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Numerical study of long-range surface diffusion influence on catalytic reactivity of spatially inhomogeneous planar surfaces

V. Skakauskas · P. Katauskis

Abstract   A phenomenological (mean-field) mathematical model of unimolecular reactions proceeding onto inhomogeneous planar surfaces is presented and investigated numerically in two-dimensional in space case taking into account the adsorption and desorption of reactant particles, long-range surface diffusion of the adsorbed particles, and an instantaneous product desorption from an adsorbent. The model also involves the bulk diffusion of the reactant from the bounded vessel towards the adsorbent and the product bulk one from the adsorbent into the same vessel. Simulations were performed using the finite difference technique. The influence of the long-range surface diffusion of adsorbed particles on the kinetics for processes catalyzed by inhomogeneous surfaces with a different arrangement of reactive and non-reactive adsorption sites is studied.

Keywords   Heterogeneous reactions · Adsorption · Desorption · Surface diffusion

1 Introduction

Diffusion of adsorbed particles (atoms, molecules, or small clusters) on solid surfaces occurs in a number of modern technologies involving crystal and film growth, catalysis, and surface-bound nanostructures by variety of mechanisms [1,2]. Usually it is assumed that surface diffusion of adsorbed particles occurs via their jumps to nearest-neighbor vacant sites [3]. If, however, the energy-exchange between adsorbed particles and substrate is slow and corrugation of the adsorption potential is weak or if the temperature is sufficiently high, the long-range jumps may

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be significant as well [4–6]. The experiments [6–9] have led to observation that long-range jumps of adsorbed particles may, upon occasion, play a dominant role. Theoretically, by using the Langevin equation with thermal noise, the contribution of long-range jumps of a single particle to diffusion coefficient was discussed in papers [1,10–13].

In most of the former studies of heterogeneous reactions, surface diffusion of the adsorbate was either neglected or considered as a rapid process (see [14] and references therein). In recent works concerning heterogeneous catalytic reactions occurring on nanostructured surfaces the diffusion of adsorbed particles is taken into account and Monte Carlo simulations technique [14–18] or mean-field modeling [14,16,19–21] are employed. However, these last four works were dealing only with uniform surfaces [14,16], while in [14] two mean-field models of the kinetics of unimolecular and bimolecular catalytic reactions occurring on heterogeneous surfaces involving a local arrangement of reactive and non-reactive surface sites are studied. Derivation and the structure of these models [22] show that they are based on the particles jumps to nearest-neighbor vacant sites.

We consider unimolecular surface reactions coupled with the reactant and product bulk diffusion and present a phenomenological (mean-field) model taking into account the long-range diffusion (all possible jumps lengths) of adsorbed particles on a spatially inhomogeneous planar surfaces that involve a heterogeneous or non-uniform homogeneous arrangement of reactive and non-reactive surface sites. Adsorption, desorption, and diffusion are allowed to proceed at each site while reaction only on the reactive ones. We also study the bulk diffusion of the reactant towards the surface and the bulk one of the product from the adsorbent letting the product desorption from the surface to be instantaneous and all processes to proceed at a constant temperature.

The paper is organized as follows. In Sect. 2, the model is presented. In Sect. 3 we discuss numerical results. Some remarks in Sect. 4 conclude the paper.

2 The model

Let reactant A and product B of concentrations $a(t, x)$ and $b(t, x)$ occupy a bounded domain Ω with surface $\partial\Omega = S_1 \cup S_2$. Here t is time, $x \in \Omega$ is a position, S_2 is a surface of the adsorbent, $S_1 = \partial\Omega \setminus S_2$ is impermeable surface to the reactant and product. Let $s_2(x)$ and $s_1(x)$, $x \in S_2$, be the surface density of active and inactive adsorption sites in the surface reaction. Assume that $s_2\theta_2$ and $s_1\theta_1$, $\theta_i(t, x) \in [0, 1]$, $i = 1, 2$, are densities of active and inactive sites occupied by the reactant molecules. Let $P_{ij}(x, y)$ be the rate by which the reactant particle adsorbed on a site of type j located in position $y \in S_2$ diffuses (jumps) to a vacant site of type i located in position $x \in S_2$. Also assume that k is a constant of the reaction rate and k_{f1}, k_{f2}, k_{r1}, k_{r2} are the adsorption and desorption rate constants. Denoting by κ_a and κ_b diffusivities of reactant a and product b and using the law of mass action and the Langmuir mechanism of unimolecular reactions we derive the following coupled system for surface coverages, θ_1 and θ_2:

