

THEORY OF HETEROGENEOUS / HOMOGENEOUS CATALYTIC REACTION WITH PRESATURATION

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In this communication we present a theoretical study of chemical reactions in a system of solid particles, immersed in a fluid environment. Our primary concern here is investigation of the systems of catalytic particles in a liquid media; however with some slight modifications our results are applicable to aerosol systems as well. We consider a second-order reaction, which proceeds both homogeneously in the environment, and heterogeneously at surfaces of catalyst particles. The Langmuir adsorption-desorption kinetics is considered explicitly. For definiteness, we are considering the so-called “three-step mechanism” of the heterogeneous reaction.

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1. INTRODUCTION

For the heterogeneous chemical reaction at the surface of catalyst particles, the complete process involves several steps: mass transfer of reactants in the fluid phase, adsorption to the surface of catalyst particles, and chemical reaction at the surface. This is followed by desorption of the reaction product in the liquid phase, the subsequent mass transfer of the product, and possibly some additional homogeneous chemical reactions. Some of these steps can become determining. To determine the rate of the entire process we must identify each such step (or steps) and estimate the rate of this step.

Research in physics and chemistry of heterogeneous systems often has as its objective the understanding and prediction of spatio-temporal distributions of reactants and reaction products on a macroscopic scale (a scale much larger than particle sizes and distances between them). That is why the “coarse-grained” description of such systems may be useful [1–5]. The heterogeneous nature of the chemical reaction is taken into account by distinguishing the mean concentrations of the reagents in the liquid bulk and the mean local concentrations in the vicinity of particles’ surfaces as macroscopic variables of the system. Thus, the distribution of each reagent is characterized by two different scalar fields, the global and the local concentrations.

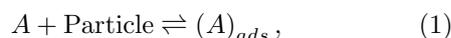
In the present paper we consider the catalyst particles of same constant size immersed in a liquid medium. We are considering a second-order reaction, which occurs both homogeneously in the environment, and heterogeneously at the surfaces of catalyst particles. Adsorption-desorption Langmuir kinetics

is taken into account explicitly. For definiteness, we consider the so-called “three-step mechanism” of the heterogeneous reaction.

In the experiments designed to study the binary heterogeneous reaction researchers sometimes use preliminary saturation with only one of the reactants, to reduce the role of the homogeneous reaction; so first we will consider the problem of adsorption-desorption in the absence of reaction.

2. PRESATURATION

We start by considering the processes at the surface of a single particle. At the surface of the particle the adsorbed complex of reagent A molecule with an active site of the surface is formed [6]



and if for the adsorption of A the Langmuir kinetics is assumed, the mass balance at the surface is given by:

$$\frac{dn_1}{dt'} = \left[\vec{k}_1 N_1^s (n_0 - n_1) - \bar{k}_1 n_1 \right] P_0, \quad (2)$$

where n_0 is the total number of active sites for adsorption of molecules A at the surface of a single particle; n_1 – the number of adsorbed molecules A at the surface of a single particle; N_1^s – a number of molecules A per unit volume in the immediate vicinity of the particle surface; \vec{k}_1 – the rate constant of adsorption for molecules A ; \bar{k}_1 – the rate constant of desorption for molecule A ; P_0 – the surface area of a single particle; t' – time.

If N_0 is the average number of atoms (molecules) per unit volume of the environment, and $c_1^{(s)} = \frac{N_1^s}{N_0}$

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is concentration of A in the immediate vicinity of the particle surface, we can rewrite the equation (2) in terms of relative surface coating of the particle with A -molecules $s_1 = \frac{n_1}{n_0}$:

$$\frac{ds_1}{dt'} = \left(P_0 \vec{k}_1 N_0 \right) \left[c_1^{(s)} (1 - s_1) - a_1 s_1 \right], \quad (3)$$

where $a_1 = \frac{\bar{k}_1}{\vec{k}_1 N_0}$.

