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

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Abstract. In this paper two mathematical models of the dimer–dimer reaction on supported catalysts are compared. The PDE model describes 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 various 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.
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1 The mathematical model

The dimer–dimer heterogeneous surface reaction that occurs on a composite catalyst, \( 2A_2 + B_2 \rightarrow 2A_2B \), 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 \( B_2 \):

\[
\begin{align*}
A_2 + 2S \xrightleftharpoons[k_{-11}]{k_{11}} 2AS, \\
B_2 + 2S \xrightleftharpoons[k_{-22}]{k_{22}} 2BS, \\
AS + BS \xrightarrow{k_3} ABS + S, \\
AS + ABS \xrightarrow{k_{13}} P + 2S, \\
2ABS \xrightarrow{k_5} P + BS + S.
\end{align*}
\]

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 \( \Omega \) with surface \( \partial \Omega = \bar{S} \cup \bar{\bar{S}} \). The catalyst surface \( \bar{S} \) is composed from two active and inactive in reaction regions \( S_1 \) and \( S_2 \). Let \( k_{11}, k_{22} \) be the adsorption and \( k_{-11}, k_{-22} \) 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 \( x_s \in (0, 1) \) be the catalyst–support interface then \( S_2 = (0, x_s) \) and \( S_1 = (x_s, 1) \) 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. Differences \( s_1 = u_{11} - u_{21} - u_{31} \) and \( s_2 = u_{12} - u_{22} - u_{32} \) are densities of the vacant adsorption sites of strips \( S_1 \) and \( S_2 \).

Let \( \lambda_{21}, \lambda_{21}, \lambda_{231} \) be the constants of the jump rates via the catalyst–support interface \( x_s \) of particles of \( AS, BS \) and \( ABS \) from the inactive position \( x_s + 0 \) into the nearest-neighbour free active site \( x_s - 0 \). Similarly, \( \lambda_{112}, \lambda_{122} \) and \( \lambda_{132} \) present the constants of the jump rates via \( x_s \) of particles of adsorbates \( AS, BS \) and \( ABS \) from the active position \( x_s - 0 \) into the nearest-neighbour vacant inactive site \( x_s + 0 \).

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:

\[
\begin{align*}
\alpha' &= -(1 - x_*) (k_{11} a (s_1 - u_{11} - u_{21} - u_{31})^2 - k_{-11} u_{11}^2) \\
&\quad - x_* (k_{12} a (s_2 - u_{12} - u_{22} - u_{32})^2 - k_{-12} u_{12}^2), \quad a(0) = a_0; \\
\beta' &= -(1 - x_*) (k_{21} b (s_1 - u_{11} - u_{21} - u_{31})^2 - k_{-21} u_{21}^2) \\
&\quad - x_* (k_{22} b (s_2 - u_{12} - u_{22} - u_{32})^2 - k_{-22} u_{22}^2), \quad b(0) = b_0; \\
\gamma' &= x_* (k_5 u_{32}^2 + k_4 u_{12} u_{32}), \quad p(0) = 0.
\end{align*}
\]

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

\[
\begin{align*}
\alpha_{11}' &= 2 (k_{11} a (s_1 - u_{11} - u_{21} - u_{31})^2 - k_{-11} u_{11}^2) \\
&\quad - (1 - x_*)^{-1} (\lambda_{2111} u_{11} (s_2 - u_{12} - u_{22} - u_{32}) \\
&\quad - \lambda_{1121} u_{12} (s_1 - u_{11} - u_{21} - u_{31})), \\
\alpha_{11}(0) &= 0, \\
\beta_{21}' &= 2 (k_{21} b (s_1 - u_{11} - u_{21} - u_{31})^2 - k_{-21} u_{21}^2) \\
&\quad - (1 - x_*)^{-1} (\lambda_{2211} u_{21} (s_2 - u_{12} - u_{22} - u_{32}) \\
&\quad - \lambda_{1222} u_{22} (s_1 - u_{11} - u_{21} - u_{31})), \\
\beta_{21}(0) &= 0, \\
\gamma_{31}' &= -(1 - x_*)^{-1} (\lambda_{2311} u_{31} (s_2 - u_{12} - u_{22} - u_{32}) \\
&\quad - \lambda_{1322} u_{32} (s_1 - u_{11} - u_{21} - u_{31})), \\
\gamma_{31}(0) &= 0, \\
\alpha_{12}' &= 2 (k_{12} a (s_2 - u_{12} - u_{22} - u_{32})^2 - k_{-12} u_{12}^2) - k_3 u_{12} u_{22} - k_{21} u_{12} u_{32} \\
&\quad + x_*^{-1} (\lambda_{2112} u_{12} (s_2 - u_{12} - u_{22} - u_{32}) - \lambda_{1212} u_{12} (s_1 - u_{11} - u_{21} - u_{31})), \\
\alpha_{12}(0) &= 0, \\
\beta_{22}' &= 2 (k_{22} b (s_2 - u_{12} - u_{22} - u_{32})^2 - k_{-22} u_{22}^2) - k_3 u_{12} u_{22} + k_5 u_{32}^2 \\
&\quad + x_*^{-1} (\lambda_{2212} u_{22} (s_2 - u_{12} - u_{22} - u_{32}) - \lambda_{1222} u_{22} (s_1 - u_{11} - u_{21} - u_{31})), \\
\beta_{22}(0) &= 0, \\
\gamma_{32}' &= k_3 u_{12} u_{22} - k_4 u_{12} u_{32} - 2 k_5 u_{32}^2 \\
&\quad + x_*^{-1} (\lambda_{2312} u_{32} (s_2 - u_{12} - u_{22} - u_{32}) - \lambda_{1322} u_{32} (s_1 - u_{11} - u_{21} - u_{31})), \\
\gamma_{32}(0) &= 0.
\end{align*}
\]

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

\[
\begin{align*}
2a + 2p + x_*(u_{12} + u_{32}) + (1 - x_*) (u_{11} + u_{31}) &= 2a_0, \\
2b + p + x_*(u_{22} + u_{42}) + (1 - x_*) (u_{21} + u_{41}) &= 2b_0.
\end{align*}
\]

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

\[
z = \left( k_5 u_{32}^2 + k_4 u_{12} u_{32} \right) / S_2.
\]

Problem (1)–(7) is written in dimensionless form. In what follows all variables and parameters are non-dimensional.
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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: $k_{12} = k_{22} = 0$, $k_{11} = k_{21} = 0.017$; $k_{21} = k_{22} = 0.017$. The turn-over rate $z(t)$ determined by the ODE model is applied.

Two variants of reactants adsorption are studied: both reactant can adsorb 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 $z(t)$ determined by the 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 $\kappa_B = 0.1$.

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 $\kappa_B = 0.1$. 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 $\kappa_S$ 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

Liet. matem. rink. Proc. LMS, Ser. A, 58, 2017, 10–15.
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.
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