$$
\begin{cases}
\dfrac{\partial \theta_1}{\partial t} = (1 - \theta_1(t,x))\Big\{ k_{f1}a + \int_{S_2} \big(\theta_1(t,y)s_1(y)P_{11}(x,y) \\
\qquad\qquad + \theta_2(t,y)s_2(y)P_{12}(x,y)\big)\,\mathrm{d}y \Big\} \\
\qquad - \theta_1(t,x)\Big\{ k_{r1} + \int_{S_2}\big((1-\theta_1(t,y))s_1(y)P_{11}(y,x) \\
\qquad\qquad + (1-\theta_2(t,y))s_2(y)P_{21}(y,x)\big)\,\mathrm{d}y \Big\}, \quad t>0,\ x\in S_2, \\[4pt]
\theta_1|_{t=0} = 0, \quad x\in S_2, \\[4pt]
\dfrac{\partial \theta_2}{\partial t} = (1 - \theta_2(t,x))\Big\{ k_{f2}a + \int_{S_2}\big(s_1(y)\theta_1(t,y)P_{21}(x,y) \\
\qquad\qquad + s_2(y)\theta_2(t,y)P_{22}(x,y)\big)\,\mathrm{d}y \Big\} \\
\qquad - \theta_2(t,x)\Big\{ k_{r2} + k + \int_{S_2}\big((1-\theta_1(t,y))s_1(y)P_{12}(y,x) \\
\qquad\qquad + (1-\theta_2(t,y))s_2(y)P_{22}(y,x)\big)\,\mathrm{d}y \Big\}, \quad t>0,\ x\in S_2, \\[4pt]
\theta_2|_{t=0} = 0, \quad x\in S_2.
\end{cases}
\tag{1}
$$

Here $a = a(t,x)$ is an unknown reactant concentration at S_2. The first integral gain term on the right-hand side of the first equation of this system is conditioned by the surface diffusion (jumps) of the adsorbed reactant particles from the inactive and active sites located on surface S_2 to the vacant inactive sites located in the position $x \in S_2$. The lost integral term of the first equation is conditioned by the surface diffusion (jumps) of the adsorbed reactant particles from the inactive sites located in position $x \in S_2$ to vacant inactive and active sites located on S_2. Similarly can be explained the rise of the integral gain and lost terms of the second equation of this system. To close this system we add equations describing the bulk diffusion of reactant a and product b,

$$
\begin{cases}
\dfrac{\partial a}{\partial t} = \kappa_a \Delta a, \quad x\in \Omega,\ t>0, \\[4pt]
\partial_n a|_{S_1} = 0, \quad t>0, \\[4pt]
\kappa_a \partial_n a|_{S_2} = -k_{f1}s_1(1-\theta_1)a|_{S_2} + k_{r1}s_1\theta_1 \\
\qquad\qquad - k_{f2}s_2(1-\theta_2)a|_{S_2} + k_{r2}s_2\theta_2, \quad t>0, \\[4pt]
a|_{t=0} = a_0(x), \quad x\in \Omega,
\end{cases}
\tag{2}
$$

$$
\begin{cases}
\dfrac{\partial b}{\partial t} = \kappa_b \Delta b, \quad x\in \Omega,\ t>0, \\[4pt]
\partial_n b|_{S_1} = 0, \quad t>0, \\[4pt]
\kappa_b \partial_n b|_{S_2} = ks_2\theta_2, \quad t>0, \\[4pt]
b|_{t=0} = 0, \quad x\in \Omega.
\end{cases}
\tag{3}
$$

Here Δ is the Laplace operator, $\partial_n a$ and $\partial_n b$ are the outward normal derivatives, and a_0 is an initial distribution of the reactant concentration. A system based on the Fick law is proposed in [23] for the description of unimolecular surface reactions coupled

with the bulk diffusion of the reactant and product and surface diffusion of the reactant particles adsorbed on a surface with all sites of reactive type. However, the model considered in [23] cannot describe the long-range surface diffusion.

