Lietuvos matematikos rinkinys
Proc. of the Lithuanian Mathematical Society, Ser. A
DOI: 10.15388/LMR.A.2017.03

ISSN 0132-2818
Vol. **58**, 2017
pages 10–15

Comparison of two models of the dimer–dimer reaction on composite catalyst

Pranas Katauskis

Faculty of Mathematics and Informatics, Vilnius University
Naugarduko 24, LT-03225, Vilnius, Lithuania
E-mail: pranas.katauskis@mif.vu.lt

Abstract. In this paper two mathematical models of the dimer–dimer reaction on supported catalysts are compared. The PDE model describe the bulk diffusion of both reactants and product, adsorption and desorption, the surface diffusion of adsorbates and intermediate. The ODE model is derived from the first, assuming that all materials are well-mixed. The catalytic reactivity, calculated using the PDE and ODE models, is compared for two variants of reactants adsorption and variuos bulk and surface diffusion.

Keywords: surface reaction, adsorption; desorption, spillover.

Introduction

Adsorption is an essential first step in heterogeneous catalysis when a molecule in the gas phase or in solution binds to atoms on the solid surface. The molecule that is binding is called the adsorbate and the surface to which it binds is the adsorbent. In heterogeneous catalysis the reactants diffuse to the catalyst surface and adsorb onto it via the formation of chemical bonds. A part of the adsorbates split from the adsorbent. The product molecules desorb and diffuse away from the catalyst surface.

The surface of catalyst can consist of small active catalyst particles affixed on solid material which is inactive in reaction but active in adsorption process. The spillover, when adsorbates can migrate from the catalyst particle to support and from the support to catalyst particle, 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. Spillover increases or decreases the concentrations of adsorbates or product molecules on active parts of the catalyst surface [1, 2, 5].

The dimer–dimer heterogeneous surface reaction proceeding on supported catalyst was examined in [5] using a rather complicated mathematical model of parabolic PDEs. One part of partial differential equations was solved in 2D domain. Another part of PDEs was determined on a boundary of the domain. Two-molecular reaction with spillover effect was investigated in [4] assuming that materials are well-mixed.

The purpose of this study was to compare the results obtained using two models: (a) the PDE model given in [5], which takes into account the bulk diffusion of both reactants and the reaction product and the surface diffusion of the adsorbed molecules of each reactant; (b) the simplified model based on ODEs if all species are well-mixed.

1 The mathematical model

The dimer–dimer heterogeneous surface reaction that occurs on a composite catalyst, $2A_2+B_2 \to 2A_2B$, is examined, provided that the reactants and reaction product are well-mixed. The following is the reaction scheme, where S is the vacant adsorption site, A_2 and B_2 are reactants, and $P = A_2B$ is the product of the reaction of A_2 and B_2:

$$\begin{cases} A_2 + 2S \underset{k_{-1i}}{\overset{k_{1i}}{\rightleftarrows}} 2AS, \\ B_2 + 2S \underset{k_{-2i}}{\overset{k_{2i}}{\rightleftarrows}} 2BS, \\ AS + BS \xrightarrow{k_3} ABS + S, \\ AS + ABS \xrightarrow{k_4} P + 2S, \\ 2ABS \xrightarrow{k_5} P + BS + S. \end{cases}$$

Here AS, BS and ABS are adsorbates of reactants A, B and intermediate AB. Let reactants A, B and product P fill in the domain Ω with surface $\partial\Omega = \tilde{S} \cup \bar{S}$. The catalyst surface $\bar{S}$ is composed from two active and inactive in reaction regions S_1 and S_2. Let k_{1i}, k_{2i} be the adsorption and k_{-1i}, k_{-2i} the desorption rates constants for inactive site ($i = 1$) and for active one ($i = 2$) of reactants A and B. k_3 is the reaction between adsorbates AS and BS rate constant, k_4 is the reaction between adsorbate AS and intermediate ABS rate constant, and k_5 is the conversion rate constant of ABS into product P.