On a scale of a single particle, both the molecular diffusion and the convection contribute to the 3-dimensional mass transfer between the environment and the particle. Even for a well-mixed system, each particle is surrounded by a boundary layer of essentially stationary liquid; the mass transfer through this layer is determined by molecular diffusion. The driving force behind the flow of materials to / from the surface is the difference between the global $c_i = \frac{N_i}{N_0}$ and the surface $c_i^{(s)} = \frac{N_i^s}{N_0}$ concentrations. The flux density is presented conventionally as

$$j_i^s = \kappa_i N_0 \left(c_i - c_i^{(s)} \right), \quad (4)$$

where κ_i are mass transfer coefficients [7]. The global concentrations c_i are defined as the concentration of reactants and reaction products far away from the particle (i.e., at distances much larger than the particle size). In general, to determine the flow of reactants to the particles, it is necessary to determine the concentration distribution around each particle, which tends towards the concentration $c_i^{(s)}$ at the surface and to c_i far from the particle.

For species A the total flux to one particle, i.e. $(j_1^s P_0)$ should be equal to the right-hand side of equation (2), or

$$\kappa_1 \left(c_1 - c_1^{(s)} \right) = \left(\vec{k}_1 n_0 \right) \left[c_1^{(s)} (1 - s_1) - a_1 s_1 \right]. \quad (5)$$

Microphysics of the model is contained in equations (3) and (5). Our goal at this stage is to derive macroscopic equations to describe the dynamics of the concentration on large scales. Therefore, we must average out the small-scale phenomena (on a scale of a single particle), but take into account their averaged effect on the large-scale dynamics. Thus, we need to introduce new variables, averaged over the ensemble of particles. At this stage we introduce the concept of local concentration. In general, the local concentrations \tilde{c}_i are the result of averaging of the surface concentrations $c_i^{(s)}$ over all particles of the same size in a physically small volume, still containing a large number of particles, located at coordinates (x, y, z) and time t' . The size of this volume is assumed to be much smaller than the size of reactor, but much larger than the particle size. For a well-mixed reservoir the dependence on macroscopic coordinates is absent. Thus, for a macroscopically homogeneous system, the local concentrations $\tilde{c}_i(t')$ are the macroscopic variables which depend on the macroscopic time. We consider first the ensemble of

identical catalytic particles. In this case, the averaging procedure is simplified, and it is possible to identify local concentrations \tilde{c}_1 with the mean values of surface concentrations $c_1^{(s)}$. This allows the next step – to average the relative surface s_1 coverage, and arrive, by averaging equations (3), (5), at the equations for the macroscopic variables, c_1, \tilde{c}_1 and \bar{s}_1 :

$$\frac{d\bar{s}_1}{dt'} = \left(P_0 \vec{k}_1 N_0 \right) \left[\tilde{c}_1 (1 - \bar{s}_1) - a_1 \bar{s}_1 \right], \quad (6)$$

$$\kappa_1 (c_1 - \tilde{c}_1) = \left(\vec{k}_1 n_0 \right) \left[\tilde{c}_1 (1 - \bar{s}_1) - a_1 \bar{s}_1 \right]. \quad (7)$$

Now let's turn to the macrophysics of the problem. On large scales the dynamics of global concentrations c_i of all species is controlled by the mass balance equation with a sink/source in the right-hand side

$$\frac{dc_i}{dt'} = -\Phi_i. \quad (8)$$

On the scale of the entire system (reactor), i.e. on a scale that is much larger than the size of the particle, Φ_i are sinks/sources due to adsorption-desorption and chemical reaction. The difference in scale allows us to consider the mesoscale (scale of a single particle) mass transfer, by introducing a macroscopic distribution of sinks and sources Φ_i , phenomenologically averaging the mesoscale phenomena, such as local mass transfer to and from the particle surface. According to (4), we shall write the sinks/sources in the usual manner

$$\Phi_i = S \kappa_i (c_i - \tilde{c}_i), \quad (9)$$

where S is the reactive surface per unit volume; $S = P_0 M_0$, where M_0 is the number of catalyst particles per unit volume. Thus, for particles of the same type, we arrive at the macroscopic equations of balance for each species

$$\frac{dc_i}{dt'} = -S \kappa_i (c_i - \tilde{c}_i). \quad (10)$$

It is convenient to take the characteristic time $\tau = \frac{1}{S \kappa_1}$ of the mass transfer of reagent A as the time scale. Introducing the dimensionless time $t = \frac{t'}{\tau}$, we can write the presaturation equations system (6), (7) and (10) in the dimensionless form (for convenience, we have dropped the bar over s_1):