It is easy to prove that system (1)–(3) possesses the mass conservation law

$$\int_{\Omega} (a + b)\, dx + \int_{S_2} (s_1\theta_1 + s_2\theta_2)\, dx = \int_{\Omega} a_0\, dx. \tag{4}$$

We determine the specific conversion rate of the reactant molecules (turn-over rate) by the formula

$$z(t) = k \int_{S_2} s_2(x)\theta_2(t, x)\, dx \Big/ \int_{S_2} s_2(x)\, dx. \tag{5}$$

In the case where $P_{ij}(x, y) = \kappa_{ij}(x, y)\delta(x - y)$, $x \notin \partial S_2$, with $\delta(x - y)$ the Dirac delta function, Eq. (1) reduce to the system of ODEs,

$$\begin{cases} \dfrac{d\theta_1}{dt} = (1 - \theta_1)\{k_{f1}a + s_2\kappa_{12}(x, x)\theta_2\} \\ \qquad\quad - \theta_1\{k_{r1} + s_2(1 - \theta_2)\kappa_{21}(x, x)\}, \quad \theta_1|_{t=0} = 0, \\ \dfrac{d\theta_2}{dt} = (1 - \theta_2)\{k_{f2}a + s_1\kappa_{21}(x, x)\theta_1\} \\ \qquad\quad - \theta_2\{k_{r2} + k + s_1(1 - \theta_1)\kappa_{12}(x, x)\}, \quad \theta_2|_{t=0} = 0, \end{cases} \tag{6}$$

that, for fixed $x \in S_2$, are the same as those used in [22]. We stress that x involved in Eq. (6) is a parameter. Equation (6) show that, in the case where $\alpha_{ij} \to 0$, parameters κ_{11} and κ_{22} do not influence evolution of θ_1 and θ_2.

3 Numerical results

We consider system (1)–(3) in domain $\Omega = \{(x_1, x_2, x_3) : x_i \in [0, l], i = 1, 2, 3\}$ with $S_2 = \{(x_1, x_2) : x_i \in [0, l], i = 1, 2\}$. To simplify the three-dimensional problem we study the case where the initial distribution of reactant a_0 is a constant and densities s_1 and s_2 depend only on x_1. We also take into account jumps of adsorbed particles only in x_1 direction. In this case surface integrals involved in Eq. (1) reduce to integrals over $[0, l]$ multiplied by l. Therefore, in what follows we consider Eqs. (2) and (3) in $\tilde{\Omega} = \{(x_1, x_2) : x_i \in [0, l], i = 1, 2\}$ with $\tilde{S}_2 = \{(x_1, x_2) : x_2 = 0, x_1 \in [0, l]\}$. For numerical calculations we apply function

$$P_{ij}(x, y) = \frac{\kappa_{ij}}{\sqrt{\pi\alpha_{ij}}} \exp\left\{\frac{-|x - y|^2}{\alpha_{ij}}\right\} \tag{7}$$

where $\alpha_{ij}/2$, $i, j = 1, 2$, are the dispersions of jumps lengths of adsorbed particles, κ_{ij} is their surface diffusion (jumps) rate constants, and $|x - y|$ with $x, y \in [0, 1]$ is
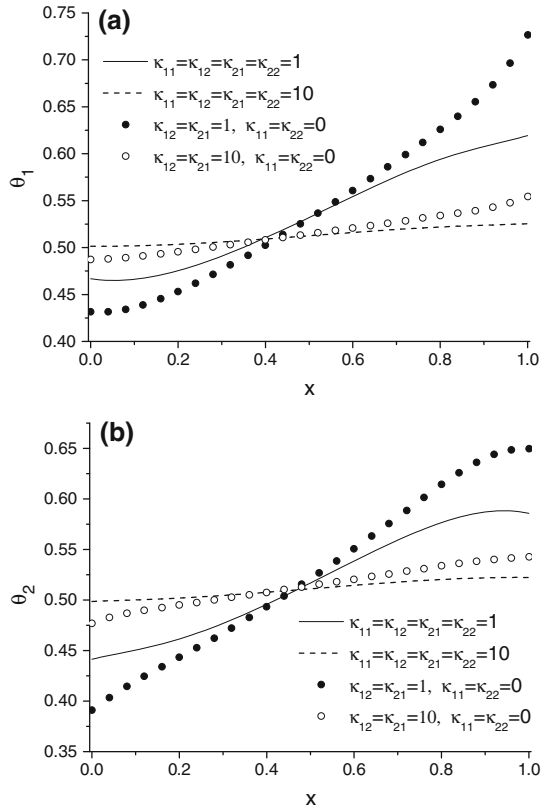
a jump length from point y to x. It is evident that

