

# Numerical study of two-molecular catalytic reaction on composite catalyst

Pranas Katauskis, Živilė Vidutytė

*Faculty of Mathematics and Informatics, Vilnius University*

Naugarduko str. 24, LT-03225 Vilnius, Lithuania

E-mail: pranas.katauskis@mif.vu.lt, zivile.vidutyte@mif.stud.vu.lt

**Abstract.** In this paper a nonlinear mathematical model of the kinetics of two-molecular heterogeneous catalytic reaction proceeding on a supported catalyst is investigated numerically. The model is based on the Langmuir–Hinshelwood type kinetics of the surface reactions assuming that all species are well-mixed. The effect of the catalytic surface size, adsorption rate constants and jump rate via the catalyst-support interface constants on the catalytic reactivity and product concentration is studied for different arrangements of the adsorption sites.

**Keywords:** surface reaction, adsorption, desorption, spillover.

## Introduction

Catalytic reactions occurring on the surface of a solid (named the adsorbent) include the bulk diffusion of one or more reactants towards the adsorbent, adsorption of the reactant molecules on the catalyst surface forming one or more adsorbates, the conversion of the adsorbates into one or more products. A part of the adsorbates can desorb from the catalyst surface. The product molecules desorb and diffuse away from the catalyst surface. Molecules of the reactants that are physisorbed can diffuse along the catalytic surface before the conversion into the product molecules. The surface of real catalyst can consist of small active catalyst particles placed on inactive in reaction but active in adsorption process support. One of kinetic effects associated with composite catalysts is the spillover effect which has an important influence on catalytic reactions proceeding on supported catalyst. Parts of the catalyst surface that are inactive in the surface reaction are active for adsorption and desorption process. It increases or decreases the concentrations of adsorbates or product molecules on active parts of the catalyst surface through the migration of the adsorbed particles across the interface between the active and inactive in reaction parts of the catalyst [1, 2, 5]. In [4] the two-molecular catalytic reaction proceeding on a composite catalyst was studied using the coupled systems of parabolic PDEs and ODEs in case the concentrations of the reactants are given. Effect of the catalytic surface size was investigated in [3] in case the catalyst consists from three parts and the reactants can adsorb only in inactive in reaction domains. The goal of this paper is to study the influence of the catalytic surface size, adsorption and jump rate via the catalyst-support interface constants on the catalytic reactivity and product concentration when there is one active and one inactive in reaction region.

## 1 The mathematical model

We study the problem of two-molecular catalytic heterogeneous surface reaction proceeding on a supported catalyst based on the Langmuir–Hinshelwood kinetics and Gorban’s diffusion mechanism in case of the well-mixed species assumption:



Here  $A_1$  and  $A_2$  are the reactants,  $S$  is the vacant adsorption site,  $B = A_1A_2$  is the product,  $A_1S$  and  $A_2S$  are the adsorbates. The catalyst is composed from two active and inactive in reaction regions.  $S_2 = [0, x_*)$  and  $S_1 = (x_*, 1]$  are the regions of the active and inactive in reaction sites, respectively.  $k_{ij}$  and  $k_{-ij}$  are the adsorption and desorption rate constants of reactant  $A_i$ ,  $i = 1, 2$ , in region  $S_j$ ,  $j = 1, 2$ .  $k_{32}$  is the reaction between adsorbates  $A_1S$  and  $A_2S$  in region  $S_2$  rate constant. Assume that  $s_1, s_2$  are densities of the inactive and active in reaction sites of strips  $S_1$  and  $S_2$ . Let  $u_{ij}$  be densities of the active ( $j = 2$ ) and inactive ( $j = 1$ ) in reaction sites occupied by the adsorbed particles of reactants  $A_i$ ,  $i = 1, 2$ . We use  $\lambda_{1,i2}$ ,  $i = 1, 2$ , for the constants of the jump rate via the catalyst-support interface  $x_*$  of an adsorbed  $A_i$  particle from the position  $x_* - 0$  into the nearest-neighbour vacant site  $x_* + 0$ . Similarly,  $\lambda_{2,i1}$ ,  $i = 1, 2$ , denote the constants of the jump rate via the catalyst-support interface of an adsorbed  $A_i$  molecule from the position  $x_* + 0$  into the nearest-neighbour free site  $x_* - 0$ .