$$\eta \frac{ds_1}{dt} = \tilde{c}_1 (1 - s_1) - a_1 s_1, \quad (11)$$

$$\eta (c_1 - \tilde{c}_1) = \omega [\tilde{c}_1 (1 - s_1) - a_1 s_1], \quad (12)$$

$$\frac{dc_1}{dt} = - (c_1 - \tilde{c}_1), \quad (13)$$

where $\eta = \frac{M_0 \kappa_1}{N_0 \vec{k}_1}$, $\omega = \frac{M_0 n_0}{N_0}$.

The dimensionless parameter ω has a simple meaning: it is the ratio of the number of “best available heterogeneous sites” per unit volume to the average total number of atoms (molecules) per unit volume of the environment; usually this ratio should be very small. The dimensionless parameter η is the ratio of characteristic time for adsorption to characteristic time of local mass transfer, which usually must also be very small; but the relative size of these

parameters may be different for different physical situations.

The system (11) - (13) must be supplemented by the initial conditions:

$$c_1|_{t=0} = c_{10}, s_1|_{t=0} = s_{10}. \quad (14)$$

The initial value s_{10} takes into account some (probably small) number of A , which has already been adsorbed during the introduction of this substance into the system.

The system (11) - (13) could be solved exactly:

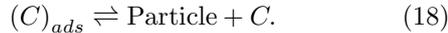
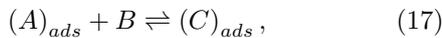
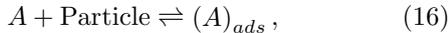
$$\left(\frac{c_1 - c_{1e}}{c_{10} - c_{1e}} \right)^{E_1} \left(\frac{c_1 + d}{c_{10} + d} \right)^{E_2} = \exp(-t), \quad (15)$$

where $b = \sqrt{(\bar{c}_{10} - \omega - a_1)^2 + 4a_1\bar{c}_{10}}$, $c_{1e} = \frac{1}{2}[\bar{c}_{10} - \omega - a_1 + b]$, $d = \frac{1}{2}[-\bar{c}_{10} + \omega + a_1 + b]$, $E_1 = \frac{1}{2}[1 + \frac{2\eta + \omega - \bar{c}_{10} - a_1}{b}]$, $E_2 = \frac{1}{2}[1 - \frac{2\eta + \omega - \bar{c}_{10} - a_1}{b}]$. The standard approach to the Langmuir kinetics is to assume quasi-stationarity with respect to the adsorption-desorption, that is to set $\eta = 0$ in the left-hand side of (11). This does not change the equilibrium state; the slight difference in dynamics may be significant only if a large coverage $s_1 \sim 1$ is achieved; this is possible only for very small a_1 . This means that for pure saturation (i.e. without a reaction) the quasi-stationary approximation works quite well. However, this does not hold for the combined adsorption and reaction.

3. REACTION

Suppose now that in the system pre-saturated with reagent A the generation of the reagent B (with a constant rate) is started; and the reaction of A and B produces C .

We will consider first a single second-order reaction with a single product, which occurs both heterogeneously and homogeneously. We presume the following so-called three-step heterogeneous reaction mechanism:



Proceeding along the same lines the basic system for averaged coverages s_i and for bulk and local concentrations c_i , \tilde{c}_i could be obtained¹:

$$\eta \frac{ds_1}{dt} = [\tilde{c}_1(1 - s_1 - s_3) - a_1s_1] - \eta \frac{\sigma}{\omega} (\tilde{c}_2s_1 - \xi s_3), \quad (19)$$

$$\eta \frac{ds_3}{dt} = \theta[\tilde{c}_3(1 - s_1 - s_3) - a_3s_3] + \eta \frac{\sigma}{\omega} (\tilde{c}_2s_1 - \xi s_3), \quad (20)$$

$$\eta(c_1 - \tilde{c}_1) = \omega[\tilde{c}_1(1 - s_1 - s_3) - a_1s_1], \quad (21)$$

$$\nu_3\eta(c_3 - \tilde{c}_3) = \omega\theta[\tilde{c}_3(1 - s_1 - s_3) - a_3s_3], \quad (22)$$

