Stochastic model of oxygen adsorption

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Abstract. The authors propose a microscopic stochastic model of the process of oxygen adsorption on the surface of a solid object. As a first approximation, the constructed model describes the dynamics of the system in terms of a planar surface coating with oxygen adatoms. A simplified diagram of the adsorbent surface oxidation mechanism is presented in five stages. The reaction conditions are determined by the temperature of the crystal surface and the partial pressure of the reagent in the gas phase. The reaction is considered as a random Markov process with a discrete set of states for a stream of elementary events occurring on a fragment of an ideal square lattice of ferrous sulfide with periodic boundary conditions. For the constructed model, numerical calculations are done using a software solution and the results of computational experiments are presented. The research results analysis suggests that the presented mathematical process model of oxygen adsorption on the ferrous sulfide surface along with the software solution for simulation studies can be used to determine control parameters for various technological processes.

1. Introduction

Superficially, the study of processes of various nature, including chemical processes, represents a random and chaotic interaction. However, upon close examination, the outlines of tendencies appear along with steady patterns. Such patterns suffice to form an idea of the factors influencing these processes and to predict the further behavior of reaction systems. The reactions where the reagents are in different phases, and the reaction happens at the phase boundary, are widespread in chemical technology. The study of the heterophase reaction features appears to be advantageous in relation to fundamental studies of elements reactivity and numerous applications.

Despite the abundance of research and considerable progress in understanding the process of gas adsorption on various surfaces, the mechanism of this process requires further study. The actual adsorbents are typically heterogeneous, and the properties exhibited by the compounds during adsorption (chemisorption) process are anomalous compared with the properties of ordinary substances. In this case, the theoretical justification of surface phenomena, based on mathematical modeling, serves as an approach for calculating the adsorption characteristics.

The modeling of the processes occurring at the solid/gas interphase shows that an attempt to bring the model closer to the real process is fundamental to microscopic stochastic models selection [1], [2]. The use of such models makes it possible to register processes on the surface with a very high spatial resolution (at the scale of several interatomic distances) and to predict the behavior of individual atoms or a group of atoms. A microscopic stochastic model of the oxygen adsorption process on the surface of a solid body is proposed. The ferrous sulfide \((FeS)\), the crystal lattice of which is spatially...
heterogeneous, but has a symmetrical structure and represents an alternation of $S$ and $Fe$ nodes, was chosen as an adsorbent.

The oxygen adsorption reaction on the crystal surface is a multi-stage process and is always accompanied by a rearrangement of the surface layer. Provided that the infill of the surface layer is sufficient, the restructuring of the surface layer can be ignored in a first approximation. Thus, the constructed model describes the system dynamics in terms of a planar surface coating with oxygen adatoms [3].

2. Physical-Chemical Model

The oxidation mechanism of the adsorbent surface goes in accordance with the Langmuir theory of mono-molecular adsorption and the lattice gas model, the adsorption centers of which are located at the nodes of an ideal square lattice [4], [5]. A simplified diagram of the process in the $O_2 - FeS$ system consists of monomolecular adsorption – desorption of $O_2$; dissociation of $O_2$ into adatoms; the interaction of adsorbed oxygen adatoms between themselves or with the surface of the crystal; longitudinal migration of adsorbed oxygen adatoms on the crystal surface. The described mechanism is presented in the form of the following acts of the kinetic scheme:

$$
1) \left( O_2 \right)_{gas} + \{\} \rightarrow O_{adc,i} + O_{adc,j} - \text{adsorption of} \ O_2;
2) \left( O \right)_{adc,i} + \left( O \right)_{adc,j} \rightarrow \left( O_2 \right)_{gas} + \{\} + \{\} - \text{desorption of} \ O_2;
3) \left( O_2 \right)_{adc,i} + \left( S \right) \rightarrow \left( SO \right)_{gas} + \{\} + \{\} - \text{formation of} \ SO_2;
4) \left( O \right)_{adc,j} + \{\} \rightarrow \{\} + \left( O \right)_{adc,j} - \text{migration of} \ O_2 \ \text{adatoms};
5) \left( O \right)_{adc,j} + \left( FeO \right) \rightarrow \left( Fe_2O \right) - \text{formation of} \ FeO,
$$

