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ORIGINAL PAPER

Spillover in monomer–monomer reactions on supported catalysts: dynamic mean-field study

V. Skakauskas · P. Katauskis

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Abstract The kinetics of a $A_1 + A_2 \rightarrow A_1A_2$ reaction on supported catalysts is investigated numerically using a phenomenological model which includes: the bulk diffusion of reactants from a bounded vessel towards the adsorbent and the product bulk one into the same vessel, adsorption and desorption of reactants molecules, and surface diffusion of adsorbed particles. The model is based on the Langmuir–Hinshelwood surface reaction mechanism coupled with the Eley–Rideal step. The model based only on the Langmuir–Hinshelwood mechanism is also studied. Simulations were performed using the finite difference technique. Three cases of reactants adsorption are considered: each reactant can adsorb on the active in reaction catalyst surface and inactive support, one of reactants adsorbs on the catalyst surface while the other one adsorbs on the support, both reactants adsorb only on the support. The surface diffusion and catalytic surface size influence on the catalytic reactivity of a supported catalyst is studied.

Keywords Heterogeneous reactions · Adsorption · Desorption · Surface diffusion · Spillover

1 Introduction

Heterogeneous catalytic reactions constitute around 90 % of all processes in the chemical industry [1]. Modelling of catalytic processes plays a central role in study of kinetics in heterogeneous catalysis and catalysts design in chemical industry [1–5]. The rate constants of kinetic processes are usually obtained either from single crystal studies

V. Skakauskas (✉) · P. Katauskis
Faculty of Mathematics and Informatics, Vilnius University,
Naugarduko 24, 03225 Vilnius, Lithuania
e-mail: vladas.skakauskas@maf.vu.lt

or experimentally from real catalysts [6]. The latter consist of small active catalyst particles placed on inactive in reaction supports. One of kinetic effects associated with small catalyst particles on a support is the spillover effect. Spillover is an effect accompanying heterogeneous surface reactions when inactive in reactions surface regions significantly influence the kinetics of the overall catalytic process [7]. It is caused by the fact that parts of the surface which are inactive in the surface reaction can be active for other processes that occur during the catalytic process, i.e. adsorption–desorption process and increase or decrease concentrations of either substrate or product particles on active parts of the surface through the diffusion of the adsorbed reactant particles across the interface between the catalyst particles and the support [1,7,8]. The term "spillover" originally was used only for diffusion from active in reaction particles onto a support, whereas the diffusion in reverse direction is called "reverse-spillover" [4,9–11]. In the present paper the term spillover will be used for diffusion in both directions. The spillover effect is observed and plays a key role in catalytic reactions on supported metal catalysts [4,9]. The bibliography of the current state of theoretical research of reactions with spillover effects include: experimental works [12–19], papers based on the Monte Carlo simulations technique [7,9,20,21], numerical solving of mean-field models [22–25], and the analytical description of such effect [2,6]. In [20], the uni-molecular $A \rightarrow B$ and bimolecular $2A \rightarrow B$ reversible reactions are studied on heterogeneous surfaces consisting of active and inactive in reaction sites.

In [7,9,21], the three-molecular $2A + B_2 \rightarrow 2AB$ reaction which models the CO oxidation on Pd/Al_2O_3 heterogeneous catalyst, is studied. In [22,23], these reactions are studied numerically by using mean-field equations for the steady-state case. The long-range surface diffusion influence on the uni-molecular reactions proceeding on the heterogeneous catalysts is studied numerically in [24,25]. Under some restrictions on rate constants and ratio of reactants pressures authors of [2] derived approximate analytical formulas to describe dynamics of $2A + B_2 \rightarrow 2AB$ reaction with spillover effect. Using analytical methods and scaling concepts a model for steady-state uni-molecular reactions on supported catalysts including reactant adsorption, desorption, and diffusion of adsorbed particles is examined in [1].

In this paper, by employing a mean-field model and its numerical simulations we consider a monomer–monomer heterogeneous reaction, $A_1 + A_2 \rightarrow B$, $B = A_1A_2$, on a supported (composite) catalyst taking into account: the bulk diffusion of both reactants from a bounded vessel with an impermeable boundary toward the adsorbent and the reaction product bulk one from the adsorbent into the same vessel, adsorption, desorption, and surface diffusion of adsorbed particles of each reactant. The model is based on the Langmuir–Hinshelwood surface reaction mechanism coupled with the Eley–Rideal step. In particular, the model based only on the Langmuir–Hinshelwood mechanism is studied. Adsorption, desorption, and surface diffusion are allowed to proceed at a constant temperature and the product desorption is assumed to be instantaneous. We consider three adsorption cases of reactants A_1 and A_2: (i) each reactant can adsorb on both active catalyst particle and inactive support, (ii) one of reactants A_1 and A_2 adsorbs on the catalyst particle while the other one adsorbs on the inactive in reaction support, (iii) both reactants adsorb only on the inactive support. The goal of this paper is a numerical study of the surface diffusion and catalytic particle size influence on the catalytic reactivity of supported catalysts.

The paper is organized as follows. In Sect. 2 we present the model. In Sect. 3 we discuss numerical results. A summary of main results in Sect. 4 concludes the paper.