¹Here we have assumed the kinetic Mass Action Law (MAL) both for the surface and homogeneous reactions.

$$\nu_2(c_2 - \tilde{c}_2) = \sigma(\tilde{c}_2s_1 - \xi s_3), \quad (23)$$

$$\frac{dc_1}{dt} = -(c_1 - \tilde{c}_1) - \rho(c_1c_2 - \zeta c_3), \quad (24)$$

$$\frac{dc_2}{dt} = -\nu_2(c_2 - \tilde{c}_2) - \rho(c_1c_2 - \zeta c_3) + J, \quad (25)$$

$$\frac{dc_3}{dt} = -\nu_3(c_3 - \tilde{c}_3) + \rho(c_1c_2 - \zeta c_3). \quad (26)$$

Where in addition to the notation already introduced above, here $\theta = \frac{\bar{k}_3}{\bar{k}_1}$, $\nu_2 = \frac{\kappa_2}{\kappa_1}$, $\nu_3 = \frac{\kappa_3}{\kappa_1}$, $\rho = \frac{r_h}{S\kappa_1}$,

$J = \frac{J'}{N_0S\kappa_1}$ and $\sigma = \frac{\bar{r}n_0}{\kappa_1P_0} = \frac{\bar{r}n_0M_0}{S\kappa_1}$; \bar{k}_3 and \bar{k}_3^- - the rate constants for the adsorption and desorption of C -molecules; $\xi = \frac{\bar{r}}{\bar{r}N_0}$ is the reciprocal of the equilibrium constant K in the Law of Mass Action, $K = \frac{1}{\xi} = \frac{\bar{r}N_0}{\bar{r}}$. \bar{r} and \bar{r}^- - the rate constants of forward and reverse reactions, respectively; r_h - the rate constant for homogeneous reaction; $\zeta = \frac{1}{K_h}$, K_h - the equilibrium constant in the MAL for a homogeneous reaction; J' - the rate of homogeneous generating of reagent B .

As before the time scale is $\tau = \frac{1}{S\kappa_1}$. Initial conditions are:

$$\begin{aligned} c_1|_{t=0} &= c_{1e}; s_1|_{t=0} = s_{1e}; c_2|_{t=0} = 0; \\ c_3|_{t=0} &= 0; s_3|_{t=0} = 0. \end{aligned} \quad (27)$$

4. PRELIMINARY ANALYSIS OF THE SYSTEM OF EQUATIONS

Combining equations we obtain the ‘‘conservation law’’ for substances A and C and an additional time-dependent constraint:

$$\omega \frac{d}{dt}(s_1 + s_3) = (c_1 - \tilde{c}_1) + \nu_3(c_3 - \tilde{c}_3), \quad (28)$$

$$\omega s_1 + c_1 - c_2 = \omega s_{1e} + c_{1e} - \int_0^t J dt. \quad (29)$$

In accordance with the standard assumption for the Langmuir kinetics, the adsorption-desorption is assumed to be very fast, i.e. $\eta \ll 1$. However, in the presence of a surface chemical reaction the distinction is more subtle. If the adsorption-desorption and the reaction are comparably fast, that is $\eta \frac{\sigma}{\omega} \approx 1$, the quasi-homogenous assumption for equations (19) - (20) is still justified; however on the mesoscopic time scale (on the time scale of local mass transfer) there is no ‘‘storing’’ of molecules A on the surface of the catalyst particle; the local flux densities are proportional manifesting the stoichiometry condition.

Comparison of exact and approximate (for quasi-stationarity) balance equations makes it obvious that the assumption of quasi-stationarity means simultaneously that the number of adsorbed A -molecules per unit volume is small compared to their number per unit volume in the environment. If ω is not too small, it means that s_1 is vanishingly small, i.e. the coating of particles with A - and C -molecules will be also always small. This means that the adsorbed A -molecules are immediately consumed; the

C-molecules produced by the reaction are immediately desorbed. The A- molecules stored during pre-saturation will be “wasted” very (probably unobservably) quickly during the initial period of the experiment; it will probably be impossible to find any trace of the product C on the particles later. So this is definitely not the experimental situation that we are interested in.