where $\{\}$, $\{\}$ are free grid nodes with numbers $i$ and $j$; $j \in \omega_\eta(i)$; $\omega_\eta(i)$ is a plurality of lattice nodes located at a distance of the $\eta$-th neighborhood from the node with number $i$, ($\eta = 1, 2$); $\left( O \right)_{adc,i}$ represents adsorbed particles in the site $i$; $\left( SO \right)_{gas}$, $\left( O_2 \right)_{gas}$ are the molecules in the gas phase [6]. The first two stages describe the exchange between the molecules of the gas phase and the surface of the crystal, the third and fifth stages describe the rearrangement of the surface layer. Particles migrate due to individual “jumps” to neighboring empty nodes. All stages except the fifth are dual node. The reaction conditions are determined by the temperature of the crystal surface $T[K]$ along with the partial pressure of the reagent in the gas phase $P_{O_2}$ [2], [6], [7].

The reaction is considered as a random Markov process with a discrete set of states for a stream of elementary events on a fragment $\Omega_{sq}(M,N)$ of an ideal square lattice of ferrous sulfide containing $L = M \cdot N$ nodes with periodic boundary conditions. Elementary events are acts 1)-5) of the kinetic scheme (1). The state of a lattice fragment $S(t)$ at time $t$ is determined by the set of occupation numbers $s_i(t)$ of all its nodes $i \in \{1, L\}$. Each state $s_i(t)$ takes one of the values [2], [6-8]:

$$
s_i(t) = \begin{cases} 0, & \text{if the node } i \text{ is empty at time } t, \\
1, & \text{if the node } i \text{ is occupied by adatom } O.
\end{cases}
$$

The considered Markov process obeys the basic kinetic (master) equation:

$$
\frac{dP(S,t)}{dt} = \sum_{S^*} \left[ V(S \rightarrow S^*) \cdot P(S,t) - V(S^* \rightarrow S) \cdot P(S^*,t) \right], \quad S \in \{S\},
$$

where $\{S\}$ is the set of all possible states of a $\Omega_{sq}(M,N)$ fragment of the lattice; $P(S,t)$ is the probability of the state $S$ at time $t$; $S^*$ is a new state that can be obtained from the state $S$ as a result
of implementation of one of the elementary acts; \( V(\mathcal{S} \rightarrow \mathcal{S}^*) \) are transition frequencies calculated using the reaction rate formulae [2], [9].

The basic kinetic equation is a system of linear homogeneous equations. However, due to the high dimension of the system, its direct solution is infeasible using numerical and analytical methods. Separate implementations of the examined random process were obtained using the dynamic Monte Carlo method.

3. Mathematical Model

The mathematical model takes into account the crystal morphology, which allows to consider the adsorbent surface as a \( m \times n \) size matrix \( \mathbf{A} = (a_{ij}) \). The alternation of surface nodes is reflected by the values of the matrix element indices. For the indices \( i = 2k - 1, j = 2k - 1, k \in \mathbb{N} \) and \( i = 2k, j = 2k, k \in \mathbb{N} \), the \( a_{ij} \) element equates to the lattice node containing \( S \). For the indices \( i = 2k - 1, j = 2k, k \in \mathbb{N} \) and \( i = 2k, j = 2k - 1, k \in \mathbb{N} \), the \( a_{ij} \) element \((i = \overline{1, m}; j = \overline{1, n})\) equates to the lattice node containing \( Fe \). The matrix elements can possess one of the \( a_{ij} = \begin{cases} 0, & \text{if } s_i(t) = 0, \\ 1, & \text{if } s_i(t) = 1, \end{cases} \)

where \( s_i(t) \) is the state of the lattice node at time \( t \) [6].