2 The model

To study the problem of two-molecular catalytic heterogeneous reaction, $A_1 + A_2 \to B$, proceeding on a supported catalyst we use a mean-field approach. Assume that reactants A_1, A_2 and product $B = A_1A_2$ of concentrations $a_1(t, x)$, $a_2(t, x)$, and $b(t, x)$ occupy a bounded domain $\Omega = \{x = (x_1, x_2, x_3) : x_i \in [0, l],\ i = 1, 2, 3\}$ with boundary $\tilde{S} = S_1 \cup S_2$, where $S_2 = \{x = (x_1, x_2, x_3) : x_i \in [0, l],\ i = 1, 3, x_2 = 0\}$ and $S_1 = \tilde{S} \setminus S_2$. Here t is time, x is a position, S_2 is the surface of the adsorbent, and S_1 is a surface impermeable to the reactants and product. Obviously, $x_2 > 0$ for S_1. Let $s_2(x)$ and $s_1(x)$, $x = (x_1, x_3) \in S_2$, be the surface densities of the active and inactive sites in the surface reaction, respectively. Assume that $u_{i2} = s_2\theta_{i2}$ and $u_{i1} = s_1\theta_{i1}$, $\theta_{ij}(t, x) \in [0, 1]$, $j = 1, 2$, are the densities of the active and inactive in reaction sites occupied by the adsorbed molecules of reactant A_i, $i = 1, 2$. Then $s_j(1-\theta_{ij})$, $i, j = 1, 2$, are the densities of the free sites. Since according to Langmuir one molecule adsorbs on only one adsorption site, function u_{ij} also present density of molecules of reactant A_i adsorbed on sites of type j ($j = 1$ for inactive sites, $j = 2$ for active ones) that are located at point x. Assume that $S_2 = S_{22} \cup S_{21}$ where $S_{22} = \{(x_1, x_2, x_3) : x_1 \in [0, x_*),\ x_2 = 0,\ x_3 \in [0, l]\}$ and $S_{21} = \{(x_1, x_2, x_3) : x_1 \in (x_*, l],\ x_2 = 0,\ x_3 \in [0, l]\}$, $x_* \in (0, l)$, are planes consisting of the active and inactive sites, respectively. Let k_{ij} and k_{-ij} be the adsorption and desorption rates constants and let κ_{ij}, $i, j = 1, 2$, be the surface diffusivity of adsorbed particles of reactant A_i on the surface S_{2j}. To simplify the model we restrict ourselves to the case where densities s_1 and s_2 depend only on variable x_1 and the initial values a_1^0 and a_2^0 of concentrations a_1 and a_2 are constants. In this case we can reduce the three-dimensional problem into two-dimensional one. Let $\lambda_{1,i2}$, $i = 1, 2$, be the constant of the jump rate via the catalyst-support interface x_* of an adsorbed A_i particle from the active position $x_* - 0$ into the nearest-neighbour vacant inactive site $x_* + 0$. Similarly, let $\lambda_{2,i1}$, $i = 1, 2$, be the constant of the jump rate via the catalyst-support of an adsorbed A_i particle from the inactive position $x_* + 0$ into the nearest-neighbour vacant active site $x_* - 0$.

To construct the model we employ the Langmuir–Hinshelwood (LH) mechanism

$$A_1 + S \underset{k_{-1j}}{\overset{k_{1j}}{\rightleftarrows}} A_1S, \quad A_2 + S \underset{k_{-2j}}{\overset{k_{2j}}{\rightleftarrows}} A_2S, \quad A_1S + A_2S \xrightarrow{k_3} A_1A_2 + 2S.$$

Here S is the adsorption site and k_3 is the reaction between A_1S and A_2S rate constant in LH step. In principle the product $B = A_1A_2$ formation may occur via one or both Eley–Rideal (ER) steps

$$A_1 + A_2S \xrightarrow{k_1} A_1A_2 + S, \quad A_2 + A_1S \xrightarrow{k_2} A_1A_2 + S$$

where k_1 is the reaction between A_1 and A_2S rate constant and k_2 is the reaction between A_2 and A_1S rate one. Assuming that product desorption is instantaneous and employing the LH and ER mechanisms we get the following system for densities u_{ij}:

$$\begin{cases} \partial_t u_{11} = k_{11}a_1(s_1 - u_{11} - u_{21}) - k_{-11}u_{11} + \kappa_{11}\frac{\partial^2 u_{11}}{\partial x_1^2}, \quad x_1 \in (x_*, l), \\ \partial_t u_{21} = k_{21}a_2(s_1 - u_{11} - u_{21}) - k_{-21}u_{21} + \kappa_{21}\frac{\partial^2 u_{21}}{\partial x_1^2}, \quad x_1 \in (x_*, l), \\ \partial_t u_{12} = k_{12}a_1(s_2 - u_{12} - u_{22}) - k_{-12}u_{12} - k_3u_{12}u_{22} - k_2a_2u_{12} \\ \qquad + \kappa_{12}\frac{\partial^2 u_{12}}{\partial x_1^2}, \quad x_1 \in (0, x_*), \\ \partial_t u_{22} = k_{22}a_2(s_2 - u_{12} - u_{22}) - k_{-22}u_{22} - k_3u_{12}u_{22} - k_1a_1u_{22} \\ \qquad + \kappa_{22}\frac{\partial^2 u_{22}}{\partial x_1^2}, \quad x_1 \in (0, x_*), \end{cases} \tag{1}$$