Concentrations of the reactants and product are solutions of the system [4]:

$$\begin{cases} a'_1 = -(1 - x_*)(k_{11}a_1(s_1 - u_{11} - u_{21}) - k_{-11}u_{11}) \\ \quad - x_*(k_{12}a_1(s_2 - u_{12} - u_{22}) - k_{-12}u_{12}), & a_1(0) = a_1^0, \\ a'_2 = -(1 - x_*)(k_{21}a_2(s_1 - u_{11} - u_{21}) - k_{-21}u_{21}) \\ \quad - x_*(k_{22}a_2(s_2 - u_{12} - u_{22}) - k_{-22}u_{22}), & a_2(0) = a_2^0, \\ b' = x_*k_{32}u_{12}u_{22}, & b(0) = 0. \end{cases} \quad (1)$$

We have the following equations for densities  $u_{ij}$ :

$$\begin{cases} u'_{11} = k_{11}a_1(s_1 - u_{11} - u_{21}) - k_{-11}u_{11} \\ \quad + (1 - x_*)^{-1}(\lambda_{1,12}u_{12}(s_1 - u_{11} - u_{21}) - \lambda_{2,11}u_{11}(s_2 - u_{12} - u_{22})), \\ u_{11}(0) = 0, \end{cases} \quad (2)$$

$$\begin{cases} u'_{21} = k_{21}a_2(s_1 - u_{11} - u_{21}) - k_{-21}u_{21} \\ \quad + (1 - x_*)^{-1}(\lambda_{1,22}u_{22}(s_1 - u_{11} - u_{21}) - \lambda_{2,21}u_{21}(s_2 - u_{12} - u_{22})), \\ u_{21}(0) = 0, \end{cases} \quad (3)$$

$$\begin{cases} u'_{12} = k_{12}a_1(s_2 - u_{12} - u_{22}) - k_{-12}u_{12} - k_{32}u_{12}u_{22} \\ \quad + x_*^{-1}(\lambda_{2,11}u_{11}(s_2 - u_{12} - u_{22}) - \lambda_{1,12}u_{12}(s_1 - u_{11} - u_{21})), \\ u_{12}(0) = 0, \end{cases} \quad (4)$$

$$\begin{cases} u'_{22} = k_{22}a_2(s_2 - u_{12} - u_{22}) - k_{-22}u_{22} - k_{32}u_{12}u_{22} \\ \quad + x_*^{-1}(\lambda_{2,21}u_{21}(s_2 - u_{12} - u_{22}) - \lambda_{1,22}u_{22}(s_1 - u_{11} - u_{21})), \\ u_{22}(0) = 0. \end{cases} \quad (5)$$

Problem (1)–(5) possesses two mass conservation laws – the sum of the free, adsorbed, converted into a product reactant at time  $t > 0$  equals the initial amount of the reactant:

$$a_1 + b + (1 - x_*)u_{11} + x_*u_{12} = a_1^0, \quad a_2 + b + (1 - x_*)u_{21} + x_*u_{22} = a_2^0. \quad (6)$$

In this paper we examine the dependence of the product concentration and the turn-over rate – the catalyst surface  $S_2$  specific conversion rate of the reactants molecules into product molecules – defined by the formula

$$z = \frac{k_{32}u_{12}u_{22}}{s_2} \quad (7)$$

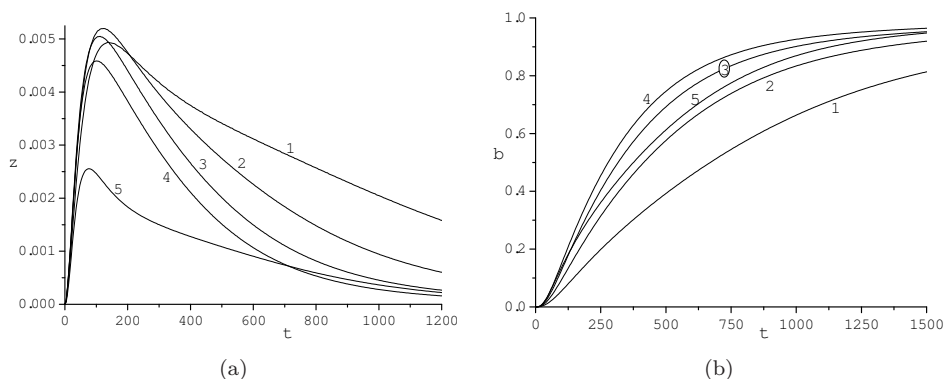
on the active domain size and rate constants. Problem (1)–(5) is written in dimensionless form. In what follows all variables and parameters are non-dimensional.

