

# Numerical study of monomer-monomer reactions on composite catalysts: well-mixed species model\*

Pranas Katauskis, Justas Sakalauskas

*Faculty of Mathematics and Informatics, Vilnius University*  
Naugarduko 24, LT-03225 Vilnius

E-mail: pranas.katauskis@mif.vu.lt, uaimedna@gmail.com

**Abstract.** A nonlinear mathematical model describing the kinetics of a bimolecular heterogeneous catalytic reaction proceeding on a supported catalyst is studied. The model is based on the Langmuir–Hinshelwood surface reaction mechanism assuming that all species are well-mixed. The catalytic surface size influence on the catalytic reactivity and product concentration is investigated numerically for different arrangements of the adsorption sites.

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

## Introduction

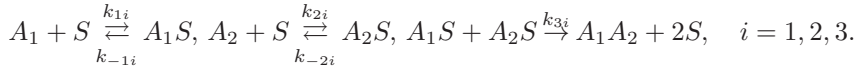
In order for the catalytic reaction on a surface to take place, one or more of the reactants must diffuse to the catalyst surface and adsorb onto it forming one or more adsorbates. After reaction of the adsorbed molecules into a product, the product molecules desorb and diffuse away from the adsorbent. A part of the adsorbed reactant molecules can desorb from the adsorbent. In case of the weak surface and reactant interaction molecules of the reactant can diffuse along the surface before the conversion into the product. The catalyst can consist of small active catalyst particles placed on inactive in reaction support. One of kinetic effects associated with small catalyst particles on a support is the spillover effect. Spillover is an effect of the heterogeneous surface reactions when inactive in reactions surface regions notably influence the kinetics of the overall catalytic process [5] The surface parts which are inactive in the surface reaction can be active for adsorption-desorption process and increase or decrease concentrations of 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, 2, 3, 5]. In [4] the kinetics of two-molecular catalytic reaction proceeding on a composite catalyst consisting from the active and inactive in reaction parts was studied using the coupled systems of parabolic PDEs and ODEs. The aim of this paper is to study the influence of the catalytic surface size on the catalytic reactivity and product concentration.

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\* The authors would like to thank Prof. V. Skakauskas for mathematical model.

### 1 The mathematical model

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



Here  $S$  is the free adsorption site,  $B = A_1A_2$  – the product. The catalyst is composed of three active and inactive in reaction regions  $S_1, S_2, S_3$ .  $x_1^*$  and  $x_2^*$  ( $x_1^* < x_2^*$ ) are the catalyst-support interface points of the interval  $[0, 1]$ .  $k_{ij}$  and  $k_{-ij}$  are the adsorption and desorption rates constants of reactant  $A_i, i = 1, 2$ , in region  $S_j, j = 1, 2, 3$ .  $k_{3j}$  are the reaction between adsorbates  $A_1S$  and  $A_2S$  in region  $S_j, j = 1, 2, 3$ , rate constants.

Let  $s_j, j = 1, 2, 3$ , be densities of the active or inactive in reaction sites of strip  $S_j$ . Functions  $u_{ij}$  present density of particles of species  $A_iS, i = 1, 2$ , bound to sites that are located in region  $S_j, j = 1, 2, 3$ . Assume that  $\lambda_{j+1,i,j}, i = 1, 2, j = 1, 2$ , are the constants of the jump rate via the catalyst-support interfaces  $x_{3-j}^*$  of an adsorbed  $A_i$  particle from the position  $x_{3-j}^* + 0$  into the nearest-neighbour vacant site  $x_{3-j}^* - 0$ . Similarly,  $\lambda_{j,i,j+1}, i = 1, 2, j = 1, 2$ , are the constants of the jump rate via the catalyst-support interfaces of an adsorbed  $A_i$  particle from the position  $x_{3-j}^* - 0$  into the nearest-neighbour free site  $x_{3-j}^* + 0$ .