Here ∂_t signifies the partial derivative with respect to time. We add to this system the initial

$$u_{ij}(0, x_1) = 0, \quad i, j = 1, 2, \tag{2}$$

and boundary conditions at points $x_1 = 0$, $x_1 = x_*$, and $x_1 = l$,

$$\begin{cases} \left.\frac{\partial u_{12}}{\partial x_1}\right|_{x_1=0} = \left.\frac{\partial u_{22}}{\partial x_1}\right|_{x_1=0} = 0, \\ \left.\frac{\partial u_{11}}{\partial x_1}\right|_{x_1=l} = \left.\frac{\partial u_{21}}{\partial x_1}\right|_{x_1=l} = 0, \end{cases} \tag{3}$$

$$\begin{cases} \kappa_{11}\left.\frac{\partial u_{11}}{\partial x_1}\right|_{x_*+0} = \kappa_{12}\left.\frac{\partial u_{12}}{\partial x_1}\right|_{x_*-0} = \lambda_{2,11}u_{11}|_{x_*+0}(s_2 - u_{12} - u_{22})|_{x_*-0} \\ \qquad\qquad - \lambda_{1,12}u_{12}|_{x_*-0}(s_1 - u_{11} - u_{21})|_{x_*+0}, \\ \kappa_{21}\left.\frac{\partial u_{21}}{\partial x_1}\right|_{x_*+0} = \kappa_{22}\left.\frac{\partial u_{22}}{\partial x_1}\right|_{x_*-0} = \lambda_{2,21}u_{21}|_{x_*+0}(s_2 - u_{12} - u_{22})|_{x_*-0} \\ \qquad\qquad - \lambda_{1,22}u_{22}|_{x_*-0}(s_1 - u_{11} - u_{21})|_{x_*+0}. \end{cases} \tag{4}$$

The first terms (gain fluxes) on the right-hand side of Eq. (4) are conditioned by the jumps via the catalyst-support interface x_* of the escaped molecules of reactant A_i, $i = 1, 2$, form the inactive position, $x_* + 0$, of the support to the nearest-neighbour vacant active one, $x_* - 0$, of the catalyst. Similarly, the other two terms (loss fluxes) on the right-hand side of Eq. (4) are conditioned by the jumps via the catalyst-support interface of the escaped molecules of the same reactant from the active position $x_* - 0$ of the catalyst to the nearest-neighbour vacant inactive one, $x_* + 0$, of the support.

Diffusion of the reactants A_1 and A_2 toward the adsorbent and the product B from the adsorbent away into the same vessel is described by the systems:

$$\begin{cases} \partial_t a_1 = \kappa_{a_1}\left(\frac{\partial^2 a_1}{\partial x_1^2} + \frac{\partial^2 a_1}{\partial x_2^2}\right), \quad (x_1, x_2) \in (0, l) \times (0, l), \\ \partial_n a_1|_{S_1} = 0, \\ \partial_n a_1 = -(k_{11} a_1 (s_1 - u_{11} - u_{21}) - k_{-11} u_{11})/\kappa_{a_1}, \\ \quad x_1 \in (x_*, l), \ x_2 = 0, \\ \partial_n a_1 = -(k_{12} a_1 (s_2 - u_{12} - u_{22}) - k_{-12} u_{12} + k_1 a_1 u_{22})/\kappa_{a_1}, \\ \quad x_1 \in (0, x_*), \ x_2 = 0, \\ a_1(0, x) = a_{10}(x), \end{cases} \tag{5}$$

$$\begin{cases} \partial_t a_2 = \kappa_{a_2}\left(\frac{\partial^2 a_2}{\partial x_1^2} + \frac{\partial^2 a_2}{\partial x_2^2}\right), \quad (x_1, x_2) \in (0, l) \times (0, l), \\ \partial_n a_2|_{S_1} = 0, \\ \partial_n a_2 = -(k_{21} a_2 (s_1 - u_{11} - u_{21}) - k_{-21} u_{21})/\kappa_{a_2}, \\ \quad x_1 \in (x_*, l), \ x_2 = 0, \\ \partial_n a_2 = -(k_{22} a_2 (s_2 - u_{12} - u_{22}) - k_{-22} u_{22} + k_2 a_2 u_{12})/\kappa_{a_2}, \\ \quad x_1 \in (0, x_*), \ x_2 = 0, \\ a_2(0, x) = a_{20}(x), \end{cases} \tag{6}$$

$$\begin{cases} \partial_t b = \kappa_b\left(\frac{\partial^2 b}{\partial x_1^2} + \frac{\partial^2 b}{\partial x_2^2}\right), \quad (x_1, x_2) \in (0, l) \times (0, l), \\ \partial_n b|_{S_1} = 0, \\ \partial_n b = (k_3 u_{12} u_{22} + k_1 a_1 u_{22} + k_2 a_2 u_{12})/\kappa_b, \quad x_1 \in (0, x_*), \ x_2 = 0, \\ \partial_n b = 0, \quad x_1 \in (x_*, l), \ x_2 = 0, \\ b(0, x) = 0. \end{cases} \tag{7}$$

Here $\partial_n f$, $f = a_1, a_2, b$, is the outward normal derivative. System (1)–(7) possesses two conservation laws

$$\int_\Omega (a_i + b)\,\mathrm{d}x + \int_0^{x_*} u_{i2}\,\mathrm{d}x_1 + \int_{x_*}^{l} u_{i1}\,\mathrm{d}x_1 = \int_\Omega a_{i0}\,\mathrm{d}x, \quad i = 1, 2. \tag{8}$$

Coupled system (1)–(7) determines densities u_{ij} (or surface coverages θ_{ij}) for all $x \in S_2$ and concentrations a_1, a_2, and b of reactants A_1, A_2 and product B for all $x \in \Omega$ and $t > 0$.

We also study system (1)–(4) with given concentrations a_1 and a_2 at the surface S_2.