$$\lim_{\alpha_{ij} \to 0} \frac{\exp\{-|x - y|^2/\alpha_{ij}\}}{\sqrt{\pi \alpha_{ij}}} = \delta(x - y).$$

Using the dimensionless variables $\bar{t} = t/T$, $\bar{x}_1 = x_1/l$, $\bar{x}_2 = x_2/l$, $\bar{x}_3 = x_3/l$, $\bar{a} = a/a_*$, $\bar{b} = b/a_*$, $\bar{s}_1 = s_1/la_*$, $\bar{s}_2 = s_2/la_*$, $\bar{k}_{f1} = k_{f1}Ta_*$, $\bar{k}_{f2} = k_{f2}Ta_*$, $\bar{k}_{r1} = k_{r1}T$, $\bar{k}_{r2} = k_{r2}T$, $\bar{k} = kT$, $\bar{\kappa}_a = \kappa_a T/l^2$, $\bar{\kappa}_b = \kappa_b T/l^2$, $\bar{\kappa}_{ij} = \kappa_{ij}Tl^2a_*$, $\bar{\alpha}_{ij} = \alpha_{ij}/l^2$, where T, l, and a_* are characteristic dimensional units, we rewrite Eqs. (1)–(7) in the same form but in dimensionless variables. Dimensionless Eqs. (1), (4), (5) involve integration over interval [0, 1]. For simplicity in what follows, we omit the bar and treat Eqs. (1)–(7) as dimensionless. To solve numerically problem (1) with given $a(t, x_1, 0)$ Euler's scheme with integrals approximated by trapezoidal quadrature formula was used. The same result was got by applying the Runge–Kutta method. We solved problem (1)–(3) by using implicit finite-difference schemes based on the alternating direction method [24]. As in [23], for all calculations we used the

Fig. 2 Effect of parameters κ_{ij}, i, j = 1, 2, on conversion rate of the reactant molecules $z(t)$ determined by (1) and (5) with densities $a(t, x_1) = 1$, $s_1(x_1) = x_1$ and $s_2(x_1) = 1 - x_1$ in the case where $\alpha = 0.02$ and **a** $k = 3 \times 10^{-3}$, **b** $k = 3 \times 10^{-2}$
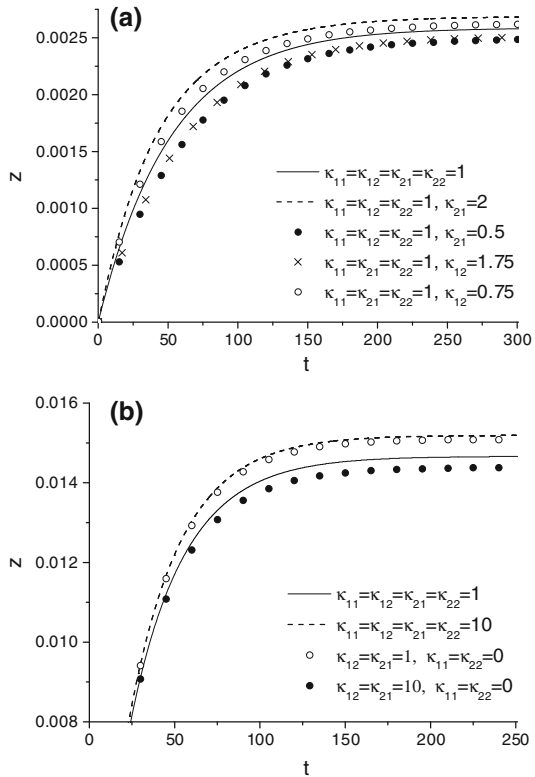
following dimensional data:

$$T = 1 \text{ s}, \quad l = 10^{-1} \text{ cm}, \quad a_* = 10^{-11} \text{ mol cm}^{-3},$$
$$s_* = la_* = 10^{-12} \text{ mol cm}^{-3}, \quad k_{f1}, k_{f2} \in [10^9, 10^{11}] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$
$$k_{r1}, k_{r2}, k \in [3 \cdot 10^{-3}, 1] \text{ s}^{-1}, \quad \kappa_a, \kappa_b \in [5 \cdot 10^{-7}, 10^{-3}] \text{ cm}^2 \text{ s}^{-1}. \tag{8}$$

