phase

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Abstract

This study is devoted to a chemical reaction, carried out in a gaseous phase under isothermal conditions and without internal convective flow. Traditionally, in the mass-balance equations, the transport of reactants and products in a porous catalyst is introduced by the diffusion phenomenon in gaseous phase. The reaction rate then is written as a function of the reactant's and product's concentrations in gaseous phase [G.F. Froment, K.B. Bischoff, Chemical Reactor Analysis and Design, Wiley, New York, 1979]. However, in stationary conditions and with the hypothesis of the thermodynamic equilibrium between the gaseous and the adsorbed phase, the existence of a concentration gradient in the gaseous phase brings about a concentration gradient in the adsorbed phase. The diffusion process occurring in the adsorbed phase is usually neglected in the traditional modeling. The present work aims to investigate the influence of the considered diffusion processes on the evaluation of the performance of the catalyzed chemical reaction. The analysis is based on the study of a simple chemical reaction and consecutive reactions. The study shows that the flux of consumed reactant, evaluated by a traditional way could be different from the flux obtained with the diffusion in the adsorbed phase. Also, in these conditions the kinetic parameters obtained by the traditional modeling of the experimental results do not represent then the real kinetic parameters.

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1. Introduction

The analysis of a simple chemical transformation carried out in gaseous phase and catalyzed by a porous solid consists of the nine following steps (see Fig. 1).

- (a) Transport of reactants from the bulk fluid to the external surface of the catalyst pellet.
- (b) Diffusion transport of the reactant A in the catalyst pores.
- (c) Adsorption process (chemisorption) of the reactant A on the active catalytic site l ($A + l \leftrightarrow Al$).
- (d) Diffusion of the reactant Al in adsorbed phase.
- (e) Chemical reaction between the adsorbed molecules. The reaction takes place only in the adsorbed phase (e.g. $Al \rightarrow Rl$, $Rl \rightarrow Sl$).
- (f) Diffusion of the products in adsorbed phase.
- (g) Desorption of the products (e.g. $Rl \leftrightarrow R + l$, $Sl \leftrightarrow S + l$).
- (h) Diffusion transport of the products in the catalyst pores.
- (i) Transport of the products back to the bulk fluid.

Chemical engineering models of heterogeneous catalysis usually consist of the seven steps a–i [1]. Two additional steps d and f are used in that study, and their existence will be discussed here after. On the other hand, the diffusion between the bulk fluid and the gaseous phase in the catalytic pore (steps a and i) is not considered in this analysis.

The association of the steps c, e and g leads to the expression of the chemical reaction rate as a function of the reagent (and product) concentration in gaseous phase (see Eqs. (9) and (10)). The analysis of the performance is usually realized with the consideration that the diffusion transport takes place only in the gaseous phase [1]. However, there exists a gradient of concentration of the components in the gaseous phase of the catalyst pellet. In stationary conditions, the reactant and the products in the adsorbed phase remain in thermodynamic equilibrium with the gaseous phase composition. Also, the

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Nomenclature

(Al), (Rl), (Sl)	concentration of the components A, R, S in the adsorbed phase (mole m^{-3})
C_A, C_R, C_S	concentration of the components A, R, S in the gaseous phase (mole m^{-3})
D_A	apparent diffusivity in the adsorbed phase (m^2 s^{-1})
D_v	apparent diffusivity in the gaseous phase (m^2 s^{-1})
k_1, k_2	rate coefficients (m^3 kg^{-1} s^{-1})
K_A, K_R, K_S	equilibrium constants of adsorption of the components A, R, S (m^3 mole^{-1})
(l)	concentration of vacant sites (mole m^{-3})
(l_0)	total concentration of active sites (mole m^{-3})
L	size of the pellet (m)
m^*	Thiele modulus in adsorbed phase
M	Thiele modulus in gaseous phase
N_i	flux transferred in the gaseous phase (mole s^{-1} kg^{-1})
N_i^*	flux transferred in the adsorbed phase (mole s^{-1} kg^{-1})
$N_{i\,\max}$	maximal flux which can be transferred in chemical regime (mole s^{-1} kg^{-1})
N_t	total transferred flux (mole s^{-1} kg^{-1})

Greek symbols

η	effectiveness factor of the catalyst, determined for the gaseous phase
η_t	effectiveness factor of the catalyst when the two fluxes coexist
η^*	effectiveness factor of the catalyst determined for the adsorbed phase
ρ_a	apparent density of the catalyst (kg m^{-3})

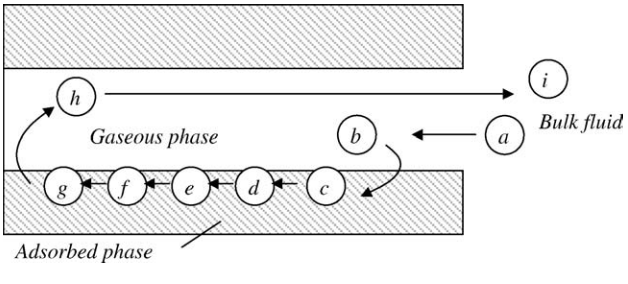

Fig. 1. Steps involved in the catalyzed chemical reaction.

concentration gradient in the gaseous phase leads necessarily to the existence of a gradient of the compositions for the adsorbed components. Consequently, a diffusion transport of the reagent and the product components occurs in the adsorbed phase (steps d and f). The concentration gradient is supposed only in the x-direction, the composition is assumed homogeneous in the z-direction (see Fig. 2). The diffusion flux in adsorbed phase is superposed then to this one in gaseous phase and it is interesting to study the influence of the transport in adsorbed phase on the evaluation of the performance of the catalytic particle.