The main characteristic that we study is the surface S_2 specific conversion rate of the reactants molecules into the product ones (turn-over rate or turn-over frequency) determined by the formula

$$z = \int_0^{x_*} (k_3 u_{12} u_{22} + k_1 a_1 u_{22} + k_2 a_2 u_{12})\,\mathrm{d}x_1 \Big/ \int_0^{x_*} s_2\,\mathrm{d}x_1. \tag{9}$$

Using the dimensionless variables $\bar{t} = t/T$, $\bar{x}_i = x_i/l$, $\bar{a}_i = a_i/a_*$, $\bar{s}_i = s_i/(la_*)$, $\bar{b} = b/a_*$ $\bar{k}_{ij} = k_{ij}Ta_*$, $\bar{k}_{-ij} = k_{-ij}T$, $\bar{k}_3 = k_3 T$, $\bar{k}_i = k_i T a_*$, $\bar{\kappa}_{a_i} = \kappa_{a_i} T/l^2$, $\bar{\kappa}_b = \kappa_b T/l^2$, $\bar{\kappa}_{ij} = \kappa_{ij} T/l^2$, $\bar{\lambda}_{1,j2} = a_* T \lambda_{1,j2}$, $\bar{\lambda}_{2,j1} = a_* T \lambda_{2,j1}$, where $i, j = 1, 2$ and T, l, a_* are the characteristic dimensional units, we rewrite Eqs. (1)–(8) in the same form, but in dimensionless variables.

In what follows we study system (1)–(7) and Eqs. (1)–(4) with given values of a_1, a_2 at the surface $x_2 = 0$ in the following three adsorption cases of the reactants A_1 and A_2:

(i) each reactant can adsorb on both intervals $[0, x_*)$ and $(x_*, 1]$,
(ii) reactant A_2 adsorbs on the interval $[0, x_*)$, while the A_1 adsorbs on the $(x_*, 1]$,
(iii) both reactants adsorb only on the interval $(x_*, 1]$.

Hence, in case (ii) we have $k_{12} = k_{21} = 0$, while in the case (iii) $k_{12} = k_{22} = 0$.

3 Numerical results

System (1)–(4) with given values of a_1 and a_2 at the surface S_2 was solved numerically using an implicit difference scheme. To solve system (1)–(7) numerically we used an implicit difference scheme based on the alternating direction method [26]. For all calculations we used the following dimensional data:

$$\begin{aligned} &T = 1\ \mathrm{s}, \quad l = 10^{-1}\ \mathrm{cm}, \quad a_* = 10^{-11}\ \mathrm{mol\ cm^{-3}},\\ &s_* = la_* = 10^{-12}\ \mathrm{mol\ cm^{-2}}, \quad k_{ij} \in [10^9, 10^{11}]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}},\\ &k_{-ij},\ k \in [3 \times 10^{-3}, 1]\ \mathrm{s^{-1}}, \quad \kappa_{a_i}, \kappa_b \in [5 \times 10^{-7}, 10^{-3}]\ \mathrm{cm^2\ s^{-1}}. \end{aligned} \tag{10}$$

In the case where values of k_{ij}, κ_{ij}, and $\lambda_{i,jn}$ for all values of indices are equal, we use $k = k_{ij}$, $\kappa = \kappa_{ij}$, and $\lambda = \lambda_{i,jn}$ for short. Of course, the case where k_{ij}, κ_{ij}, and $\lambda_{i,jn}$ do not depend on values of indices is not realistic. However, it is useful for a study of the interplay of many different physico-chemical processes. In calculations, we used $k_3 = 0.1$, $k_{-ij} = 1.66 \times 10^{-3}$ and two different arrangements of the adsorption sites $s_1 = s_2 = 1$ and $s_2 = s_1(1/x_* - 1)$, $s_1 = 1$. In the first case of the adsorption sites arrangement, the total numbers of the active and inactive sites for $x_* \neq 0.5$ are different. In the second case, these numbers are equal, i.e. $\int_0^{x_*} s_2\,\mathrm{d}x_1 = \int_{x_*}^1 s_1\,\mathrm{d}x_1$. Moreover, for $x_* = 0.5$, $s_2 = s_1 = 1$ in the second case too. The model values of dimensionless k_{ij}, κ_{ij}, and $\lambda_{i,jn}$ are given in the captions of figures. We first discuss numerical results for system (1)–(4) with given values of a_1 and a_2 at the surface S_2.

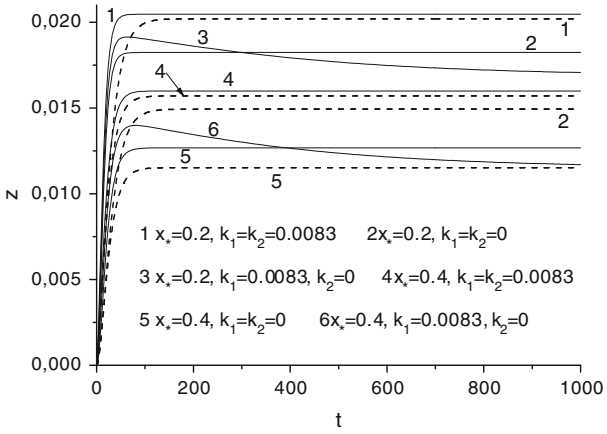

Fig. 1 Influence of the active interval length x_* and reaction rate constants, k_1 and k_2, in ER step on the turnover rate $z(t)$ determined by Eqs. (1)–(4) with $a_1 = a_2 = 1$ at the surface S_2 for densities $s_1 = s_2 = 1$ (*dashed line*) and $s_1 = 1$, $s_2 = s_1(1/x_* - 1)$ (*solid line*) in the case $\kappa = 0.5$, $\lambda = 0.5$, and $k = 0.0166$