Dynamics of the concentration of the reactants and product is described by the system:

$$\begin{cases} a'_1 = -(1 - x_2^*)(k_{11}a_1(s_1 - u_{11} - u_{21}) - k_{-11}u_{11}) \\ \quad - (x_2^* - x_1^*)(k_{12}a_1(s_2 - u_{12} - u_{22}) - k_{-12}u_{12}) \\ \quad - x_1^*(k_{13}a_1(s_3 - u_{13} - u_{23}) - k_{-13}u_{13}), \quad a_1(0) = a_{10}; \\ a'_2 = -(1 - x_2^*)(k_{21}a_2(s_1 - u_{11} - u_{21}) - k_{-21}u_{21}) \\ \quad - (x_2^* - x_1^*)(k_{22}a_2(s_2 - u_{12} - u_{22}) - k_{-22}u_{22}) \\ \quad - x_1^*(k_{23}a_2(s_3 - u_{13} - u_{23}) - k_{-23}u_{23}), \quad a_2(0) = a_{20}; \\ b' = (1 - x_2^*)k_{31}u_{11}u_{21} + (x_2^* - x_1^*)k_{32}u_{12}u_{22} + x_1^*k_{33}u_{13}u_{23}, \\ b(0) = 0. \end{cases} \tag{1}$$

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

$$\begin{cases} u'_{11} = k_{11}a_1(s_1 - u_{11} - u_{21}) - k_{-11}u_{11} - k_{31}u_{11}u_{21} \\ \quad + (1 - x_2^*)^{-1}(\lambda_{1,12}u_{12}(s_1 - u_{11} - u_{21}) - \lambda_{2,11}u_{11}(s_2 - u_{12} - u_{22})), \\ u_{11}(0) = 0, \end{cases} \tag{2}$$

$$\begin{cases} u'_{21} = k_{21}a_2(s_1 - u_{11} - u_{21}) - k_{-21}u_{21} - k_{31}u_{11}u_{21} \\ \quad + (1 - x_2^*)^{-1}(\lambda_{1,22}u_{22}(s_1 - u_{11} - u_{21}) - \lambda_{2,21}u_{21}(s_2 - u_{12} - u_{22})), \\ u_{21}(0) = 0, \end{cases} \tag{3}$$

$$\begin{cases} u'_{12} = k_{12}a_1(s_2 - u_{12} - u_{22}) - k_{-12}u_{12} - k_{32}u_{12}u_{22} \\ \quad + (x_2^* - x_1^*)^{-1}(\lambda_{2,11}u_{11}(s_2 - u_{12} - u_{22}) - \lambda_{1,12}u_{12}(s_1 - u_{11} - u_{21}) \\ \quad + \lambda_{2,13}u_{13}(s_2 - u_{12} - u_{22}) - \lambda_{3,12}u_{12}(s_3 - u_{13} - u_{23})), \\ u_{12}(0) = 0, \end{cases} \quad (4)$$

$$\begin{cases} u'_{22} = k_{22}a_2(s_2 - u_{12} - u_{22}) - k_{-22}u_{22} - k_{32}u_{12}u_{22} \\ \quad + (x_2^* - x_1^*)^{-1}(\lambda_{2,21}u_{21}(s_2 - u_{12} - u_{22}) - \lambda_{1,22}u_{22}(s_1 - u_{11} - u_{21}) \\ \quad + \lambda_{2,23}u_{23}(s_2 - u_{12} - u_{22}) - \lambda_{3,22}u_{22}(s_3 - u_{13} - u_{23})), \\ u_{22}(0) = 0, \end{cases} \quad (5)$$

$$\begin{cases} u'_{13} = k_{13}a_1(s_3 - u_{13} - u_{23}) - k_{-13}u_{13} - k_{33}u_{13}u_{23} \\ \quad + (x_1^*)^{-1}(\lambda_{3,12}u_{12}(s_3 - u_{13} - u_{23}) - \lambda_{2,13}u_{13}(s_2 - u_{12} - u_{22})), \\ u_{13}(0) = 0, \end{cases} \quad (6)$$

$$\begin{cases} u'_{23} = k_{23}a_2(s_3 - u_{13} - u_{23}) - k_{-23}u_{23} - k_{33}u_{13}u_{23} \\ \quad + (x_1^*)^{-1}(\lambda_{3,22}u_{22}(s_3 - u_{13} - u_{23}) - \lambda_{2,23}u_{23}(s_2 - u_{12} - u_{22})), \\ u_{23}(0) = 0. \end{cases} \quad (7)$$