The present analysis is realized for a simple reaction (1) and simple consecutive reactions (2) carried out in gaseous phase in stationary isothermal conditions:

$$A \rightarrow R \tag{1}$$

$$A \rightarrow R \rightarrow S \tag{2}$$

The work aims to show in these two cases the influence of the diffusion process in adsorbed phase on the evaluation of the performance of the catalyst. The analysis is based on the pellet model. The characteristic pellet length L (the distance from the particle center to the particle surface) is given by the relation $L = V_\mathrm{p}/S_\mathrm{p}$, V_p and S_p are respectively the external volume and area of the catalytic particle.

2. Mathematical formulation

When simple chemical reaction (1) or simple consecutive reactions (2) are considered, the reaction rate of transformation of the reagent A is supposed of first order with respect to the concentration of the adsorbed reactant:

$$r_1 = k_1(Al) \tag{3}$$

where r_1 introduces the reaction rate for unit weight of solid catalyst and k_1 is the reaction rate coefficient.

Considering the chemical reaction between the adsorbed molecules as determinant step, the adsorption and the desorption processes remain close to the thermodynamic equilibrium given by the following relations:

$$(Al) = K_A C_A (l) \tag{4}$$

$$(Rl) = K_R C_R (l) \tag{5}$$

and respectively for the consecutive reaction scheme given by Eq. (2):

$$(Sl) = K_S C_S (l) \tag{6}$$

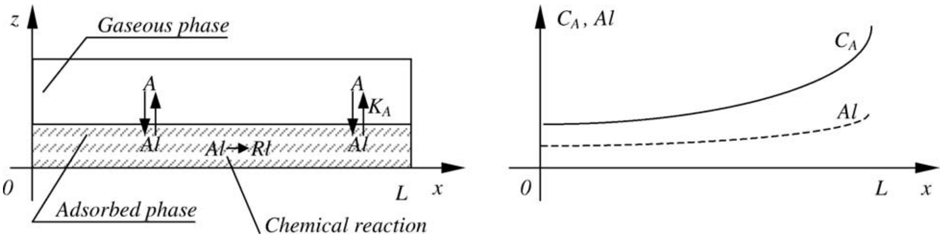

Fig. 2. Schematic representation of the existing thermodynamic equilibrium between the gaseous and the adsorbed phase, the resulting gradient and the present chemical reaction.

where K_A, K_R and K_S are the equilibrium constants. According to the conservation of the total number of active sites of the catalyst and taking into account relations (3)–(6) the total number of active site is given by Eq. (7):

$$(l_0) = (l) + (Al) + (Rl) = (l)(1 + K_A C_A + K_R C_R) \tag{7}$$

or respectively for the consecutive reactions (2) l_0 is expressed by Eq. (8):

$$\begin{aligned}(l_0) &= (l) + (Al) + (Rl) + (Sl)\\ &= (l)(1 + K_A C_A + K_R C_R + K_S C_S)\end{aligned} \tag{8}$$

The chemical reaction rate for the transformation of the reactant A can be then written as function of the concentration of the component's concentrations in gaseous phase:

$$r_1 = \frac{k_1 K_A C_A l_0}{1 + K_A C_A + K_R C_R} \tag{9}$$

$$r_1 = \frac{k_1 K_A C_A l_0}{1 + K_A C_A + K_R C_R + K_S C_S} \tag{10}$$

The expression of the reaction rate given by Eqs. (9) and (10) is classically used for the modeling of a catalytic particle.

When a gradient of concentration is present in the gaseous and adsorbed phase, a diffusion flux occurs consequently in each phase. The magnitude of the resulting fluxes depends on the concentration gradients and on the respective diffusion coefficients. In the following paragraphs the governing macroscopic mass-balance equations describing the functioning of a catalytic particle are written in the three cases given below:

- the fluxes in the gaseous and the adsorbed phases are of the same order of magnitude. The diffusion of constituents in the two phases has to be taken into account. This is the most general case;
- the diffusion of constituents occurs only in gaseous phase. This limit case supposes that the flux of constituents in the adsorbed phase is negligible. This situation is classically used in the treatment of the chemical reaction in gaseous phase catalyzed by a solid catalyst [1];
- the diffusion of constituents occurs only in adsorbed phase. The second limit case admits that the flux in the gaseous phase is supposed very weak.

2.1. *Modeling of catalyzed chemical reaction, when both the diffusions processes in the gaseous phase and in the adsorbed phase are taken into account*

The analysis is made with the assumption that the transport of the reactant A and the products R and S in the gaseous phase as in the adsorbed phase occurs only by diffusion. The apparent diffusivities in gaseous phase D_v and in adsorbed phase D_A are supposed equal for all the constituents. In stationary conditions, the mass balances of the reactant A and the products R (and S) are written as follows [2]:

$$D_\mathrm{v}\frac{\mathrm{d}^2 C_A}{\mathrm{d}x^2} + D_A\frac{\mathrm{d}^2 (Al)}{\mathrm{d}x^2} - k_1(Al)\rho_\mathrm{a} = 0 \tag{11}$$

$$D_\mathrm{v}\frac{\mathrm{d}^2 C_R}{\mathrm{d}x^2} + D_A\frac{\mathrm{d}^2 (Rl)}{\mathrm{d}x^2} + k_1(Al)\rho_\mathrm{a} = 0 \tag{12}$$