The model values of dimensionless κ_{ij} are given in the captions of figures. All figures are drawn for $k_{f1} = k_{f2} = 0.01661$ and $k_{r1} = k_{r2} = 0.001$. In what follows, we study the long-range surface diffusion influence on the kinetics of catalytic process of surfaces with active and inactive in reaction sites arrangement. This influence can be illustrated by varying parameters κ_{ij} and α_{ij}.

We first discuss the case of long-range surface diffusion where the bulk diffusion of the reactant is neglected, i.e. we study system (1) with a given value of the reactant concentration, $a = 1$, at the adsorbent $x_2 = 0$.

In the case where all α_{ij} and κ_{ij} are equal we use $\alpha = \alpha_{ij}$ and $\kappa = \kappa_{ij}$ i, $j = 1, 2$, for short.

1. *Numerical results of system (1) with a given a.* We consider a non-uniform homogeneous (every point of [0, 1] contains active and inactive sites) and heterogeneous

Fig. 3 Effect of parameters α_{ij}, $i, j = 1, 2$, on conversion rate of the reactant molecules $z(t)$ determined by (1) and (5) with densities $a(t, x_1) = 1$, $s_1(x_1) = x_1$ and $s_2(x_1) = 1 - x_1$ in the case where $k = 3 \times 10^{-2}$ and $\kappa = 1$
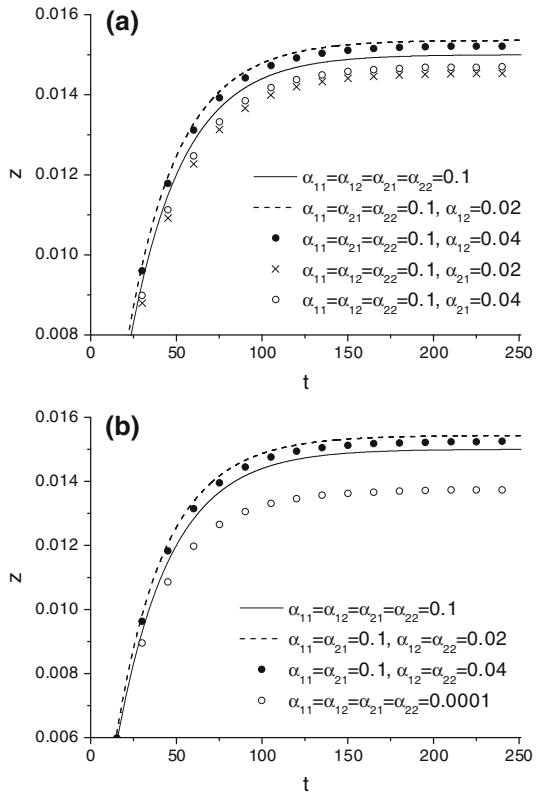
(active and inactive sites are distributed in domains alternatively) distributions of active and inactive sites. Size of sites is neglected.

1.1. *The case of non-uniform homogeneous distribution of adsorption sites.* Let $s_1(x_1) = x_1$ and $s_2(x_1) = 1 - x_1$. Note that $\int_0^1 s_1(x)\,dx = \int_0^1 s_2(x)\,dx = 1/2$. Numerical results illustrated on Figs. 1, 2, 5, 6 and 3, 4 depict the steady-state values of $\theta_1(x_1)$, $\theta_2(x_1)$ and dynamics of z, respectively. Numerical experiments show that for values of $\kappa_{12} = \kappa_{21}$ and α from a broad intervals and small reaction rate constant ($k = 3 \cdot 10^{-3}$), parameters κ_{11} and κ_{22} influence the behavior of θ_1 and θ_2 weakly. A small their influence is observed in the regions near ends of interval $[0, 1]$. But it vanishes and results tend to solution of system (6) as $\alpha_{ij} \to 0$. This result is strong because $P_{ij}(x, y) \to \kappa_{ij}\delta(x - y)$ as $\alpha_{ij} \to 0$. If α_{ij} are far from zero, from Fig. 1 we observe that this influence significantly grows as k increases. This figure also demonstrates an influence of the increase of parameter κ on the values of θ_1 and θ_2. We observe that θ_1 and θ_2 tend to values independent of position x_1 as κ grows. In this case we have a long-range diffusion effect.