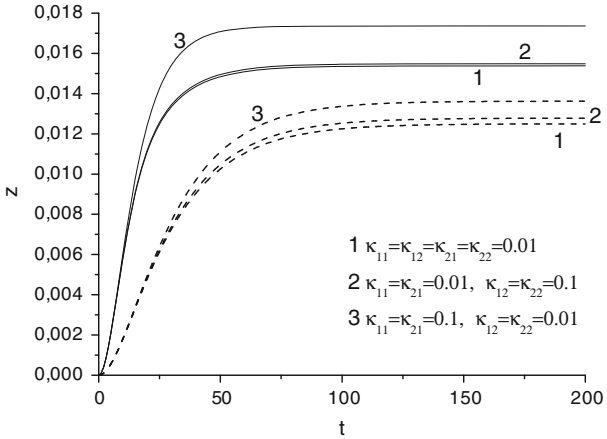

Fig. 2 Dependence of turnover rate $z(t)$ determined by (1)–(4) with $a_1 = a_2 = 1$ at the surface S_2 for densities $s_1 = s_2 = 1$ (*dashed line*) and $s_1 = 1$, $s_2 = s_1(1/x_* - 1)$ (*solid line*) on the parameters κ_{ij}, $i, j = 1, 2$, in the case $\lambda = 0.5, k_1 = k_2 = 0$, and $k = 0.0166$

3.1 Numerical results of system (1)–(4) with $a_1(t, x_1, 0) = a_2(t, x_1, 0) = 1$

Numerical results are presented in Figs. 1, 2, 3, 4 and 5.

Figure 1 illustrates the dependence of the turn-over rate z on the parameters s_1, s_2, x_*, and $k_1 = k_2$ for the case where $\kappa = \lambda = 0.5$ and each reactant can adsorb on both active and inactive intervals. In both cases of the s_1 and s_2 arrangement, Fig. 1 depicts a growth of the turn-over rate z as the size of the active interval, x_*, decreases (at the same time the length of the inactive interval, $1 - x_*$, grows). For uni-molecular reactions this effect is studied in [2]. This figure also shows that incorporation of the ER step for one or both reactants remarkably increases z compared to that determined by the model involving only the LH mechanism.

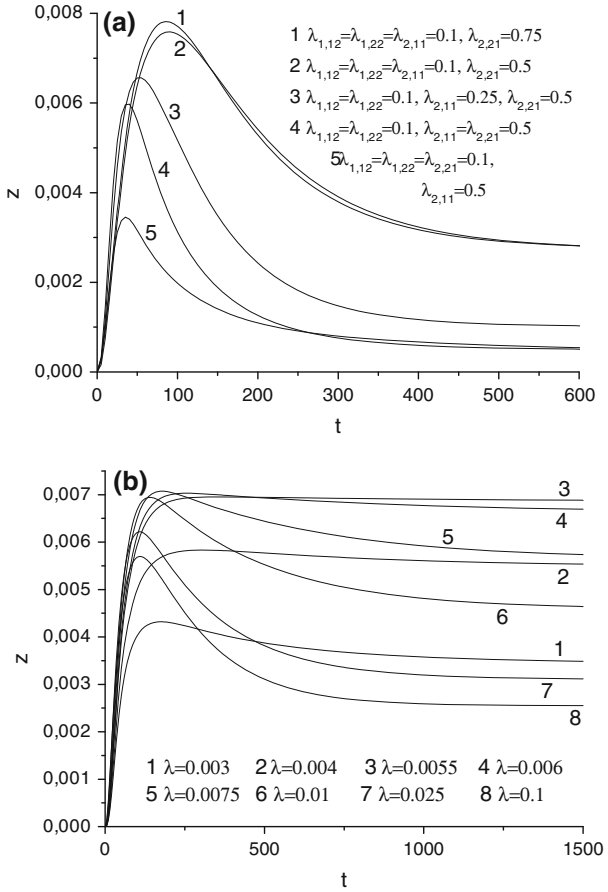

Fig. 3 Effect of increasing parameters $\lambda_{i,jn}$ (**a**) and λ (**b**) on the turnover rate $z(t)$ determined by (1)–(4) with $a_1 = a_2 = 1$ at the surface S_2 in the case $k_{11} = k_{22} = 0.0166$, $k_{12} = k_{21} = 0$, $k_1 = k_2 = 0$, $\kappa = 0.01$, and $s_1 = s_2 = 1$

Figure 2 depicts the influence of the surface diffusivity κ_{ij} on the dynamics of z for the case where the reactants A_1 and A_2 can adsorb on both active and inactive intervals and $k = 1.66 \times 10^{-2}$, $\lambda = 0.1$, $k_1 = k_2 = 0$. From this figure we see that in both cases of the distribution of s_1 and s_2 the increase of the diffusivity in the inactive interval, $\kappa_{11} = \kappa_{21}$, leads to the larger values of z compared to those corresponding to the same increase of the diffusivity $\kappa_{12} = \kappa_{22}$ in the active interval. Figs. 1 and 2 also shows that values of z for $s_2 = s_2(1/x_* - 1)$, $s_1 = 1$ are much more larger than those corresponding to the case $s_1 = s_2 = 1$.

Figures 3a, b present the dependence of z on $\lambda_{i,jn}$ and λ, respectively, for $\kappa = 0.01$, $k_1 = k_2 = 0$, $k_{11} = k_{22} = 1.66 \times 10^{-2}$ in the case where A_1 adsorbs on $(0, x_*)$ and A_2 on $(x_*, 1)$, i.e. $k_{12} = k_{21} = 0$. From Fig. 3a we observe that the increase of $\lambda_{2,21}$ or $\lambda_{2,11}$ increases values of z for small t. For large t the turn-over rate behaves vice-versa. Figure 3b shows that the steady-state value of z depending on λ possesses a maximum value at some λ_*, e.g. $\lambda_* \approx 0.055$.