Respectively, for the case of consecutive reaction, the mass balance of the product R have to introduce the term of chemical transformation of R in S (13). The mass balance of the product S have to be added also (14):

$$D_\mathrm{v}\frac{\mathrm{d}^2 C_R}{\mathrm{d}x^2} + D_A\frac{\mathrm{d}^2 (Rl)}{\mathrm{d}x^2} + k_1(Al)\rho_\mathrm{a} - k_2(Rl)\rho_\mathrm{a} = 0 \tag{13}$$

$$D_\mathrm{v}\frac{\mathrm{d}^2 C_S}{\mathrm{d}x^2} + D_A\frac{\mathrm{d}^2 (Sl)}{\mathrm{d}x^2} + k_2(Rl)\rho_\mathrm{a} = 0 \tag{14}$$

where ρ_a is the apparent density of the catalyst. The coupled equations (11)–(14) are solved simultaneously using the finite volume method [3]. The boundary conditions are specified as follows:

- in the particle center ($x = 0$) the mass fluxes are null: $\frac{\mathrm{d}C_A}{\mathrm{d}x} = \frac{\mathrm{d}C_R}{\mathrm{d}x} = 0$ (and for the scheme (2) $\frac{\mathrm{d}C_S}{\mathrm{d}x} = 0$);
- at the surface of the catalytic particle ($x = L$) the concentrations of the reactant C_A and the products C_R (and C_S) are equal to those in the overflowing gas stream: $C_A = C_{A_i}$, $C_R = C_{R_i}$, $C_S = C_{S_i}$.

The resulting total fluxes given by Eqs. (15)–(17) are obtained numerically.

$$N_{\mathrm{t},A} = S_\mathrm{p}\left[D_\mathrm{v}\frac{\mathrm{d}C_A}{\mathrm{d}x} + D_A\frac{\mathrm{d}(Al)}{\mathrm{d}x}\right]_{x=L} \tag{15}$$

$$N_{\mathrm{t},R} = S_\mathrm{p}\left[D_\mathrm{v}\frac{\mathrm{d}C_R}{\mathrm{d}x} + D_A\frac{\mathrm{d}(Rl)}{\mathrm{d}x}\right]_{x=L} \tag{16}$$

$$N_{\mathrm{t},S} = S_\mathrm{p}\left[D_\mathrm{v}\frac{\mathrm{d}C_S}{\mathrm{d}x} + D_A\frac{\mathrm{d}(Sl)}{\mathrm{d}x}\right]_{x=L} \tag{17}$$

For every simulation it was verified that the sum of the fluxes (Eqs. (15)–(17)) is equal to zero. The maximal flux of the reactant A which can be transferred in is the flux which can occurs in chemical regime (Eq. (18)):

$$N_{i\,\mathrm{max}} = V_\mathrm{p} k_1 (Al)_i \rho_\mathrm{a} \tag{18}$$

The normalized fluxes will be called here for more simplicity the effectiveness factors. They are defined [1] as the ratio of the transferred flux of the respective constituents in the gaseous and the adsorbed phases (Eqs. (15)–(17)) to the maximal flux of the reactant A (Eq. (19)–(21)):

$$\eta_{\mathrm{t},A} = \frac{N_{\mathrm{t},A}}{N_{i\,\mathrm{max}}} \tag{19}$$

$$\eta_{\mathrm{t},R} = \frac{N_{\mathrm{t},R}}{N_{i\,\mathrm{max}}} \tag{20}$$

$$\eta_{\mathrm{t},S} = \frac{N_{\mathrm{t},S}}{N_{i\,\mathrm{max}}} \tag{21}$$

Usually in the literature, the effectiveness factor η_t is plotted as a function of the generalized Thiele modulus m^* which for the given reaction schemes is written as follows:

$$m^* = L\sqrt{\frac{r_1\rho_\mathrm{a}}{D_A(Al)_i}} \tag{22}$$

The chemical reaction rate in Eq. (22) is expressed by Eq. (3), for the two reaction schemes (1) and (2).

2.2. *Traditional modeling of catalyzed chemical reaction, when only the gaseous phase diffusion is considered*

Usually in the literature [1], the fluxes in adsorbed phase are considered very weak compared to the fluxes in the gaseous phase. With this hypothesis, traditional modeling takes into account only the gaseous phase diffusion process. In stationary conditions, the mass balances of the reactant A and the products R (and S) are given by Eqs. (23) and (24) for the simple reaction (1), and (23), (25), (26) for the consecutive reactions (2):

$$D_\mathrm{v}\frac{\mathrm{d}^2C_A}{\mathrm{d}x^2} - k_1(Al)\rho_\mathrm{a} = 0 \tag{23}$$

$$D_\mathrm{v}\frac{\mathrm{d}^2C_R}{\mathrm{d}x^2} + k_1(Al)\rho_\mathrm{a} = 0 \tag{24}$$

$$D_\mathrm{v}\frac{\mathrm{d}^2C_R}{\mathrm{d}x^2} + k_1(Al)\rho_\mathrm{a} - k_2(Rl)\rho_\mathrm{a} = 0 \tag{25}$$

$$D_\mathrm{v}\frac{\mathrm{d}^2C_S}{\mathrm{d}x^2} + k_2(Rl)\rho_\mathrm{a} = 0 \tag{26}$$

The coupled equations (23)–(26) are solved numerically with specified boundary conditions:

- at $x = 0$ the mass fluxes are null: $\frac{\mathrm{d}C_A}{\mathrm{d}x} = \frac{\mathrm{d}C_R}{\mathrm{d}x} = \frac{\mathrm{d}C_S}{\mathrm{d}x} = 0$;
- at $x = L$ the concentrations are respectively: $C_A = C_{A_i}$, $C_R = C_{R_i}$, $C_S = C_{S_i}$.