The mathematical model of the surface reaction proceeding on a composite catalyst is written using the Langmuir–Hinshelwood kinetics and the surface diffusion mechanism based on the particle jumping into a nearest vacant adsorption site [3].

Assume that s_1, s_2 are densities of the inactive and active in reaction adsorption sites of strips S_1 and S_2. In case where densities s_1, s_2 depend only on variable x_1 and the initial concentrations of reactants are constants the 3D in space problem can be reduced in the 2D problem (see [5]). Let $x_* \in (0,1)$ be the catalyst–support interface then $S_2 = [0, x_*)$ and $S_1 = (x_*, 1]$ are domains consisting of the active and inactive in reaction adsorption sites.

Assume that u_{12}, u_{22}, u_{32} are densities of the active in the surface reaction sites occupied by the adsorbed molecules of reactants A, B and particles of intermediate AB. Similarly, u_{11}, u_{21}, u_{31} denote densities of particles of adsorbates AS, BS and ABS bound to the inactive in reaction sites. Differencies $s_1 - u_{11} - u_{21} - u_{31}$ and $s_2 - u_{12} - u_{22} - u_{32}$ are densities of the vacant adsorption sites of strips S_1 and S_2.

Let $\lambda_{2,11}$, $\lambda_{2,21}$ and $\lambda_{2,31}$ be the constants of the jump rates via the catalyst–support interface x_* of particles of AS, BS and ABS from the inactive position $x_* + 0$ into the nearest-neighbour free active site $x_* - 0$. Similarly, $\lambda_{1,12}$, $\lambda_{1,22}$ and $\lambda_{1,32}$ present the constants of the jump rates via x_* of particles of adsorbates AS, BS and ABS from the active position $x_* - 0$ into the nearest-neighbour vacant inactive site $x_* + 0$.

A simplified mathematical model based on the ODEs is derived from the PDE model given in [5] using the averaging procedure. Concentrations $a(t)$, $b(t)$ and $p(t)$ of reactants A_2, B_2 and their reaction product $P = A_2B$, respectively, are solutions of the system:

$$\begin{cases} a' = -(1-x_*)\big(k_{11}a(s_1-u_{11}-u_{21}-u_{31})^2-k_{-11}u_{11}^2\big) \\ \qquad -x_*\big(k_{12}a(s_2-u_{12}-u_{22}-u_{32})^2-k_{-12}u_{12}^2\big), \quad a(0)=a_0; \\ b' = -(1-x_*)\big(k_{21}b(s_1-u_{11}-u_{21}-u_{31})^2-k_{-21}u_{21}^2\big) \\ \qquad -x_*\big(k_{22}b(s_2-u_{12}-u_{22}-u_{32})^2-k_{-22}u_{22}^2\big), \quad b(0)=b_0; \\ p' = x_*\big(k_5u_{32}^2+k_4u_{12}u_{32}\big), \quad p(0)=0. \end{cases} \tag{1}$$

System (1) is solved together with the following equations to find the unknown values of densities u_{ij}:

$$\begin{cases} u_{11}' = 2\big(k_{11}a(s_1-u_{11}-u_{21}-u_{31})^2-k_{-11}u_{11}^2\big) \\ \qquad -(1-x_*)^{-1}\big(\lambda_{2,11}u_{11}(s_2-u_{12}-u_{22}-u_{32}) \\ \qquad -\lambda_{1,12}u_{12}(s_1-u_{11}-u_{21}-u_{31})\big), \\ u_{11}(0)=0, \end{cases} \tag{2}$$

$$\begin{cases} u_{21}' = 2\big(k_{21}b(s_1-u_{11}-u_{21}-u_{31})^2-k_{-21}u_{21}^2\big) \\ \qquad -(1-x_*)^{-1}\big(\lambda_{2,21}u_{21}(s_2-u_{12}-u_{22}-u_{32}) \\ \qquad -\lambda_{1,22}u_{22}(s_1-u_{11}-u_{21}-u_{31})\big), \\ u_{21}(0)=0, \end{cases} \tag{3}$$