If only κ_{21} increases (or κ_{12} decreases) then θ_1 decreases and θ_2 increases (results not presented here). This effect can be also seen from Eq. (6).

Figure 2a depicts a growth of the turn-over rate $z(t)$ as parameter κ_{21} increases or κ_{12} decreases in the case where $k = 3 \times 10^{-3}$ and $\alpha = 0.02$.

Fig. 4 Comparison of the steady-state surface coverages determined by (1) with densities $a(t, x_1) = 1$, $s_1(x_1) = x_1$ and $s_2(x_1) = 1 - x_1$ on parameters α_{ij}, $i, j = 1, 2$, in the case where $k = 3 \times 10^{-2}$ and $\kappa = 1$
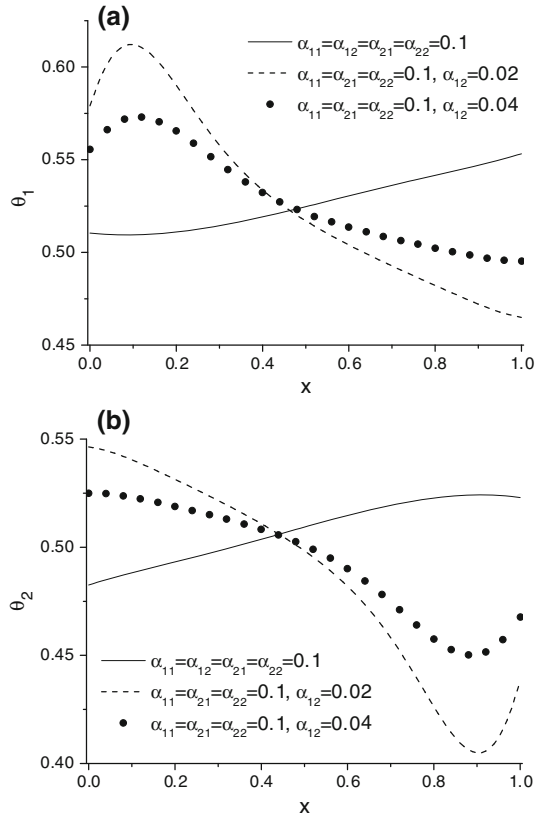

(a)

$\alpha_{11}=\alpha_{12}=\alpha_{21}=\alpha_{22}=0.1$
$\alpha_{11}=\alpha_{21}=\alpha_{22}=0.1,\ \alpha_{12}=0.02$
$\alpha_{11}=\alpha_{21}=\alpha_{22}=0.1,\ \alpha_{12}=0.04$

θ_1

x

(b)

θ_2

$\alpha_{11}=\alpha_{12}=\alpha_{21}=\alpha_{22}=0.1$
$\alpha_{11}=\alpha_{21}=\alpha_{22}=0.1,\ \alpha_{12}=0.02$
$\alpha_{11}=\alpha_{21}=\alpha_{22}=0.1,\ \alpha_{12}=0.04$

x

Figure 2b demonstrates an effect of the increase of κ or only of $\kappa_{11} = \kappa_{22}$ on the dynamics of z for $\alpha = 0.02$ and $k = 3 \times 10^{-2}$. Curves in this figure demonstrate the increase of $z(t)$ as κ or only $\kappa_{11} = \kappa_{22}$ grows.

Figure 3a depicts a dependence of z on the parameters α_{12} and α_{21}. The decrease of α_{12} increases z. The decrease of α_{21} decreases values of $z(t)$.