The fluxes of the consumed reactant are defined by Eqs. (27) and (28) and are also obtained numerically:

$$N_{i,A} = S_\mathrm{p}D_\mathrm{v}\left(\frac{\mathrm{d}C_A}{\mathrm{d}x}\right)_{x=L} \tag{27}$$

$$N_{i,R} = S_\mathrm{p}D_\mathrm{v}\left(\frac{\mathrm{d}C_R}{\mathrm{d}x}\right)_{x=L} \tag{28}$$

$$N_{i,S} = S_\mathrm{p}D_\mathrm{v}\left(\frac{\mathrm{d}C_S}{\mathrm{d}x}\right)_{x=L} \tag{29}$$

The effectiveness factors, η_A, η_R and η_S are calculated in the same manner than the in the previous (Eqs. (19)–(21)) as the ratio between the consumed respective consumed flux and the maximal flux of the reactant A (Eq. (18)).

2.3. *Modeling of a catalyzed chemical reaction, when only the adsorbed phase diffusion is considered*

Let us study now the evaluation of the performance of the reaction catalyzed by a porous solid when the diffusion transport of the reactant A and the product R (and S) occurs only in the adsorbed phase. This case considers that the gaseous phase fluxes is very weak compared to the adsorbed phase flux. The mass balances in stationary conditions are written here after:

$$D_\mathrm{A}\frac{\mathrm{d}^2(Al)}{\mathrm{d}x^2} - k_1(Al)\rho_\mathrm{a} = 0 \tag{30}$$

$$D_\mathrm{A}\frac{\mathrm{d}^2(Rl)}{\mathrm{d}x^2} + k_1(Al)\rho_\mathrm{a} = 0 \tag{31}$$

and respectively:

$$D_\mathrm{A}\frac{\mathrm{d}^2(Rl)}{\mathrm{d}x^2} + k_1(Al)\rho_\mathrm{a} - k_2(Rl)\rho_\mathrm{a} = 0 \tag{32}$$

$$D_\mathrm{A}\frac{\mathrm{d}^2(Sl)}{\mathrm{d}x^2} + k_2(Rl)\rho_\mathrm{a} = 0 \tag{33}$$

The boundary conditions are specified as follows:

- in $x = 0$, the mass fluxes are null: $\frac{\mathrm{d}(Al)}{\mathrm{d}x} = \frac{\mathrm{d}(Rl)}{\mathrm{d}x} = \frac{\mathrm{d}(Sl)}{\mathrm{d}x} = 0$;
- at $x = \mathrm{L}$, the component concentrations are obtained with respect to the equilibrium conditions (Eqs. (4)–(6)): $(Al)_i = K_\mathrm{A}C_{A_i}(l)$, $(Rl)_i = K_RC_{R_i}(l)$, $(Sl)_i = K_SC_{S_i}(l)$. The number of free active sites (l) is obtained according to Eqs. (7) and (8).

The coupled equations (30)–(33) are solved numerically. Eq. (30) can be solved also analytically and the (Al) profile over the pellet is given by Eq. (34):

$$(Al) = (Al)_i\frac{\cosh\left[\left(\sqrt{\frac{k_1\rho_\mathrm{a}}{D_A}}\right)x\right]}{\cosh\left[\left(\sqrt{\frac{k_1\rho_\mathrm{a}}{D_A}}\right)L\right]} \tag{34}$$

The flux of the reactant consumed in adsorbed form (Al) can be obtained directly by deriving Eq. (34):

$$\begin{aligned} N^*_{i,A} &= S_\mathrm{p}D_A\left(\frac{\mathrm{d}(Al)}{\mathrm{d}x}\right)_{x=L} \\ &= S_\mathrm{p}D_A(Al)_i\sqrt{\frac{k_1\rho_\mathrm{a}}{D_A}}\,\mathrm{th}\left(\sqrt{\frac{k_1\rho_\mathrm{a}}{D_A}}L\right) \end{aligned} \tag{35}$$

The product fluxes are calculated from the numerical results by Eqs. (36) and (37):

$$N^*_{i,R} = S_\mathrm{p}D_\mathrm{v}\left(\frac{\mathrm{d}(Rl)}{\mathrm{d}x}\right)_{x=L} \tag{36}$$

$$N^*_{i,S} = S_\mathrm{p}D_\mathrm{v}\left(\frac{\mathrm{d}(Sl)}{\mathrm{d}x}\right)_{x=L} \tag{37}$$

The symbol "*" is used to describe the adsorbed phase. The effectiveness factors η^*_A, η^*_R and η^*_S are defined as the ratio of the transferred flux in the adsorbed phase to the maximal flux which can be transferred in chemical regime $N_{i\,\max}$.