$$\begin{cases} u_{31}' = -(1-x_*)^{-1}\big(\lambda_{2,31}u_{31}(s_2-u_{12}-u_{22}-u_{32}) \\ \qquad -\lambda_{1,32}u_{32}(s_1-u_{11}-u_{21}-u_{31})\big), \\ u_{31}(0)=0, \end{cases} \tag{4}$$

$$\begin{cases} u_{12}'=2\big(k_{12}a(s_2-u_{12}-u_{22}-u_{32})^2-k_{-12}u_{12}^2\big)-k_3u_{12}u_{22}-k_4u_{12}u_{32} \\ \qquad +x_*^{-1}\big(\lambda_{2,11}u_{11}(s_2-u_{12}-u_{22}-u_{32})-\lambda_{1,12}u_{12}(s_1-u_{11}-u_{21}-u_{31})\big), \\ u_{12}(0)=0, \end{cases} \tag{5}$$

$$\begin{cases} u_{22}'=2\big(k_{22}b(s_2-u_{12}-u_{22}-u_{32})^2-k_{-22}u_{22}^2\big)-k_3u_{12}u_{22}+k_5u_{32}^2 \\ \qquad =+x_*^{-1}\big(\lambda_{2,21}u_{21}(s_2-u_{12}-u_{22}-u_{32})-\lambda_{1,22}u_{22}(s_1-u_{11}-u_{21}-u_{31})\big), \\ u_{22}(0)=0, \end{cases} \tag{6}$$

$$\begin{cases} u_{32}' = k_3u_{12}u_{22}-k_4u_{12}u_{32}-2k_5u_{32}^2 \\ \qquad +x_*^{-1}\big(\lambda_{2,31}u_{31}(s_2-u_{12}-u_{22}-u_{32})-\lambda_{1,32}u_{32}(s_1-u_{11}-u_{21}-u_{31})\big), \\ u_{32}(0)=0. \end{cases} \tag{7}$$

From (1)–(7) it follows two mass conservation laws:

$$\begin{aligned} 2a+2p+x_*(u_{12}+u_{32})+(1-x_*)(u_{11}+u_{31}) &= 2a_0, \\ 2b+p+x_*(u_{22}+u_{32})+(1-x_*)(u_{21}+u_{31}) &= 2b_0. \end{aligned} \tag{8}$$

In this paper the turn-over rate – the catalyst surface S_2 specific conversion rate of the reactants molecules into product molecules – is studied. This time function is defined by the formula

$$z = \big(k_5u_{32}^2+k_4u_{12}u_{32}\big)/s_2. \tag{9}$$

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

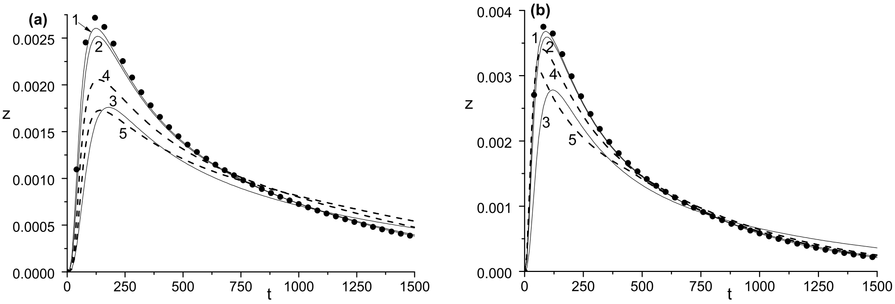

Fig. 1. Comparison of the turnover rate $z(t)$ determined by the ODE (Eqs. (1)–(7)) and PDE (system (2)–(9) from [5]) models. **(a)** – $k_{12} = k_{22} = 0$, $k_{11} = k_{21} = 0.017$; **(b)** – $k_{11} = k_{12} = k_{21} = k_{22} = 0.017$. • – ODE model. 1 – $\kappa_B = 0.1$, 2 – $\kappa_B = 0.01$, 3 – $\kappa_B = 0.001$ when $\kappa_S = 0.1$ and 4 – $\kappa_S = 0.01$, 5 – $\kappa_S = 0.005$ when $\kappa_B = 0.1$.