## 2 Numerical results

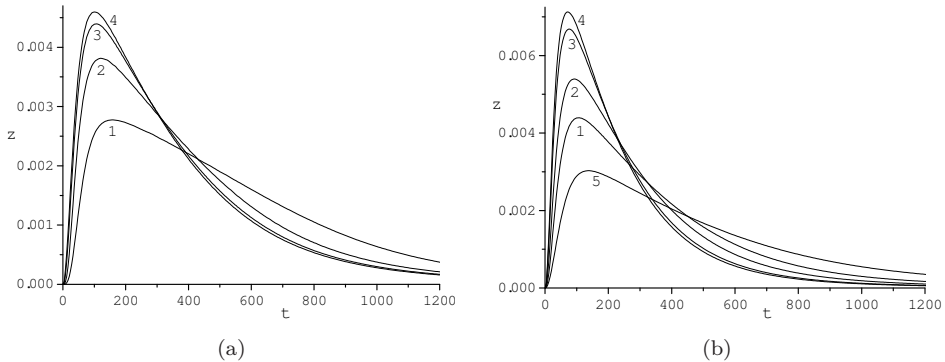
To solve systems (1)–(5) numerically the standard MATLAB ODE solver ode45 was used. The following values of parameters were used in calculations:  $k_{ij} = 0.015$ ,  $k_{-ij} = 0.0015$ ,  $i, j = 1, 2$ ;  $k_{32} = 0.1$ ;  $\lambda_{j+1,ij} = \lambda_{j,ij+1} = 0.1$ ,  $i = 1, 2$ ,  $j = 1$ ;  $a_1^0 = a_2^0 = 1$ . If values of  $k_{ij}$ ,  $\lambda_{j,il}$  do not depend on the values of indices we use  $k$  and  $\lambda$  for short. In all cases laws (6) were fulfilled with  $10^{-8}$  accuracy.

All calculations were performed for two different arrangements of the adsorption sites (a)  $s_1 = s_2 = 1$  and (b)  $s_1 = 0.5s/(1 - x_*)$ ,  $s_2 = 0.5s/x_*$ ,  $s = 1$ . In the second case the total numbers of the active and inactive sites are equal  $0.5s$ . Three variants of reactants adsorption are studied: both reactant can adsorb on the active in reaction catalyst surface and inactive in reaction support; one of reactants adsorbs on the active in reaction domain while the other one adsorbs on the inactive domain; both reactants adsorb only on the support.

Fig. 1 presents the comparison of turn-over rate  $z$  and product concentration  $b$  dynamics when reactant  $A_1$  adsorbs on the inactive region  $S_1$ , while reactant  $A_2$  adsorbs on the active region  $S_2$ , i.e.  $k_{12} = k_{21} = 0$ , for densities  $s_1 = s_2 = 1$ . The



**Fig. 1.** Effect of the catalytic surface size  $x_*$ : 0.2 (1), 0.3 (2), 0.4 (3), 0.5 (4), 0.75 (5) on turn-over rate  $z$  (a) and product concentration  $b$  (b) in case  $k_{12} = k_{21} = 0$ ,  $k_{11} = k_{22} = 0.015$ .