3. Numerical resolution

The differential equations presented in the previous section are solved by the finite volume method described by [3]. The

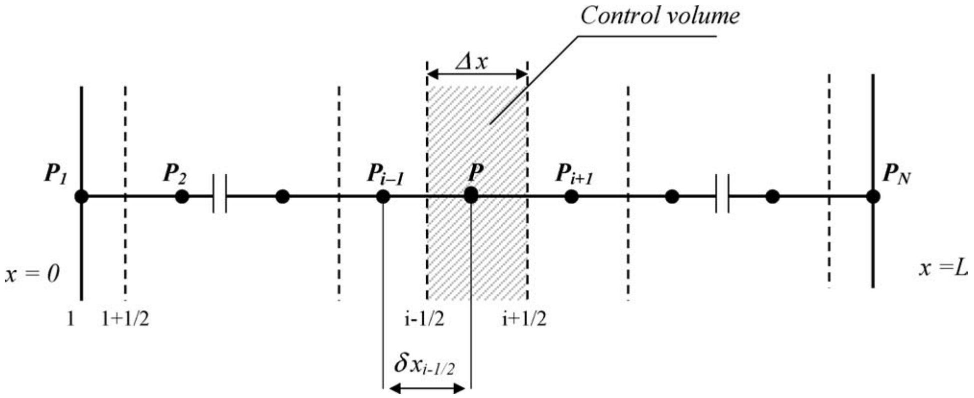

Fig. 3. Grid of points covering the integration domain.

integration domain is recovered by a grid of points P_i. A control volume is constructed around each point P_i (see Fig. 3). The surfaces of these volumes are commune for two adjacent volumes. The fluxes are evaluated through these surfaces.

The discretization aims on focusing attention on the values at the grid points. The continuous information contained in the exact solution of the differential equations is replaced with the discrete values at each grid point P_i. The discretization concept makes possible to replace the governing differential equations with simple algebraic equations, which can be solved with relative ease. When the number of grid points covering the integration domain is large enough, the solution of the discretization equations is expected to approach the exact solution on the differential equations. The most attractive feature of the control-volume formulation is that the resulting solution would imply that the integral conservation of quantity such as mass is exactly satisfied over any group of control volumes and over whole the calculation domain.

Fig. 3 shows the characteristics of the control volume surrounding a grid point P_i situated at half distance of the volume surfaces (dashed lines) with coordinates "$i-1/2$" and "$i+1/2$". A regular grid is applied here. Δx_i represents the control volume width and $\delta x_{i-1/2}$ denotes the distance between the two adjacent grid points P_i and P_{i-1}.

The discretization method will be illustrated using the steady state equation (23), which can be written in a simplest way:

$$D_{\mathrm{v}}\frac{\mathrm{d}^2C_A}{\mathrm{d}x^2}-S=0 \tag{38}$$

Here, the term introducing the chemical reaction $S=-k_1(\mathrm{A}l)\rho_{\mathrm{a}}$ is treated as a source term. In order to derive the discretization equation the grid point scheme given by Fig. 3 is used. The attention is focused on the grid point P_i and its neighbors points P_{i-1} and P_{i+1}. The integration of Eq. (38) over the control volume gives:

$$\left(D_{\mathrm{v}}\frac{\mathrm{d}C_A}{\mathrm{d}x}\right)_{i+1/2}-\left(D_{\mathrm{v}}\frac{\mathrm{d}C_A}{\mathrm{d}x}\right)_{i-1/2}+\int_{i-1/2}^{i+1/2}S\,\mathrm{d}x=0 \tag{39}$$

It is assumed that the value of C_A at a given grid point prevails over the control volume surrounding it. The discretization equation takes then the form:

$$\frac{D_{\mathrm{v},i+1/2}(C_{A,P_{i+1}}-C_{A,P_i})}{\delta x_{i+1/2}}-\frac{D_{\mathrm{v},i-1/2}(C_{A,P}-C_{A,P_{i-1/2}})}{\delta x_{i-1/2}}+\bar{S}\Delta x_i=0 \tag{40}$$

where $C_{A,P_{i+1}}$ is the concentration of the reactant at the grid point P_i and will be denoted afterward by simplicity as C_i. $\bar{S}$ is the averaged value of S over the control volume. In our study, the diffusivity is considered constant and equal to D_{v} for the entire integration domain. It is useful to cast Eq. (40) in the following form:

$$a_iC_i=a_{i+1}C_{i+1}+a_{i-1}C_{i-1}+b \tag{41}$$

where

$$a_{i+1}=\frac{D_{\mathrm{v}}}{\delta x_{i+1/2}} \tag{42}$$

$$a_{i-1}=\frac{D_{\mathrm{v}}}{\delta x_{i-1/2}} \tag{43}$$

$$a_i=a_{i+1}+a_{i-1} \tag{44}$$

$$b=\bar{S}\Delta x \tag{45}$$

The solution of the discretization equations for the one-dimensional situation can be solved by the standard Gaussian-elimination method.

4. Numerical simulation and results

The present work aims on comparing the flux of consumed reactant when the diffusion process is considered simultaneously in the gaseous and the adsorbed phases with the two limit cases where only the gaseous phase flux or the adsorbed phase flux are considered. As it was underlined in the introduction, the chemical reaction always occurs in the adsorbed phase on the catalytic surface. The study is realized for steady state conditions (gas temperature is equal to 400 °C and pressure equal to 1 atm). The surface concentration of the reactant A and the reaction products R and S are respectively $C_{A_i}=12\,\mathrm{mole\,m^{-3}}$, $C_{R_i}=8\,\mathrm{mole\,m^{-3}}$ and $C_{S_i}=4\,\mathrm{mole\,m^{-3}}$.