Problem (1)–(7) possesses mass conservation laws – the sum of the free, adsorbed, converted into a product reactant equals the initial amount of the reactant:

$$\begin{aligned} a_1 + b + (1 - x_2^*)u_{11} + (x_2^* - x_1^*)u_{12} + x_1^*u_{13} &= a_{10}, \\ a_2 + b + (1 - x_2^*)u_{21} + (x_2^* - x_1^*)u_{22} + x_1^*u_{23} &= a_{20}. \end{aligned} \quad (8)$$

The first characteristic that we examine in this paper is the turn-over rate – the catalyst surface specific conversion rate of the reactants molecules into product molecules defined by the formula

$$z = \frac{k_{33}x_1^*u_{13}u_{23} + k_{32}(x_2^* - x_1^*)u_{12}u_{22} + k_{31}(1 - x_2^*)u_{11}u_{21}}{x_1^*s_3 + (1 - x_2^*)s_1 + (x_2^* - x_1^*)s_2}. \quad (9)$$

The second important characteristic is the product concentration.

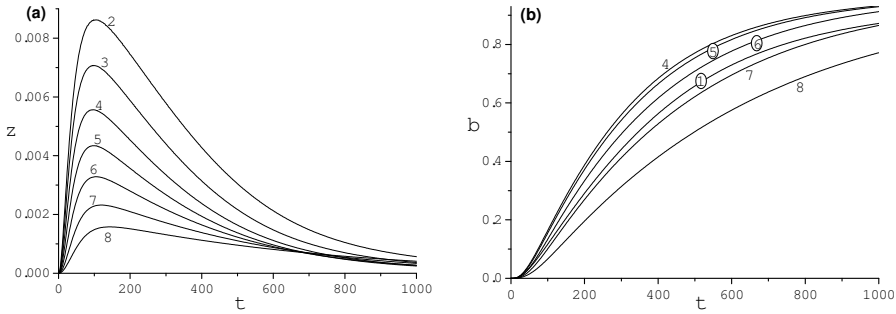
Problem (1)–(7) is written in dimensionless form. In what follows all variables and parameters are non-dimensional.

## 2 Numerical results

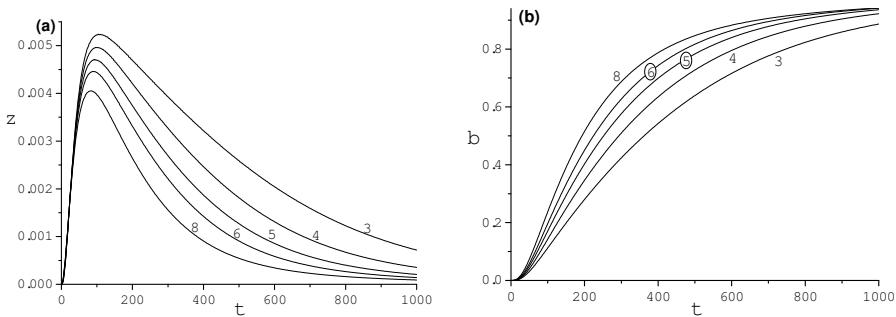
The standard MATLAB ODE solver ode45 was used in our numerical calculations. The following values of parameters were used in calculations:  $k_{ij} = 0.017$ ,  $k_{-ij} = 0.0017$ ,  $k_{3j} = 0.1$ ,  $j = 1, 2, 3$ ,  $i = 1, 2$ ;  $\lambda_{j+1,ij} = \lambda_{j,ij+1}$ ,  $j, i = 1, 2$ ;  $a_1^0 = a_2^0 = 1$ . In all cases laws (8) were fulfilled with  $10^{-7}$  accuracy.

All calculations were performed for two different arrangements of the adsorption sites (a)  $s_1 = s_2 = s_3 = 1$  and (b)  $s_2 = s_1(1 + x_1^* - x_2^*)/(x_2^* - x_1^*)$ ,  $s_1 = s_3 = 1$ . In the second case, the total numbers of the active and inactive sites are equal, i.e.  $x_1^*s_3 + (1 - x_2^*)s_1 = (x_2^* - x_1^*)s_2$ . Numerical results are given for such pairs  $(x_1^*; x_2^*)$  of the catalyst-support interface points  $x_1^*$  and  $x_2^*$ :

$$\begin{cases} 1 - \left(\frac{1}{12}, \frac{11}{12}\right), 2 - \left(\frac{1}{8}, \frac{7}{8}\right), 3 - \left(\frac{1}{6}, \frac{5}{6}\right), 4 - \left(\frac{7}{32}, \frac{25}{32}\right), \\ 5 - \left(\frac{13}{48}, \frac{35}{48}\right), 6 - \left(\frac{31}{96}, \frac{65}{96}\right), 7 - \left(\frac{3}{8}, \frac{5}{8}\right), 8 - \left(\frac{5}{12}, \frac{7}{12}\right). \end{cases} \quad (10)$$