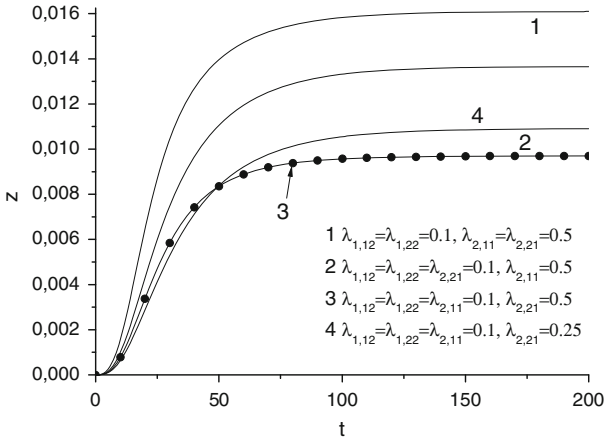

Fig. 4 Effect of increasing parameters $\lambda_{i,jn}$ on the turnover rate $z(t)$ determined by (1)–(4) with $a_1 = a_2 = 1$ at the surface S_2 for densities $s_1 = s_2 = 1$ in the case $k_{11} = k_{21} = 0.0166$, $k_{12} = k_{22} = 0$, and $k_1 = k_2 = 0$, $\kappa = 0.01$

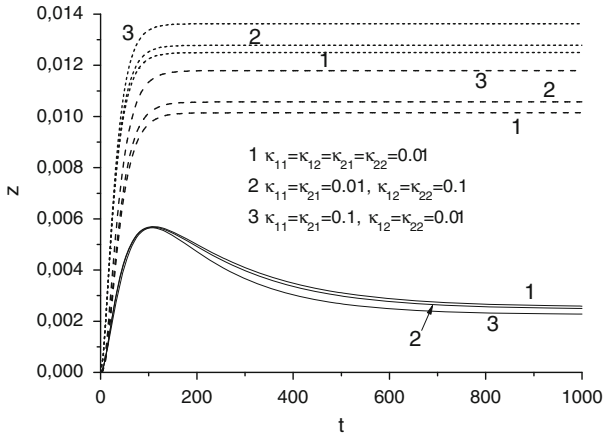

Fig. 5 Dependence of the turnover rate $z(t)$ determined by Eqs. (1)–(4) with $a_1 = a_2 = 1$ at the surface S_2 on the parameters κ_{ij} and k_{ij}, $i, j = 1, 2$, in the case $s_1 = s_2 = 1$, $k_1 = k_2 = 0$ and $\lambda = 0.1$. $k_{11} = k_{22} = 0.0166$, $k_{12} = k_{21} = 0$—*solid line*, $k_{11} = k_{21} = 0.0166$, $k_{12} = k_{22} = 0$—*dashed line*, $k_{11} = k_{12} = k_{21} = k_{22} = 0.0166$—*short dashed line*

Figure 4 depicts the dependence of z on $\lambda_{i,jn}$ for $k_1 = k_2 = 0$ and $k_{11} = k_{21} = 1.66 \times 10^{-2}$ in the case where both reactants adsorb on the inactive interval $(x_*, 1)$, i.e. $k_{12} = k_{22} = 0$. We observe that, for all $t > 0$, z increases as the jump rates, $\lambda_{2,11} = \lambda_{2,21}$, of both reactants from the inactive position $x_* + 0$ into the active vacant location $x_* - 0$ grows. Curves 3 and 4 show that this behaviour of z is not true if only the jump rate $\lambda_{2,21}$ of reactant A_2 increases.

In Fig. 5, we compare dynamics of z for $\lambda = 0.1$ and $k_1 = k_2 = 0$ in all three adsorption cases of reactants A_1 and A_2 ($k = 1.66 \times 10^{-2}$; $k_{12} = k_{21} = 0$, $k_{11} = k_{22} = 1.66 \times 10^{-2}$; $k_{12} = k_{22} = 0, k_{11} = k_{21} = 1.66 \times 10^{-2}$). In each case we compare

the turn-over rate z corresponding to $\kappa = 0.01$; $\kappa_{11} = \kappa_{21} = 0.01$, $\kappa_{12} = \kappa_{22} = 0.1$; and $\kappa_{11} = \kappa_{21} = 0.1$, $\kappa_{12} = \kappa_{22} = 0.01$. We observe a similar behaviour of z in cases where A_1 and A_2 adsorb only on the inactive interval or were each reactant adsorbs on both intervals. Figure 5 shows that in these two adsorption cases the increase of the diffusivity $\kappa_{11} = \kappa_{21}$ in the inactive interval determines larger values of z compared to those corresponding to the same increase of the reactants diffusivity $\kappa_{12} = \kappa_{22}$ in the active interval. In the case where A_1 adsorbs on the inactive interval and A_2 on the active one, the increase of the diffusivity $\kappa_{11} = \kappa_{21}$ in the inactive interval decreases z and determines values of z that are smaller those corresponding to the same increase of the diffusivity $\kappa_{12} = \kappa_{22}$ in the active interval (see solid lines in this figure).

3.2 Numerical results of system (1)–(7)

Numerical results are presented in Figs. 6, 7, 8 and 9.

Figure 6 depicts the increase of z as x_* decreases in the case $k = 1.66 \times 10^{-2}$, $k_1 = k_2 = 0$, $\kappa = \lambda = 0.5$. This result is similar to that illustrated in Fig. 1 for system (1)–(4) with given $a_1 = a_2 = 1$ at the surface S_2.