The equilibrium constant are fixed to $K_A = 0.0333\,\mathrm{m^3\,mole^{-1}}$, $K_R = 0.0250\,\mathrm{m^3\,mole^{-1}}$ $K_S = 0.02\,\mathrm{m^3\,mole^{-1}}$. The pellet size used in this study is equal to $L = 5 \times 10^{-4}$ m and the apparent density of the catalyst $\rho_a = 1500\,\mathrm{kg\,m^{-3}}$. The apparent diffusivity in the gaseous phase is fixed to be $D_v = 10^{-7}\,\mathrm{m^2\,s^{-1}}$, and the study have been carried out for diffusivity ratios D_A/D_v less then 1 and respectively equal to 10^{-1}, 10^{-2} and 10^{-3}. The reason to choice such diffusivity ratios is that in the adsorbed phase the diffusivity of constituents can be close to the liquid phase diffusivity. Consequently, the ratio D_A/D_v is expected to be close to 10^{-3}. As this study aims on underline the importance of the consideration of both the gaseous and the adsorbed phases fluxes the simulation is made in bringing some values included between a limit case ($D_A/D_v = 10^{-1}$) to a realistic one ($D_A/D_v = 10^{-3}$). For the consecutive reactions, it has be chosen that the reaction rate coefficients are related by $k_1 = 2k_2$.

The effectiveness factors η, η^* and η_t are calculated for a large range of Thiele modulus and plotted as a function of the Thiele modulus characterizing the adsorbed phase m^* (Eq. (22)) in view of the fact that the reaction occurs in this phase. Results concerning the effectiveness of the consumed flux of the reactant A by a simple chemical reaction are presented in Fig. 4a–c. Results η_A, η_A^* and $\eta_{t,A}$ for the consecutive reactions are shown in Fig. 5a–c.

For the two reaction schemes (Eqs. (1) and (2)) it can be observed in Figs. 4a–c and 5a–c that in chemical regime (for

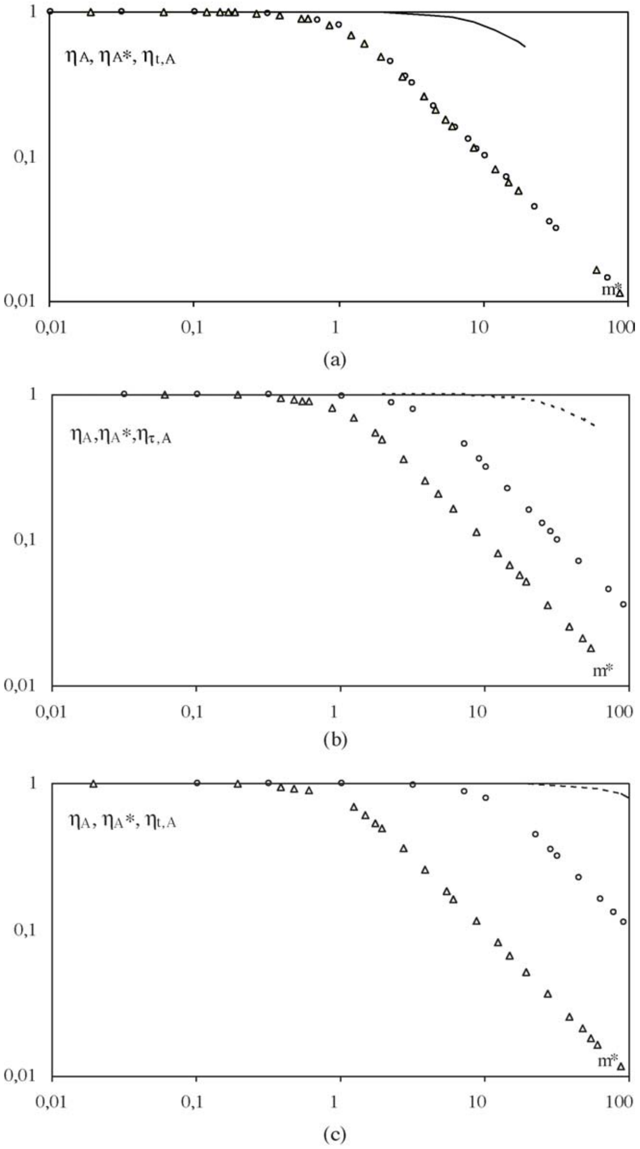

Fig. 4. (a) Effectiveness factors obtained with a simple reaction for $D_A/D_v = 10^{-1}$ (◯, η_A; Δ, η_A^*; −−−, $\eta_{t,A}$). (b) Effectiveness factors obtained with a simple reaction for $D_A/D_v = 10^{-2}$ (◯, η_A; Δ, η_A^*; −−−, $\eta_{t,A}$). (c) Effectiveness factors obtained with a simple reaction for $D_A/D_v = 10^{-3}$ (◯, η_A; Δ, η_A^*; −−−, $\eta_{t,A}$).