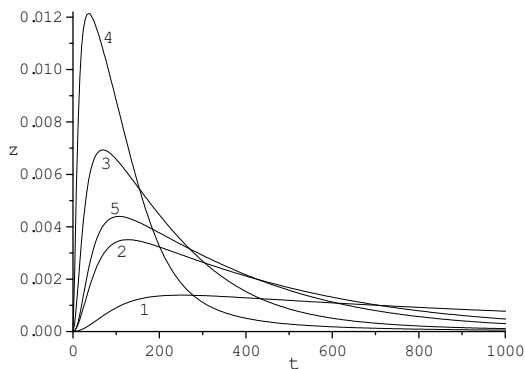


**Fig. 2.** Dependence of the catalytic reactivity  $z$  on jump rate constants  $\lambda$ : 0.01 (1), 0.03 (2), 0.1 (3), 0.3 (4) (a) and  $\lambda = 0.1$  (1);  $\lambda_{2,21} = 0.5$  (2);  $\lambda_{2,11} = 0.3$ ,  $\lambda_{2,21} = 0.5$  (3);  $\lambda_{2,11} = \lambda_{2,21} = 0.5$  (4);  $\lambda_{1,22} = 0.5$  (5) and  $\lambda_{i,jl} = 0.1$  for other values of indices (b) in case  $k_{12} = k_{22} = 0$ ,  $k_{11} = k_{21} = 0.015$ .

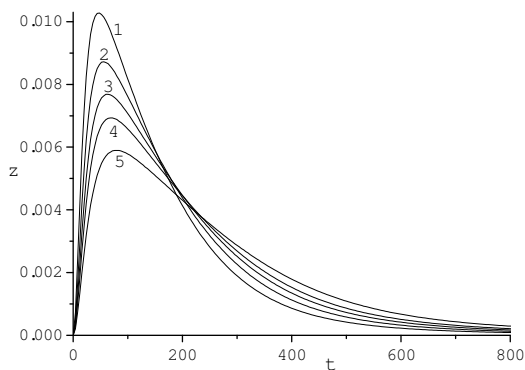
reaction occurs when  $A_1$  is transported in domain  $S_2$  due to the spillover. The number of the active in reaction adsorption sites increases and the number of the inactive sites decreases as  $x_*$  grows. The turn-over rate is non-monotonic active interval size and time function. For fixed values of parameters  $z(t)$  grows as time increases, reaches a maximum and then decreases. The maximum value of  $z$  weakly depends on time, but strongly on parameter  $x_*$ . The peak of conversion rate is reached for  $x_* \approx 0.3$ . The turn-over rate  $z(t)$  is a monotonically decreasing function of  $x_*$  for  $220 \lesssim t \lesssim 600$   $z(t)$ . The product concentration is monotonically increasing time function, but non-monotonic active in reaction domain size function. Function  $b(t)$  grows as  $x_*$  increases till 0.5 where it reaches the maximal values (curves 1–4, Fig. 1b) and then decreases (curves 4, 5).

Fig. 2 demonstrates the effect of the variation of the particle jumping rate constants  $\lambda_{1,i2}$  and  $\lambda_{2,i1}$ ,  $i = 1, 2$  for  $s_1 = s_2 = 1$  and  $x_* = 0.5$  in the case where  $A_1$  and  $A_2$  can adsorb only on the inactive interval. The surface reaction proceeds only due to spillover effect.  $z(t)$  grows as time increases, possesses a maximum and then tends to zero. Fig. 2(a) shows the increase of function  $z(t)$  as the jumping rate constant  $\lambda = \lambda_{1,12} = \lambda_{1,22} = \lambda_{2,11} = \lambda_{2,21}$  grows for small time, while for large time the behaviour of  $z(t)$  is opposite. We observe that  $z(t)$  grows for small time as the jump rates,  $\lambda_{2,11}$  or  $\lambda_{2,21}$ , of  $A_1$  or  $A_2$  from the inactive position  $x_* + 0$  into the active free position  $x_* - 0$  increase (curves 1–4, Fig. 2b).  $z(t)$  decreases for small time as the jump rate of  $A_2$ ,  $\lambda_{1,22}$ , from the active position  $x_* - 0$  into the inactive vacant position  $x_* + 0$  grows (curves 1, 5, Fig. 2(b)). For large time turn-over rate behaves vice-versa.