2 Numerical results

An implicit difference scheme based on the alternating direction method was used to solve the PDE problem. To get the numerical solution of systems (1)–(7) the standard MATLAB ODE solver ode45 was applied. The following values of parameters were used in calculations: $k_{ij} = 0.017$, $k_{-ij} = 0.0017$, $i, j = 1, 2$; $k_3 = 0.1$; $k_4 = 0.1$; $k_5 = 0.1$; $\lambda_{j+1,i\,j} = \lambda_{j,i\,j+1} = 0.1$, $i = 1, 2, 3$, $j = 1$; $a_1^0 = a_2^0 = 1$. Assume that $\kappa_B =: \kappa_a = \kappa_b = \kappa_p$ and if values of κ_{ij} do not depend on the values of indices we use κ_S for the PDE model from [5]. In the calculations laws (8) were satisfied with 10^{-6} accuracy for both models.

Calculation the values of the turnover rate $z(t)$ for $t \in [0, 1500]$ s using the PDE model requires approximately 180 times more the computer time than calculation these values when the ODE model is applied.

Two variants of reactants adsorption are studied: both reactant can adsorb on the active in reaction catalyst surface and inactive in reaction support; both reactants adsorb only on the support.

Fig. 1(a) demonstrates the influence of the variation of the bulk diffusion coefficients of both reactants and product in the case where the reactants A and B can adsorb only on the support, i.e. $k_{12} = k_{22} = 0$. The surface reaction occurs only due to spillover. The turn-over rate $z(t)$ grows faster, reaches a large maximum, and approaches the curve $z(t)$ calculated using the ODE model if the diffusion coefficients κ_B increase. The maximal values of $z(t)$ are given in Table 1. We observe that curves 1 and 2 practically not differ from the ODE line for $t > 300$ if $\kappa_B = 0.1$ or 0.01 and $\kappa_S = 0.1$. The catalytic reactivity calculated by the PDE and ODE models differs significantly if the bulk diffusion is small (curve 3 with $\kappa_B = 0.001$). The maximum values of $z(t)$, corresponding to the bulk diffusion coefficients 0.1, 0.01, 0.001, are 95.96, 92.65 and 64.71 percent of the maximum $z(t)$ determined by the ODE model.

The effect of the surface diffusivity κ_S of adsorbates AS, BS and particles of intermediate ABS on the turn-over rate is more noticeable (see Fig. 1(a) and Table 1) although the qualitative behavior of $z(t)$ is similar. Plots in Fig. 1(a) show noticeable differences between maximal values of $z(t)$ corresponding to the surface diffusivity 0.01, 0.005 and the fixed bulk diffusivity $\kappa_B = 0.1$. In this case the maximum values

Table 1. Maximal values of the turn-over rate $z(t)$ of PDE and ODE models in case $k_{12} = k_{22} = 0$, $k_{11} = k_{21} = 0.017$.

PDE model			
$\kappa_a = \kappa_b = \kappa_c$	κ	$t_{\max}$ (s)	$z_{\max}$
0.1	0.005	145.5	$1.73 \cdot 10^{-3}$
0.1	0.01	135.5	$2.05 \cdot 10^{-3}$
0.1	0.1	124.5	$2.61 \cdot 10^{-3}$
0.01	0.1	130.8	$2.52 \cdot 10^{-3}$
0.001	0.1	180.3	$1.76 \cdot 10^{-3}$
ODE model		120.5	$2.72 \cdot 10^{-3}$

Table 2. Maximal values of the turn-over rate $z(t)$ of PDE and ODE models in case $k_{12} = k_{22} = k_{11} = k_{21} = 0.017$.