The increase of α or decrease of $\alpha_{12} = \alpha_{22}$ demonstrates on Fig. 3b the increase of z.

The increase of parameters α, $\alpha_{12} = \alpha_{22}$, or only α_{12} strongly influences dynamics of θ_1 and θ_2 which tend to values independent of position x_1 as well (see Fig. 4). This behavior of θ_1 and θ_2 demonstrates a long-range diffusion effect as well.

1.2. *The case of heterogeneous distribution of adsorption sites.* We consider three cases of active and inactive sites distribution where they are arranged in the form of stripes of decreasing width:

Case I. $s_1 = 1$, $s_2 = 0$, if $x_1 \in [0, 1/2]$; $s_1 = 0$, $s_2 = 1$, if $x_1 \in (1/2, 1]$;

Case II. $s_1 = 1$, $s_2 = 0$, if $x_1 \in [0, 1/4] \cup [2/4, 3/4]$; $s_1 = 0$, $s_2 = 1$, if $x_1 \in (1/4, 2/4) \cup (3/4, 1]$;
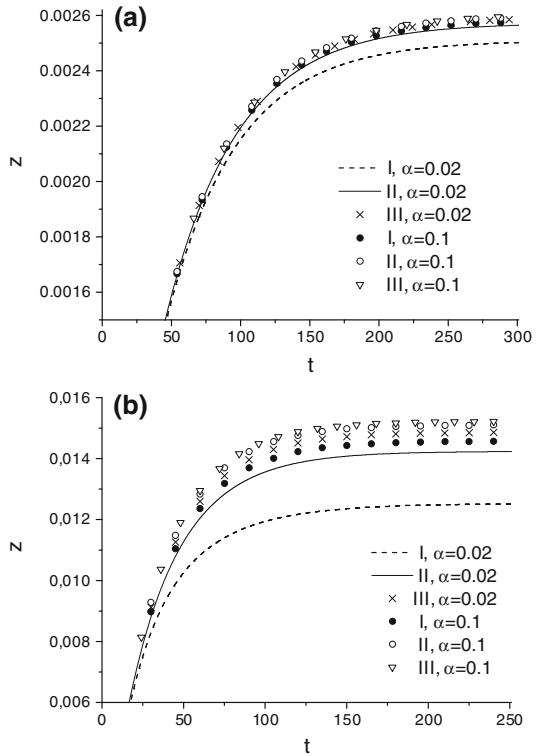
Case III. $s_1 = 1$, $s_2 = 0$, if $x_1 \in [0, 1/8] \cup [2/8, 3/8] \cup [4/8, 5/8] \cup [6/8, 7/8]$;
$s_1 = 0$, $s_2 = 1$, if $x_1 \in (1/8, 2/8) \cup (3/8, 4/8) \cup (5/8, 6/8) \cup (7/8, 1]$.

In all three cases $\int_0^1 s_1(x)\, dx = \int_0^1 s_2(x)\, dx = 1/2$ as well.

Figure 5 depicts the dependence of z on parameters k and α for three cases (I–III) of the active and inactive sites distribution. We observe that function z grows as the width of stripes decreases and achieves maximal values in the third case of the surface arrangement. Function z also increases as α grows.

2. *Numerical results of system (1)–(3).*

This system was also solved for the same as above uniform homogeneous and heterogeneous distributions of sites. In the case where $s_1 = x_1$ and $s_2 = 1 - x_1$, the dependence of z on parameters α, κ, or $\kappa_{12} = \kappa_{22}$, $\kappa_{11} = \kappa_{21}$ is depicted in Fig. 6a for $k = 3 \times 10^{-3}$. This figure demonstrates a different behavior of z as $\kappa_{12} = \kappa_{22}$ increases. We observe that values of z for every fixed $t \in (0, t_*)$, $t < t_* \approx 1100$ s, increase as $\kappa_{12} = \kappa_{22}$ grows, while their behavior is vice versa if $t > t_*$.