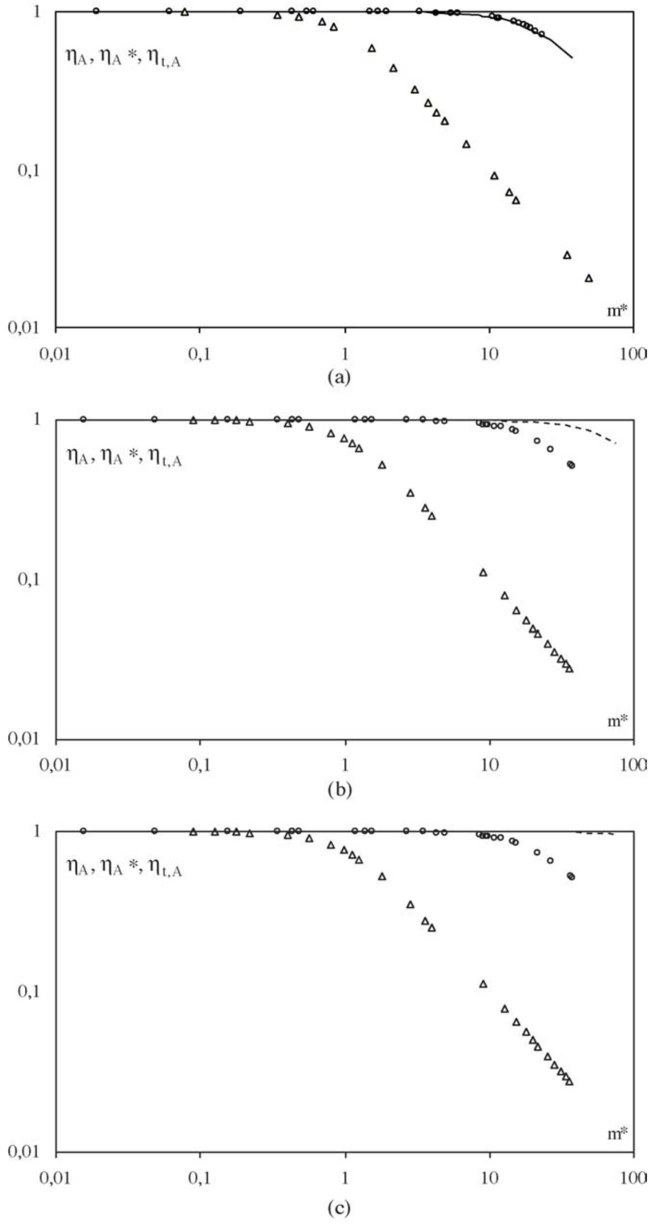

Fig. 5. (a) Effectiveness factors obtained with consecutive reactions for $D_A/D_v = 10^{-1}$ (◯, η_A; Δ, η_A^*; −−−, $\eta_{t,A}$). (b) Effectiveness factors obtained with consecutive reactions for $D_A/D_v = 10^{-2}$ (◯, η_A; Δ, η_A^*; −−−, $\eta_{t,A}$). (c) Effectiveness factors obtained with consecutive reactions for $D_A/D_v = 10^{-3}$ (◯, η_A; Δ, η_A^*; −−−, $\eta_{t,A}$).

small values of m^*), the consumed fluxes are identical and the effectiveness factors are very close to 1 whatever the considered diffusions. Even though, in the intermediate and diffusion regime, the obtained consumed fluxes are quite different. The difference depends on the ratio between the reactant's apparent diffusivity in adsorbed (D_A) and gaseous phase (D_v) and the trend of numerical result is different according to the investigated reaction scheme. When a simple chemical reaction is considered, apart from the chemical regime, the consumed fluxes are different for the three described cases of diffusion taken into account. Fig. 5a concerns the scheme of consecutive chemical reactions characterized by chemical reaction rate coefficients such that $k_1 = 2k_2$ for small values of the ratio $D_A/D_\mathrm{v} = 10^{-1}$. The consumed flux of the reactant A when the coexistence of the diffusion processes is considered is equivalent to the consumed flux when only the gaseous phase diffusion is taken into account in this case. The differences appear in the intermediate and the diffusion regime for values of D_A/D_v equal to 10^{-2} and 10^{-3}. The consumed flux when both diffusion fluxes coexist (Eq. (11)) is always greater then these obtained when every diffusion process is considered separately. These numerical results allow concluding that the diffusion in the adsorbed phase could not be neglected and in general for given operating conditions, the fluxes of consumed reactant are not identical.