PDE model			
$\kappa_a = \kappa_b = \kappa_c$	κ	$t_{\max}$ (s)	$z_{\max}$
0.1	0.005	50.1	$3.13 \cdot 10^{-3}$
0.1	0.01	78.8	$3.41 \cdot 10^{-3}$
0.1	0.1	90	$3.68 \cdot 10^{-3}$
0.01	0.1	90.5	$3.59 \cdot 10^{-3}$
0.001	0.1	120.2	$2.78 \cdot 10^{-3}$
ODE model		90.5	$3.77 \cdot 10^{-3}$

of $z(t)$, corresponding to the surface diffusion coefficients 0.01 and 0.005, equal to 75.37 and 63.6 percent of the maximum $z(t)$ determined by the ODE model.

We observe a qualitatively similar dependence of the catalytic reactivity on the bulk diffusion of reactants and the product, and the surface diffusion of adsorbates and intermediate when the reactants can adsorb on both active and inactive intervals (Fig. 1(b)). The maximal values of $z(t)$ are written in Table 2. In this case, the differences between curves calculated using the PDE and ODE models are smaller. Now the maximum values of $z(t)$ are 97.61, 95.23, 73.74 percent for the bulk diffusivity 0.1, 0.01, 0.001, and 90.19, 83.02 percent for the surface diffusivity 0.01 and 0.005 of the maximum $z(t)$ determined by the ODE model.

3 Conclusions

The catalytic reactivity of the heterogeneous dimer–dimer catalytic reaction on a composite catalyst, calculated using the PDE and simplified ODE models, was compared for two versions of reactants adsorption. The bulk diffusivity of reactants and the surface diffusivity of adsorbates and intermediate strongly influence the catalytic reactivity. The results of the numerical study are as follows: (a) The effect of change in the surface diffusion of adsorbates and intermediate, and the change in the bulk diffusion of reactants on the turn-over rate is notably appreciable for small time. (b) The simplified ODE model can be used for calculations, if the bulk diffusion of reagents and the surface diffusion of adsorbates and intermediate is greater than 0.1.

References

[1] L. Cwiklik. Influence of surface diffusion on catalytic reactivity of spatially inhomogeneous surfaces – mean field modeling. *Chem. Phys. Lett.*, **449**:304–308, 2007.

[2] L. Cwiklik, B. Jagoda-Cwiklik and M. Frankowicz. Influence of the spacing between metal particles on the kinetics of reaction with spillover on the supported metal catalyst. *Appl. Surf. Sci.*, **252**:778–783, 2005.

[3] A.N. Gorban, H.P. Sargsyan and H.A. Wahab. Quasichemical models of multicomponent nonlinear diffusion. *Math. Model. Nat. Phenom.*, **6**:184–262, 2011.

[4] P. Katauskis and Ž. Vidutytė. Numerical study of two-molecular catalytic reaction on composite catalyst. *Liet. matem. rink. Proc. LMS, Ser. A*, **57**:35–40, 2016.

[5] V. Skakauskas and P. Katauskis. Modelling dimer–dimer reactions on supported catalysts. *J. Math. Chem.*, **53**:604–617, 2015.

REZIUMĖ

Dviejų modelių, aprašančių dimerų katalitinę reakciją kompozitinio katalizatoriaus paviršiuje, palyginimas

Pranas Katauskis

Palyginami du dimerų katalitinės reakcijos, vykstančios kompozitinio katalizatoriaus paviršiuje, modeliai. Dalinių išvestinių modelis aprašo reagentų ir produkto tūrinę bei adsorbatų ir tarpinio produkto paviršinę difuziją, adsorbciją ir desorpciją. Paprastųjų išvestinių modelis išvedamas iš pirmojo, kai reakcijoje dalyvaujančios medžiagos yra vienodai pasiskirsčiusios. Lyginamas abiem metodais apskaičiuotas katalitinis reaktyvumas, keičiant difuzijos koeficientus.

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