From Fig. 7 we see that, for $k = 1.66 \times 10^{-2}$, $k_1 = k_2 = 0$, $\kappa = 0.01$ and small t, the increase of λ increases z. For large t, function z behaves vice-versa. Similarly, for $\lambda = 0.01$ and small t, function z increases as κ grows but, for large t, its behaviour is opposite. Moreover, for large t, z decreases to zero, because concentrations $a_1(t, x)$ and $a_2(t, x)$ tend to zero. For comparison we also present dynamics of z determined by Eqs. (1)–(4) with given a_1 and a_2 at the surface S_2. In this case z increases for all $t > 0$ as λ or κ increases.

Figure 8 presents the comparison of z dynamics for $\lambda = 0.1$ and $k_1 = k_2 = 0$ in three adsorption cases of A_1 and A_2. If each reactant adsorbs on both active and inactive interval or both reactants adsorb only on the inactive interval then, for small t, the increase of diffusivity $\kappa_{11} = \kappa_{21}$ of both reactants in the inactive interval increases

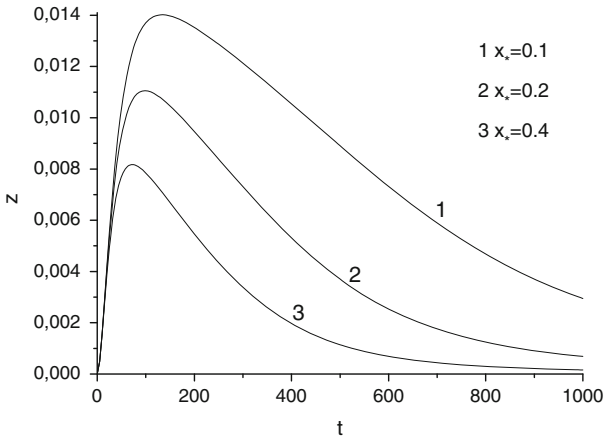

Fig. 6 Influence of the active interval length x_* on the turnover rate $z(t)$ determined by system (1)–(7) with densities $a_1^0(x_1, x_2) = a_2^0(x_1, x_2) = 1$ and $s_1 = s_2 = 1$ in the case $k_1 = k_2 = 0$, $\kappa = 0.5$ and $\lambda = 0.5$

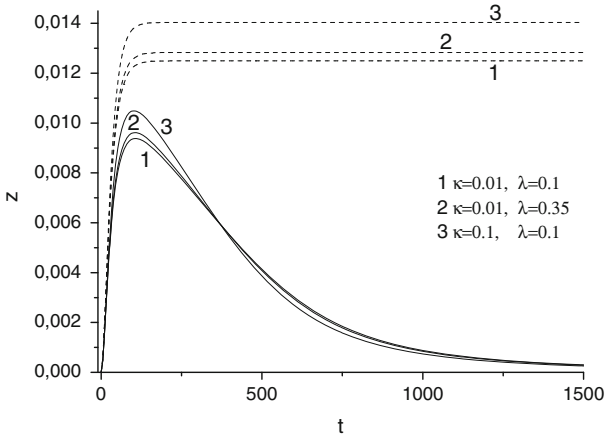

Fig. 7 Dependence of the turnover rate $z(t)$ determined by Eqs. (1)–(4) with $a_1(t, x_1, 0) = a_2(t, x_1, 0) = 1$ (*dashed line*) and by system (1)–(7) with densities $a_1^0(x_1, x_2) = a_2^0(x_1, x_2) = 1$ (*solid line*) on parameters κ and λ in the case $s_1 = s_2 = 1$ and $k_1 = k_2 = 0$

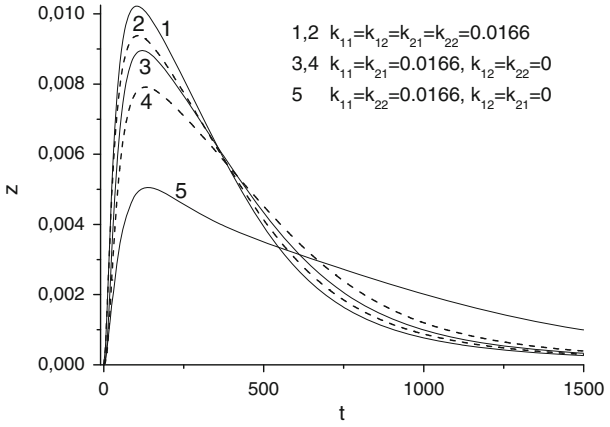

Fig. 8 Effect of increasing parameters k_{ij} and κ_{ij}, $i, j = 1, 2$, on the turnover rate $z(t)$ determined by system (1)–(7) with densities $a_1^0(x_1, x_2) = a_2^0(x_1, x_2) = 1$ and $s_1 = s_2 = 1$ in the case $k_1 = k_2 = 0$ and $\lambda = 0.1$. $\kappa_{11} = \kappa_{21} = 0.1$, $\kappa_{12} = \kappa_{22} = 0.01$—*solid line*, $\kappa_{11} = \kappa_{12} = \kappa_{21} = \kappa_{22} = 0.01$—*dashed line*

z. For large t, its influence is opposite. Simulations show that the increase of the diffusivity $\kappa_{12} = \kappa_{22}$ of both reactants in the active interval also increases z for small t but this increase is smaller than that corresponding to the same diffusivity increase in the inactive interval. Curve 5 in this figure corresponds to the case where A_1 and A_2 adsorb on the inactive and active interval, respectively. For small t, values of z are smaller than those corresponding to the other two adsorption cases, but for large t its values are larger.