**Fig. 1.** Dependence of catalytic reactivity  $z$  (a) and product concentration  $b$  (b) on catalytic surface size (some of the pairs (10)) in case  $s_1 = s_2 = s_3 = 1$  and  $k_{31} = k_{33} = 0.1$ ,  $k_{32} = k_{11} = k_{21} = k_{13} = k_{23} = 0$ .

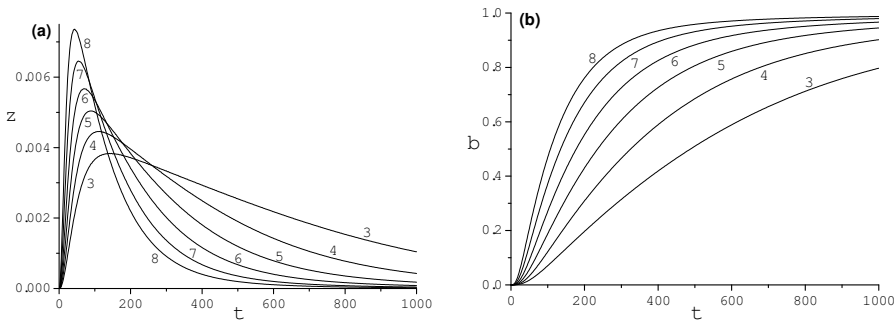


**Fig. 2.** Influence of the catalytic surface size (some of the pairs (10)) on turn-over rate  $z$  (a) and product concentration  $b$  (b) in case  $s_1 = s_3 = 1$ ,  $s_2 = s_1(1 + x_1^* - x_2^*)/(x_2^* - x_1^*)$  and  $k_{31} = k_{33} = 0.1$ ,  $k_{32} = k_{11} = k_{21} = k_{13} = k_{23} = 0$ .

We investigate the adsorption of both reactants  $A_1, A_2$  only on the inactive in reaction support and conversion of the reactants molecules into the product molecules on the active in reaction catalyst surface.

Firstly we study the case where both reactants adsorb on the interval  $(x_1^*, x_2^*)$ , i.e.  $k_{11} = k_{21} = k_{13} = k_{23} = 0$  and the reaction occurs on the intervals  $[0, x_1^*]$  and  $(x_2^*, 1]$ , i.e.  $k_{32} = 0$ . Fig. 1 presents the dependence of turn-over rate  $z$  and product concentration  $b$  on the active domain  $[0, x_1^*] \cup (x_2^*, 1]$  size for densities  $s_1 = s_2 = s_3 = 1$ . The number of active adsorption sites grows and of inactive adsorption sites drops as  $x_1^*$  increases and  $x_2^*$  decreases. The conversion rate is non-monotonic active interval length and time functions. Maximum of  $z$  strongly depends on  $x_1^*$  and  $x_2^*$ , but weakly on time  $t$ , e.g. it is equal 0.0086 at  $t = 105$ , 0.0056 at  $t = 96$  and 0.0016 at  $t = 145$  for curves 2, 4 and 8 (Fig. 1(a)), respectively. The product concentration is monotonically increasing time function, but non-monotonic active in reaction domain size function. The peak product concentration is reached for  $x_1^* \approx \frac{7}{32}$ ,  $x_2^* \approx \frac{25}{32}$  (curve 4, Fig. 1(b)). The product concentration falls as the active domain increases (curves 5–8).