Figure 6b depicts the comparison of $z(t)$ determined for the non-uniform homogeneous and heterogeneous distribution of sites. This figure demonstrates a different behavior of z determined for heterogeneous distribution of sites as α increases. Calculations show that $t^* \approx 230$ s for $k = 3 \times 10^{-2}$. The decrease of the width of stripes

Fig. 6 Dependence of conversion rate of the reactant molecules $z(t)$ determined by (1)–(3) and (5) on parameters α, and κ_{ij}, i, $j = 1, 2$. **a** Reaction rate constant $k = 3 \times 10^{-3}$, densities $s_1(x_1) = x_1$ and $s_2(x_1) = 1 - x_1$. **b** Reaction rate constant $k = 3 \times 10^{-2}$, $\kappa = 1$. *Solid* and *dashed lines* for non-uniform homogeneous distribution of sites ($s_1(x_1)=x_1$, $s_2(x_1) = 1 - x_1$), symbols for heterogeneous distribution of sites (*cases I and III*)
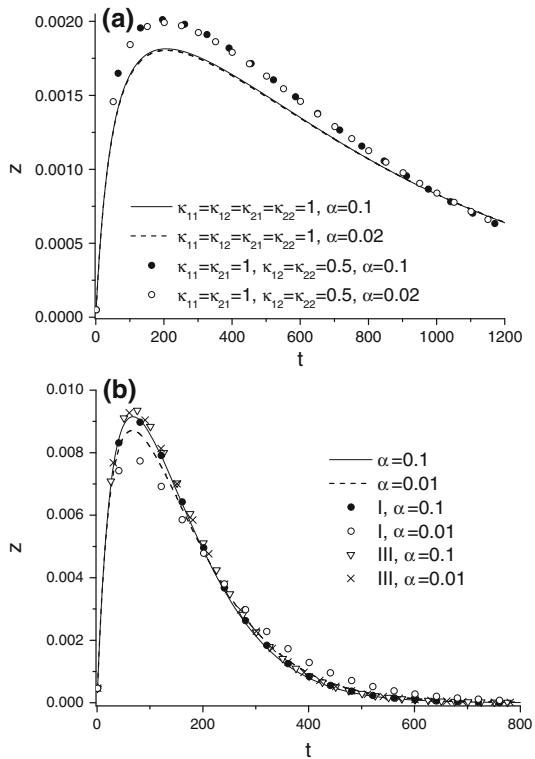
increases values of z. But these values practically coincide in the second and third cases of the active and inactive sites arrangement.

Calculation of an influence of parameter α on the dynamics of the total amount of reactant, $I_a(t) := \int_0^1 \int_0^1 a(t, x_1, x_2)\, dx_1 dx_2$, and product, $I_b(t) := \int_0^1 \int_0^1 b(t, x_1, x_2)\, dx_1 dx_2$, for distribution of active and inactive sites considered above shows that I_a practically does not depend on α. Dependence of $I_b(t)$ on α demonstrates a significant influence of α on $I_b(t)$ only in the first case of heterogeneous distribution of sites. In the second or third cases α practically does not influences I_b.

4 Conclusions

In this paper we studied theoretically the role of long-range surface diffusion of adsorbed particles on the kinetics of unimolecular heterogeneous reactions catalyzed by plane inhomogeneous surfaces. We studied a phenomenological model in two-dimensional in space case which involves a reactant adsorption and its desorption, long-range diffusion of the adsorbed particles on surfaces with different (non-uniform homogeneous and heterogeneous) arrangement of reactive and non-reactive sites, and an instantaneous product desorption from the adsorbent. The model also involves the

bulk diffusion of the reactant from the bounded vessel towards the adsorbent and the product bulk one from the adsorbent into the same vessel.

Inactive sites, due to the possibility of adsorption and surface diffusion of particles on them, constitute an additional channel transporting reactant particles onto active sites [14].

We demonstrated that surface diffusion rate constants κ_{ij} or dispersions of jumps lengths α_{ij} strongly influence the coverages θ_1 and θ_2 and turn-over rate z.

We found that:

In the case of non-uniform homogeneous distribution of sites, both coverages determined by system (1) with a given reactant concentration $a|_{S_2}$ tend to values independent of position on the surface S_2 as surface diffusion rate constants κ_{ij} or dispersions of jumps lengths α_{ij} increase.

In all cases of sites arrangement we considered as κ_{ij} or α_{ij} increase, we demonstrate a different behavior of $z(t)$ determined by system (1)–(3) or system (1) with given $a|_{S_2}$.

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