In Fig. 9, we compare the total amount of product B at time t, $I_b = \int_0^1 \mathrm{d}x_1 \int_0^1 b\,\mathrm{d}x_2$, for $k = 0.1$, $\kappa = 0.5$, $\lambda = 0.5$ in cases where $s_1 = s_2 = 1$; $s_2 = s_1(1/x_* - 1)$, $s_1 = 1$ and $x_* = 0.1,\ 0.2,\ 0.4$. In the case $s_1 = s_2 = 1$, function I_b grows as x_* increases,

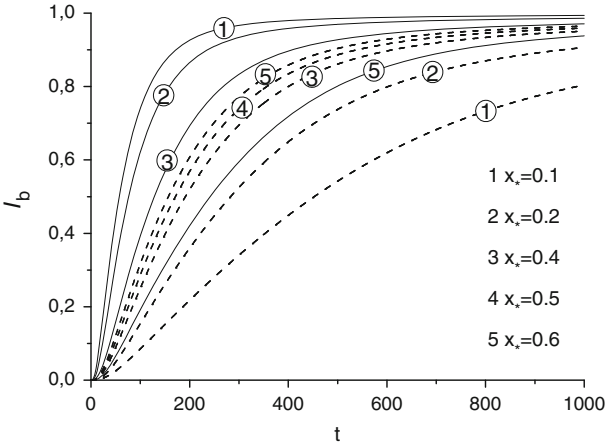

Fig. 9 Dependence of the total amount of the product I_b on the active interval length x_* in the case $a_1^0(x_1, x_2) = a_2^0(x_1, x_2) = 1$, $k_1 = k_2 = 0$, $k = 0.1$, and $\lambda = 0.5$, $\kappa = 0.5$. $s_1 = s_2 = 1$—*dashed line*, $s_1 = 1$, $s_2 = s_1(1/x_* - 1)$—*solid line*

but, in the other one, I_b decreases as x_* increases. In both cases of the s_1 and s_2 distribution, values of I_b coincide for $x_* = 0.5$.

4 Conclusions

To conclude the paper, we summarise the main results. In this paper, using a phenomenological (mean-field) model in two-dimensional space we studied numerically bimolecular surface reactions proceeding on supported catalysts coupled with both reactants and product bulk diffusion in a bounded impermeable vessel. The model includes the adsorption, desorption, surface diffusion of adsorbed particles of each reactant, and rapid product desorption from the surface. Two different arrangements of adsorption sites were used and three cases of both reactants adsorption on them are considered: (i) each reactant can adsorb on both active catalyst particle and inactive support, (ii) one of the reactants A_1 and A_2 adsorbs on the catalyst particle while the other one adsorbs on the inactive in reaction support, (iii) both reactants adsorb only on the inactive support.

Inactive in reaction sites, due to possibility of adsorption of at least one of reactants and diffusion of adsorbed particles on them, constitute an additional (to the adsorption) channel transporting particles onto active ones. In case (i) of reactants adsorption, we have the adsorption channel of both reactants and the spillover one of both reactants from the inactive interval onto the active one. In case (ii), we have the adsorption channel of reactant A_2 and the spillover one of A_1. At last, in case (iii), both reactants are transported onto active interval by the spillover channel.

The main characteristic we studied was the catalyst particle specific conversion rate (turn-over rate) of molecules of both reactants into the product ones. We analysed the effects of spillover on the turn-over rate under different conditions and demonstrated that:

1. The ER step remarkably increases the turn-over rate z compared to that corresponding to only one LH mechanism. Function z determined by system (1)–(4) with given values of a_1 and a_2 at the surface S_2 is monotonic in time for $k_1 = k_2 \geq 0$ and non-monotonic if only one of k_1 and k_2 is zero.
2. The size of the active interval strongly influence the turn-over rate. In both cases of active sites arrangement, z determined by Eqs. (1)–(4) with given a_1 and a_2 at the surface S_2 or system (1)–(7) grows as size x_* decreases. Moreover, values of z corresponding to the case $s_2 = s_1(\frac{1}{x_*} - 1)$, $s_1 = 1$ are larger than those corresponding to the case $s_1 = s_2 = 1$.
3. The increase of at least one of diffusion coefficients κ_{ij} increases z determined by system (1)–(7) or Eqs. (1)–(4) with given concentrations a_1 and a_2 at the surface S_2.
4. In the case where one of reactants adsorbs on the inactive interval and the other on the active one, $s_1 = s_2$, and $k_1 = k_2 = 0$, the steady-state value of z determined by system (1)–(4) with given $a_1 = a_2$ at the surface S_2 possesses a maximum at some value λ_*, e.g. $\lambda_* \approx 0.055$ for $k_{11} = k_{22} = 0.0166$, $k_{12} = k_{21} = 0$, $\kappa = 0.01$.
5. In the case, where both reactants adsorb only on the inactive support, the turn-over rate z is a monotonically increasing function in time.
6. z determined by system (1)–(7) is non-monotonic in time. It attains a maximum value and then tends to zero as time grows. Moreover, z grows only for small t as κ, $\kappa_{11} = \kappa_{21}$, or λ increase and behaves vice versa for large t.
7. Values of the total amount of product B for $s_1 = s_2 = 1$ monotonically increase as size of the active interval, x_*, grows and decrease for $s_2 = s_1(1/x_* - 1)$, $s_1 = 1$.

Results of simulations let us to think that the phenomenological model presented here is able to describe qualitatively processes that proceed at constant temperature during monomer–monomer reactions on supported catalysts.

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