The implementation of dual node elementary acts results from the current state of the lattice node \( i \) and its local environment. A mathematical description of such neighborhood is presented in figure 1.

\[
\begin{align*}
\mathbf{a}_{i-1j} & \quad \mathbf{a}_{ij} \quad \mathbf{a}_{i+1j} \\
\mathbf{a}_{ij-1} & \quad \mathbf{a}_{ij} \quad \mathbf{a}_{ij+1}
\end{align*}
\]

**Figure 1.** Local environment for the element \( a_{ij} \) of the matrix \( \mathbf{A} \).

The \( FeO \) forming stage is determined by the state of the \( i \) node containing \( Fe \). The reaction rates are determined by the current state of the fragment, and are calculated using the formulae [3], [10]:

1) \( V_1(i, j, t) = P_{O_2} \cdot k_1 \cdot e^{-\frac{E_1}{RT}} \cdot \delta_i(0)\delta_j(0) \cdot \exp \left[ \frac{1}{RT} \cdot \sum_k \delta_k(p)\epsilon_{11} \right] \),

2) \( V_2(i, j, t) = k_2 \cdot e^{-\frac{E_2}{RT}} \cdot \delta_i(1)\delta_j(1) \cdot \exp \left[ \frac{1}{RT} \cdot \sum_k \delta_k(p)\epsilon_{21} \right] \),

3) \( V_3(i, j, t) = k_3 \cdot e^{-\frac{E_3}{RT}} \cdot \delta_i(1)\delta_j(1) \cdot \exp \left[ \frac{1}{RT} \cdot \sum_k \delta_k(p)\epsilon_{31} \right] \),

4) \( V_4(i, j, t) = k_4 \cdot e^{-\frac{E_4}{RT}} \cdot \delta_i(0)\delta_j(0) \cdot \exp \left[ \frac{1}{RT} \cdot \sum_k \delta_k(p)\epsilon_{41} \right] \),

5) \( V_5(i, j, t) = k_5 \cdot e^{-\frac{E_5}{RT}} \cdot \delta_i(1) \cdot \exp \left[ \frac{1}{RT} \cdot \sum_k \delta_k(p)\epsilon_{51} \right] \):

\[
\delta_i(p) = \begin{cases} 1, & \text{if } s_i = p, \\
0, & \text{if } s_i \neq p, \end{cases}
\]

\[
\sum_k \delta_k(p) = 1; \quad P = 0, N_{adc}; \quad k \in \{ \omega_{ij}(i), \text{when } \alpha = 5, \omega_{ij}(i, j), \text{when } \alpha = 1,4 \}.\]
where $R$ is the universal gas constant; $k_{\alpha}, E_{\alpha}$ are the preexponential factor and the $\alpha$ stage activation energy [6].

It is assumed that the activation energies of elementary acts can depend on the local environment of the node or nodes they occur at. This dependency is calculated using the energy parameters of interactions $e_{\alpha np}$, where $\alpha$ is the stage number of $\left(\alpha = 1, N_{act}\right)$, $\eta$ is the neighborhood number ($\eta = 1, 2$) and $p$ is the type of the adsorbed particle $\left(p \in \{\star, O\}\right)$ [1]. The number of elements included in the local environment depends on its location geometry. The local environment for one of the internal locations of the dual node elementary act, represented by the configuration of the matrix elements $a_{ij-1} \leftarrow a_{ij}$, is depicted in figure 2.

Numerical calculations for the model were performed using a software solution focused on solving the following main tasks [2], [9], [11]:

1. Setting the process parameters $(k_{\alpha}, E_{\alpha})$ and forming the state of the fragment $S(t)$ at time $t$, that is either a completely unfilled surface or is formed by a random “scattering” of the certain quantity of oxygen particles over the fragment nodes.

2. According to the reaction rates formulae (3), the reaction rate for each node of the lattice is found, provided that the corresponding state $s_j(t)$ is implemented. The value of the process rate $V_R$ is determined by averaging over all the fragment nodes.

3. The contacting phases interaction time $\tau$, which is a random variable distributed exponentially with a distribution density

\[ f(\tau) = \lambda \cdot e^{-\lambda \tau} \]  

for $\tau \geq 0$, $\lambda > 0$, (where $\lambda = \lambda(t, S(t)) \neq 0$ represents the sum of all reaction rates), is calculated by the formula

\[ \tau = -\ln(\xi) / \lambda \]  

where $\xi$ is a random number distributed uniformly in the interval $(0,1)$.

The resulting model can be estimated as a stochastic approach on expanding the feasibility of describing the nonlinear dynamics of interaction in a solid/gas system.