On the other hand, if the adsorption-desorption is much faster than any other process, including the surface chemical reaction, both $\eta \ll 1$, and $\eta \frac{\sigma}{\omega} \ll 1$. In this case equations (19) and (20) for s_1 and s_3 , respectively, are still non-stationary, due to slower changes as a result of a chemical reaction.

In this paper we shall consider only the latter case.

For this case we can express the relative coverage in terms of local concentrations:

$$s_1 = \frac{\tilde{c}_1}{1 + \frac{\tilde{c}_1}{a_1} + \frac{\tilde{c}_2}{a_3}}, s_3 = \frac{\tilde{c}_3}{1 + \frac{\tilde{c}_1}{a_1} + \frac{\tilde{c}_2}{a_3}}, \quad (30)$$

which is the standard expression for the Langmuir kinetics, see [6]. Then we can express all bulk concentration in terms of local concentrations \tilde{c}_i :

$$c_2 = \tilde{c}_2 + \frac{\bar{\sigma}}{\nu_2} \frac{\tilde{c}_1 \tilde{c}_2 - \bar{\xi} \tilde{c}_3}{1 + \frac{\tilde{c}_1}{a_1} + \frac{\tilde{c}_2}{a_3}}, \quad (31)$$

$$c_1 = c_2 + \bar{c}_{1e} - G(t) - \frac{\omega}{a_1} \frac{\tilde{c}_1}{1 + \frac{\tilde{c}_1}{a_1} + \frac{\tilde{c}_2}{a_3}}, \quad (32)$$

$$c_3 = -c_2 + G(t) - \frac{\omega}{a_3} \frac{\tilde{c}_3}{1 + \frac{\tilde{c}_1}{a_1} + \frac{\tilde{c}_2}{a_3}}, \quad (33)$$

where $G(t) = \int_0^t J dt = Jt$.

Substituting (31) – (33) for c_1 , c_2 and c_3 into (24) – (26) yields, after some rearrangement of the system, three strongly nonlinear differential equations for \tilde{c}_1 , \tilde{c}_2 and \tilde{c}_3 . This means that the original system of five differential and three algebraic equations is now reduced to only three equations, without any additional approximations. Reformulation the problem in terms of local concentrations, which we call the interaction representation, was widely used in our previous work on heterogeneous reactions [1–3].

For simplicity let’s suppose that the relative coverage s_1 , s_2 , while quite observable, are still much less than a unity; then the saturation effects represented in the denominators of the right-hand side of (30) are insignificant (which corresponds to the approximation of Henry’s Law):

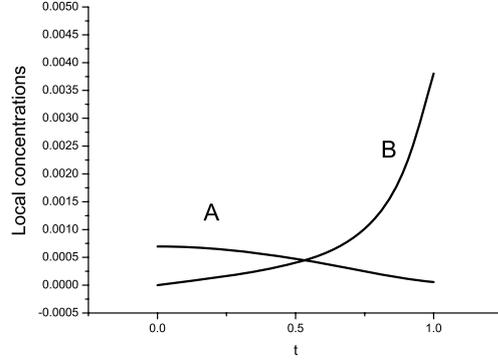
$$s_1 \simeq \frac{\tilde{c}_1}{a_1}, s_3 \simeq \frac{\tilde{c}_3}{a_3}. \quad (34)$$

Thus, the coverage is simply proportional to the concentration over the surface. This assumption is not necessary for solving the system, see [3], and is aimed to make the following calculations a little more transparent.

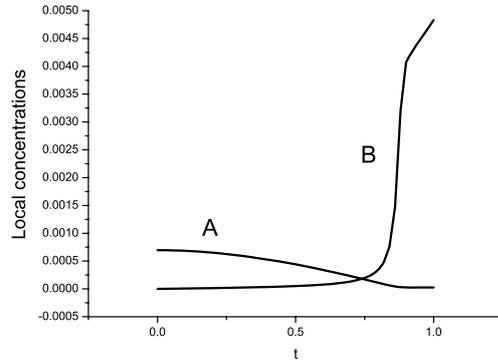
To compare the relative importance of heterogeneous and homogeneous reactions, it is appropriate to

consider both at their peak performance mode; so we assume that both heterogeneous and homogeneous reactions are irreversible $\xi = \zeta = 0$. Accordingly, equation (31) reduced to