Fig. 2 demonstrates the influence of the active domain  $[0, x_1^*] \cup (x_2^*, 1]$  size on the turn-over rate and product concentration for densities  $s_2 = s_1(1 + x_1^* - x_2^*)/(x_2^* - x_1^*)$ ,  $s_1 = s_3 = 1$ . Both functions,  $z(t)$  and  $b(t)$ , grow as the size of active interval increases (for fixed time  $x_1^*$  increases and  $x_2^*$  decreases). The differences between maximal values of conversion rate  $z$  are much smaller than those in Fig. 1(a) corresponding to the



**Fig. 3.** Effect of the catalytic surface size (some of the pairs (10)) on catalytic reactivity  $z$  (a) and product concentration  $b$  (b) for  $s_2 = s_1(1 + x_1^* - x_2^*)/(x_2^* - x_1^*)$ ,  $s_1 = s_3 = 1$  and  $k_{32} = 0.1$ ,  $k_{31} = k_{33} = k_{12} = k_{22} = 0$ .

same size of active in reaction domain, e.g. maximal values are  $z(104) = 0.00524$  (curve 3, Fig. 2(a)) and  $z(83) = 0.00405$  (curve 8, Fig. 2(a)). We observe that in this case the values of  $z$  is remarkably smaller compared to those corresponding to the same small values of active interval length of the case  $s_1 = s_2 = s_3 = 1$  for small  $t$  (curves 3 of Figs. 1(a) and 2(a)). For small  $t$  and long active interval the conversion rate  $z$  behaves vice-versa (curves 6 and 8).

Fig. 3 shows the dynamics of  $z(t)$  and  $b(t)$  for densities  $s_2 = s_1(1 + x_1^* - x_2^*)/(x_2^* - x_1^*)$ ,  $s_1 = s_3 = 1$ , when the active in reaction interval is  $(x_1^*, x_2^*)$  and both reactants can adsorb on the support  $[0, x_1^*) \cup (x_2^*, 1]$ . In this case  $k_{12} = k_{22} = 0$  and  $k_{31} = k_{33} = 0$ . The catalytic reactivity is non-monotonic active interval length and time function. For long active interval function  $z(t)$  grows in time, possesses the small maximum and then slowly decreases to zero (curve 3, Fig. 3(a)). The turn-over rate more quickly grows in time, reaches a large maximum value and sharply falls as the active in reaction domain decreases (curves 6–8, Fig. 3(a)). Fig. 3(a) demonstrates that  $z(t)$  as function of the active interval length increases for small time, but it decreases for large time as the active zone narrows – number of the active and inactive adsorption sites grows as  $x_1^*$  increases and  $x_2^*$  decreases. The product concentration is monotonically increasing time function and monotonically decreasing function of the active in reaction domain size (Fig. 3(b)). Concentration  $b(t)$  rapidly reaches a saturation value when the active interval is short (curves 7, 8). The growth of  $b(t)$  in time is slow if the number of active in reaction sites is small (curve 3, Fig. 3(b)).

### 3 Conclusions

The bimolecular surface reaction proceeding on the supported catalyst was studied numerically by using the well-mixed species model for different arrangements of adsorption sites. The size of the active in reaction domain and the arrangement of adsorption sites strongly influence the catalytic reactivity and product concentration. The results of numerical investigation are the following: (a) In case where both reactants adsorb only on interval  $(x_1^*, x_2^*)$  and  $s_1 = s_2 = s_3 = 1$  there exists the optimal active domain size for the product concentration. (b) If active interval is  $(x_1^*, x_2^*)$  and densities are  $s_2 = s_1(1 + x_1^* - x_2^*)/(x_2^* - x_1^*)$ ,  $s_1 = s_3 = 1$  the turn-over rate grows for small time and decreases for large time as the size of the active domain

decreases. (c)  $z$  is non-monotonic in time, it reaches a maximum and tends to zero as time increases.

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## REZIUMĖ

### Monomerų reakcijų kompozitinių katalizatorių paviršiuje skaitinis tyrimas: gerai išmaišytų medžiagų modelis

*P. Katauskis, J. Sakalauskas*

Nagrinėjamas netiesinis modelis aprašantis heterogeninę katalitinę dviejų reagentų reakciją, vykstančią kompozitinių katalizatorių paviršiuje. Modelis pagrįstas Langmiūro ir Hinšelvudo paviršinių reakcijų mechanizmu, laikant, kad reakcijoje dalyvaujančios medžiagos yra tolygiai pasiskirsčiusios. Tiriama aktyvios katalizatoriaus paviršiaus dalies dydžio įtaka katalitiniam reaktyvumui ir produkto koncentracijai, esant skirtingam adsorbcijos centrų išsidėstymui.

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