The catalytic reactivity is non-monotonic adsorption rate constant  $k$  and time function in the case where the reactants  $A_1$  and  $A_2$  can adsorb on both active and inactive intervals. For small  $k$  function  $z(t)$  grows in time, possesses the small maximum and then slowly decreases to zero (curves 1 and 3, Fig. 3). The turn-over rate more quickly grows in time, reaches a large maximum value and sharply falls as the adsorption rate increases (curves 3 and 4). We observe a similar behaviour of factor  $z$  in the cases where  $A_1$  and  $A_2$  can adsorb only on the inactive region or where each reactant adsorbs on both regions (curves 3 and 5). If each reactant adsorbs on both



**Fig. 3.** Influence of the adsorption rate constants  $k$ : 0.0015 (1), 0.005 (2), 0.015 (3), 0.05 (4) and  $k_{11} = k_{21} = 0.015, k_{12} = k_{22} = 0$  (5) on turn-over rate  $z$ .



**Fig. 4.** Effect of the catalytic surface size  $x_*$ : 0.2 (1), 0.3 (2), 0.4 (3), 0.5 (4), 0.7 (5) on turn-over rate  $z$  in case  $s_1 = 0.5/(1 - x_*)$ ,  $s_2 = 0.5/x_*$  and  $k_{12} = k_{21} = k_{11} = k_{22} = 0.015$ .

active and inactive regions values of  $z$  are large than those corresponding to the other adsorption case, i.e.  $k_{12} = k_{22} = 0$ , for small  $t$ , while for large  $t$  its values are smaller (curves 3 and 5). If reactant  $A_1$  adsorbs on the inactive region  $S_1$ , while reactant  $A_2$  adsorbs on the active region  $S_2$ , i.e.  $k_{12} = k_{21} = 0$ , values of  $z$  are close to those corresponding the case  $k_{12} = k_{22} = 0$  (results not shown).

Fig. 4 illustrates the dependence of catalytic reactivity on the active domain size for the case where densities are  $s_1 = 0.5/(1 - x_*)$ ,  $s_2 = 0.5/x_*$  and each reactant can adsorb on both active and inactive regions. Now the total amount of the active and inactive adsorption sites does not depend on  $x_*$  and is equal 0.5. Turn-over rate is non-monotonic time function. The increase of the active domain size increases  $z$  for small  $t$ . For large  $t$  its influence is opposite. Maximum of  $z$  strongly depends on  $x_*$ , but weakly on time  $t$ , e.g.  $z_{\max}$  is 0.01 at  $t = 48$  for  $x_* = 0.2$  and 0.006 at  $t = 78$  for  $x_* = 0.7$ .

### 3 Conclusions

The two-molecular surface reaction proceeding on the composite catalyst was studied numerically by using the well-mixed species model for two arrangements of adsorp-

tion sites. The size of the active in reaction domain, densities of adsorption sites, adsorption rate constants and jump rate via the catalyst-support interface constants strongly influence the catalytic reactivity and product concentration. The results of numerical investigation are the following: (a) In case where the reactants adsorb on different regions and  $s_1 = s_2 = 1$  the product concentration is non-monotonic active interval size, but monotonic time function. (b) The turn-over rate in this case is non-monotonic active interval size and time function. (c) If both reactants adsorb only on the support and  $s_1 = s_2 = 1$  the product concentration is non-monotonic active interval size, but monotonic jump rate via the catalyst-support interface constant  $\lambda$  function.

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## REZIUMĖ

### Dvimolekulinės katalitinės reakcijos kompozitinio katalizatoriaus paviršiuje skaitinis tyrimas

P. Katauskis, Ž. Vidutytė

Nagrinėjamas netiesinis modelis aprašantis dvimolekulinę heterogeninę katalitinę reakciją, vykstančią kompozitinio katalizatoriaus paviršiuje. Modelis pagrįstas Langmiūro ir Hinšelvudo paviršinių reakcijų kinetika, kai reakcijoje dalyvaujančios medžiagos yra vienodai pasiskirsčiusios. Tiriama aktyvios katalizatoriaus paviršiaus dalies dydžio, adsorbcijos ir šuolių per sritis skiriančią ribą greičių įtaka katalitiniam reaktyvumui ir produkto koncentracijai.

*Raktiniai žodžiai:* paviršinė reakcija, adsorbcija, desorbcija, spiloveris.