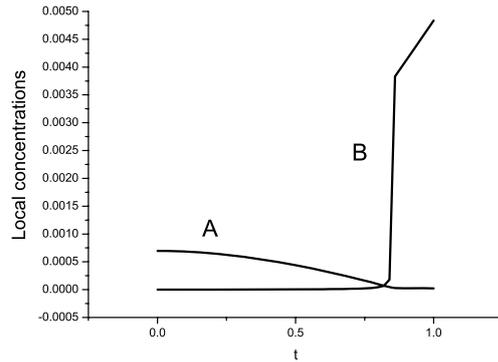
$$c_2 = \tilde{c}_2 + \frac{\bar{\sigma}}{\nu_2} \tilde{c}_1 \tilde{c}_2. \quad (35)$$



a



b



c

Changing of local concentrations with time at $\rho = 0.5$, $\omega = 0.02$, $\eta = 10^{-3}$, $a_1 = 0.01$, $J = 0.007$, $\nu_2 = 0.7$, $c_{10} = 0.002$, $c_{1e} = 6.97 \times 10^{-4}$ and σ possesses values 10^2 (a), 10^3 (b), and 10^4 (c)

5. DISCUSSION AND CONCLUSIONS

Let us consider first the case where heterogeneous reaction is infinitely fast, that is $\bar{\sigma} \rightarrow \infty$. As c_2 and \tilde{c}_2

in (35) are bounded from above, the product ($\tilde{c}_1\tilde{c}_2$) should be simultaneously approaching zero. Physically, this means that if the reaction is very fast, in the close vicinity of the particle's surface, at least one of the reactants must be immediately depleted to zero. From (35) and the initial condition (27) it is evident that at least for some time after $t = 0$ $\tilde{c}_1 \neq 0$; that is, $\tilde{c}_2 = 0$.

As usual, an important characteristic of the process is the "switch" time, i.e. the transition from a local depletion of one component to the local depletion of the other. We are interested in the case of a strong source, i.e. large J . Then the "switch" must occur at sufficiently small times. Numerical analysis shows a smooth change in the dynamics of the system at increasing rate of surface reaction. Numerical examples are presented in Figures a, b, and c.

We are interested in a situation where the main role is played by a heterogeneous reaction. In this case, the homogeneous reaction rate is low. In this case in the first approximation although the concentrations of both reagents depend on the rate of homogeneous reaction ρ , the "switch" time in the same approximation is independent on this rate.

Concluding, the approach proposed in the present communication allows the detailed analysis of the interplay between the heterogeneous and homogeneous routes of reaction and elucidates the means to make the heterogeneous route more pronounced.

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ТЕОРИЯ ГЕТЕРОГЕННОЙ/ГОМОГЕННОЙ КАТАЛИТИЧЕСКОЙ РЕАКЦИИ С ПЕРЕДНАСЫЩЕНИЕМ

С. Кёр-Турнёр, Д.Ю. Копейченко, П.О. Мчедлов-Петросян

Мы рассматриваем одну реакцию второго порядка, которая протекает как гомогенно в окружающей среде, так и гетерогенно на поверхностях каталитических частиц. Адсорбционно-десорбционная ленгмюровская кинетика учитывается явно. Для определённости мы рассматриваем так называемый "трёх-ступенчатый механизм" гетерогенной реакции.

ТЕОРИЯ ГЕТЕРОГЕННОЇ/ГОМОГЕННОЇ КАТАЛІТИЧНОЇ РЕАКЦІЇ С ПЕРЕДНАСИЧЕННЯМ

С. Кьор-Турньор, Д.Ю. Копійченко, П.О. Мчедлов-Петросян

Ми розглядаємо одну реакцію другого порядку, що протікає як гомогенно в оточуючому середовищі, так і гетерогенно на поверхнях каталітичних частин. Адсорбційно-дисорбційна ленгмюрівська кінетика враховується явно. Для визначеності ми розглядаємо так званий "триступінчатий механізм" гетерогенної реакції.