4. **Computational experiments and their results**

As a result of the research, the dependence of the reaction rate $V_R$ on the geometry of the adsorbent $(L=M \cdot N)$ and the adsorbed substance expenditure was evaluated $\left(Q = \varphi(P_{\theta_{O_2}}, \theta)\right)$. To study the dependence, a series of tasks was solved for a surface fragment containing from $L=100$ to $L=10000$ nodes. The concentration value $\theta_{O_2} = N/L$ (where $N = N(t)$ is the total number of oxygen particles on the surface) varied, and the remaining parameters were set as: $P_{O_2} = 10^{-5} Pa$, $T = 298K$ and $R = 8.31(44) J/(mole \cdot K)$. The results of computational experiments are presented in figure 3 and table 1.
Let’s consider the fragment size influence on the process rate. The qualitative analysis of the simulation results shows that chaotic fluctuations in the reaction rate arise due to the influence of spontaneous fluctuations. The influence quantity of spontaneous fluctuations on the reaction dynamics is observed on fragments containing \( L = 100 \) to \( L = 4000 \) nodes (figure 3). The occurrence frequency of high amplitude oscillations gradually decreases with the increase of the fragment size.

![Figure 3](image)

**Figure 3.** The influence of fragment size \( \Omega_{\text{sqf}}(M,N) \) on the process rate \( V_R \) depending on the average fragment infill: a) \( \theta = 25\% \); b) \( \theta = 50\% \); c) \( \theta = 100\% \)

The incipience of kinetic fluctuations of physicochemical process rates is not solely dependent on the fragment size, but also depends on the average surface fragment infill \( (\theta) \). The computational
experiment has proven that the increase of filled adsorption centers causes the process rate fluctuations to become more regular (figure 3 b), and with $\theta = 100\%$ (figure 3 c) the system gradually enters the self-oscillation mode. This kind of reaction system behavior results from the lateral interactions between adsorbed particles.

Table 1 presents the results of computational experiments allowing to evaluate the influence of $K_{\text{mig}} (k_4)$ on process rate $V_R$ fluctuations. The results comparison was made for fragments with a reaction surface $\Omega_{\text{sqr}} (100,100)$ and $\Omega_{\text{sqr}} (20,20)$, along with variations in the internal parameter $K_{\text{mig}}$ value in the range between 2 to 20. Analysis of the data obtained shows the following:

1) the process rate $V_R$ has fractional deviations from its average values on the fragment $\Omega_{\text{sqr}} (100,100)$ with coating density of $\theta = 25\%$;

2) the parameter value $K_{\text{mig}} = 5$ (while using a small sized fragment $\Omega_{\text{sqr}} (20,20)$) is sufficient to displace the macroscopic characteristics of the reaction system in an unpredictable manner.

| $k_4$ | $L = 10000$ | $L = 400$ |
|-------|-------------|-----------|
|       | $\theta = 25\%$ | $\theta = 50\%$ | $\theta = 75\%$ | $\theta = 25\%$ | $\theta = 50\%$ | $\theta = 75\%$ |
| 2     | 2564        | 1649      | 823     | 2538        | 1619      | 814     |
| 5     | 2547        | 1654      | 822     | 2599        | 1689      | 823     |
| 20    | 2568        | 1645      | 816     | 2547        | 1645      | 814     |

The estimated process time comprised $\tau = 10^{-6} - 10^{-5}$ sec. This result does not exceed the heuristic estimate of the interaction time of oxygen particles with the surface of ferrous sulfide ($\approx 10^{-3}$ sec), obtained by solving the spatially homogeneous Boltzmann potential equation using an analytical model of oxygen interaction with the ferrous sulfide surface [12].

5. Conclusion
The performed simulation studies and calculations illustrate the influence of various solid/gas reaction system parameters on the rate of the adsorption process. The calculation algorithm was developed at the scale level of individual adsorption centers ($\approx 10^{-7} - 10^{-9}$ m) using a stochastic approach to the simulation process. Taking the influence of intermolecular interactions on calculating the process rate into account makes it possible to describe the nonmonotonic dependence of the reaction rate on the fragment size and adsorbed substance expenditure, which makes it possible to use the presented mathematical model and software solution to determine control parameters for various technological processes.

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