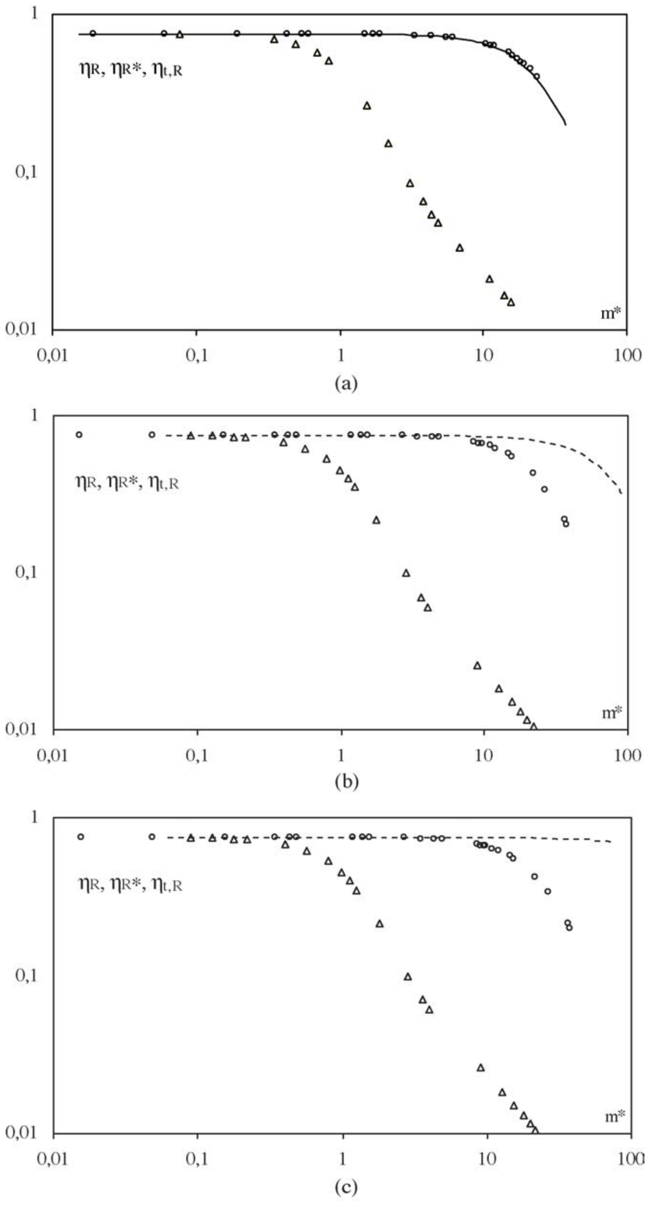

Fig. 6. (a) Effectiveness factors obtained with consecutive reactions for $D_A/D_\mathrm{v} = 10^{-1}$ (◯, η_R; Δ, η_R^*; −−−, $\eta_{\mathrm{t},R}$). (b) Effectiveness factors obtained with consecutive reactions for $D_A/D_\mathrm{v} = 10^{-2}$ (◯, η_R; Δ, η_R^*; −−−, $\eta_{\mathrm{t},R}$). (c) Effectiveness factors obtained with consecutive reactions for $D_A/D_\mathrm{v} = 10^{-3}$ (◯, η_R; Δ, η_R^*; −−−, $\eta_{\mathrm{t},R}$).

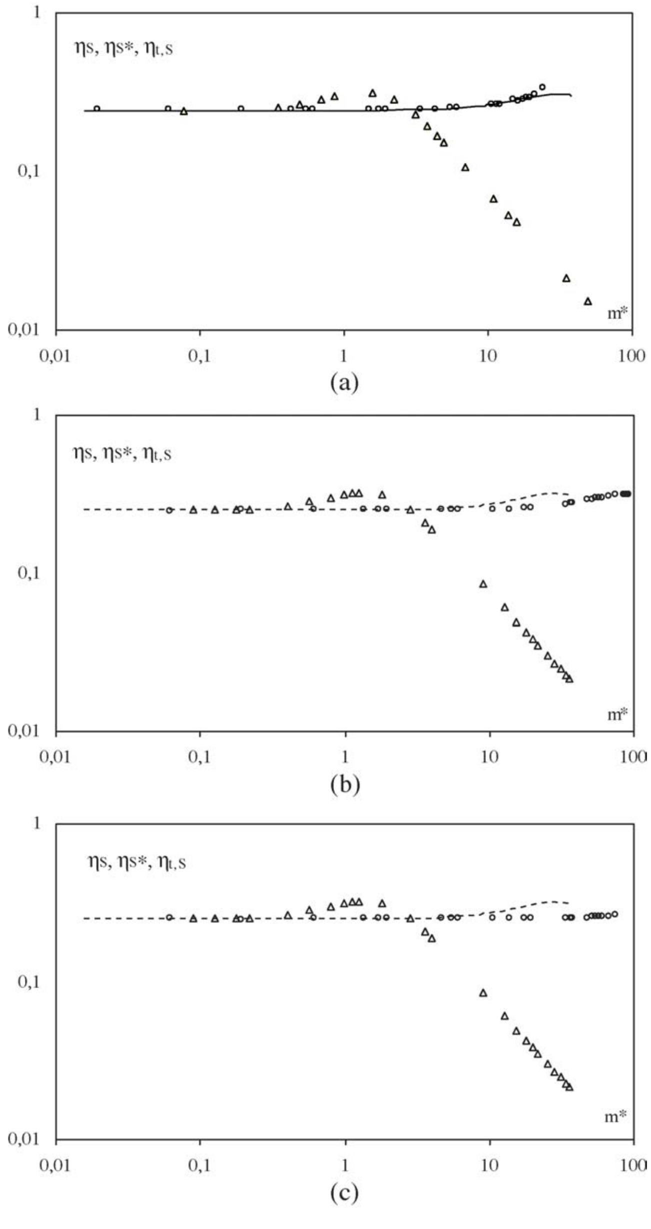

Fig. 7. (a) Effectiveness factors obtained with consecutive reactions for $D_A/D_\mathrm{v} = 10^{-1}$ (◯, η_S; Δ, η_S^*; −−−, $\eta_{\mathrm{t},S}$). (b) Effectiveness factors obtained with consecutive reactions for $D_A/D_\mathrm{v} = 10^{-1}$ (◯, η_S; Δ, η_S^*; −−−, $\eta_{\mathrm{t},S}$). (c) Effectiveness factors obtained with consecutive reactions for $D_A/D_\mathrm{v} = 10^{-1}$ (◯, η_S; Δ, η_S^*; −−−, $\eta_{\mathrm{t},S}$).

Fig. 6a–c shows the calculated normalised fluxes for the product R when for the consecutive reaction scheme, and Fig. 7a–c represents the normalised fluxes for the secondary product S. The analysis of the normalised fluxes of the intermediate product R is similar to the previous one. Numerical results depend of the fluxes considered in the mass balance equation. For the product of the secondary reaction S, performed with the reaction rate coefficients ratio $k_1 = 2k_2$ the influence of the considered diffusion in less sensible.

5. Conclusion

According to the obtained results we can deduce that if the diffusion of components in adsorbed phase is neglected, the kinetic parameters obtained from the experimental results in a catalytic bed of particles do not represent the real kinetic parameters. Therefore, it is necessary to introduce simultaneously the diffusion in the gaseous and the adsorbed phase and to keep in mind that the estimations of the apparent diffusivities of the constituents in gaseous and adsorbed phase are required.

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