Modeling of Pt-catalyst surface influence on characteristics of oxygen and carbon monoxide molecules

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A simple mathematical model of Pt-catalyst surface influence on both carbon monoxide and oxygen molecules behavior is considered. It is shown that an electric field, which is located in a near-surface layer of the Pt-catalyst, leads to a significant change of both the dipole moment and the equilibrium interatomic distance.

Keywords: diatomic molecule in electric field, catalyst phenomenon, semi-bounded metal.

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1. Introduction

A significant number of theoretical and experimental researches are devoted to investigation of carbon monoxide (CO) oxidation processes kinetics on a metal catalysts surface (based on platinum, palladium, ruthenium) [1]. Nevertheless, the research of these processes remains urgent both from the viewpoint of experimental investigations at nanocatalytic level and theoretical viewpoint because a consequent microscopic theory of reactive diffusion processes has not been investigated enough yet. Without understanding catalytic CO oxidation mechanisms on a microscopic scale, the development of a mathematical model of a quantitative description of catalytic CO oxidation process is impossible.

The catalytic CO oxidation mechanisms (Langmuir-Hinshelwood (LH) [2], Eley-Rideal (ER) [3]) were investigated in [4]. According to the LH mechanism both reactants (CO and O₂) are adsorbed on a metal catalyst surface in the beginning and then between adsorbed COad and O²ad under thermodynamically advantageous conditions a fusion reaction with a quick desorption process of the resultant product (CO₂) from the catalyst surface occur. The CO oxidation process through the ER mechanism occurs when oxygen atoms are adsorbed on the catalyst surface and a CO molecule is located in a subsurface gas zone. The energy barrier of the reaction according to such a mechanism is 0.72 eV and according to LH mechanism it is larger (0.8 – 1.05 eV). However, experimental investigations show that for CO oxidation processes on a platinum catalyst, LH mechanism is more acceptable. Although, the minimum barrier energy of a reaction for ER mechanism is less than for LH mechanism, such factors as the CO molecule structure, its orientation near a catalyst surface begin to play a determinant role. Detailed microscopic analysis of CO oxidation mechanisms on a platinum catalyst surface was conducted in [5–7] and an impurity effect on a catalytic CO oxidation was considered in [8].

ZGB model [9] and its generalization [10] a basis for theoretical investigation of catalytic CO oxidation kinetics being considered. This model assumes that a CO oxidation reaction occurs only on a catalyst surface, moreover, an adsorption of oxygen atoms occurs in consequence of a O₂ molecule decomposition near the catalyst surface. The CO molecule is adsorbed by the surface and lies on it without decomposing into atoms. However, as shown in [11], near a metal catalysts surface there exists
a strong electrostatic field (with the intensity 40 V/nm), which localization is the same as the atomic number of the metal catalyst. The influence of this field on a diatomic molecule (CO or O₂) can lead to its decomposition into atoms that henceforth can be adsorbed by the surface of metal catalysts.

In this work, a simple mathematical model of a diatomic molecule near a metal catalyst surface is developed and investigated. It is shown that existing near-surface electric field affects an equilibrium distance \( R \) between molecule atoms (leads to its increase), that implies a possibility of molecule decomposition into atoms with a consequent adsorption of O₂ molecule by the surface.

2. Problem formulation

Let us consider a motion of a diatomic molecule (CO or O₂) near a metal catalyst surface. The diatomic molecule contains atoms with atomic numbers \( Q_1 \) and \( Q_2 \) respectively, and set of electrons which general number is \( Q_1 + Q_2 \).

Whereas the metal catalyst is macroscopically large comparing to a size of the molecule, further let us assume that it is located in the lower half-space \( Z < 0 \) (\( OXYZ \) is the Cartesian coordinate system connected to the catalyst) with a flat surface \( Z = 0 \) (Fig. 1).

![Diatomic molecule near metal catalyst surface.](image)

As shown in [13], near the surface of metal there exists a non-uniform electric field with the intensity \( E(r) \).

In dipole approximation [14], the energy \( W \) of diatomic molecule in an internal electric field of the intensity \( E(r) \) can be expressed as follows:

\[
W = W_0 + \frac{1}{2} \int \varphi(r) \rho(r) \, dr - \int \left( d(r), E(r) \right) \, dr.
\]  

(1)

Here \( W_0 \) is a molecule energy at the moment when electric field is absent, \( \rho(r) \) is the electric charge density, \( \varphi(r) \) and \( E(r) \) are the potential and the intensity of the electric field respectively, \( d(r) \) is the dipole moment of the molecule, \( (, ) \) is a scalar product.

The diatomic molecule density of the electric field is

\[
\rho(r) = \rho^e(r) + Q_1 e \delta(r - R_1) + Q_2 e \delta(r - R_2).
\]  

(2)

Here \( R_1 \) and \( R_2 \) are coordinates of the nucleus atoms of the molecule in Cartesian coordinate system tied to the catalyst, \( e \) is electron charge, \( \delta() \) is Dirac delta function [14].

Let us assume that the dipole moment of the molecule is a constant vector. It allows us to write the expression for the dipole moment in the presence of the electric field in the following form

\[
d(r) = (d_0 + \varepsilon_0 E) \, \delta \left( r - R^d \right) \, n,
\]  

(3)

where \( d_0 \) is an absolute value of the dipole moment, \( \varepsilon_0 \) is the vacuum permittivity, \( \alpha \) is the molecule polarization, \( \mathbf{n} \) is a unit direction vector (in our case under influence of a field, created by the surface, the direction is perpendicular to the surface). Let us consider that dipole moment is concentrated in the molecule center of the charge \( \mathbf{R}^d \), which we denote by

\[
\mathbf{R}^d = \frac{Q_1 \mathbf{R}_1 + Q_2 \mathbf{R}_2}{Q_1 + Q_2}.
\]

For the chosen model of catalyst in case of a plane surface, the electrostatic potential is \( \varphi (\mathbf{r}) \equiv \varphi (z) \), and \( E (\mathbf{r}) \equiv E (z) \) [15], where \( z \) is a coordinate of the \( Oz \) axis that is perpendicular to the surface of the catalyst.

Considering this, let us rewrite the expression (3) as follows:

\[
W - W_0 = \frac{1}{2} \int_V \varphi (z) \rho^e (\mathbf{r}) d\mathbf{r} - \frac{1}{2} \varepsilon_0 \left( Q_1 \varphi (z_1) + Q_2 \varphi (z_2) \right) - d_0 \varepsilon_0 \alpha E^2 (z_d),
\]

(4)

where \( d_0 \) is a dipole moment projection of the molecule onto \( Oz \) axis.

3. Calculation of the electronic density, the electrostatic potential and intensity

The electronic density of molecules has been calculated using a software package Firefly (old name is PC GAMESS) [18]. In Fig. 2, it is shown scalar surfaces of the electronic density of CO molecule and in Fig. 3 of \( O_2 \). Note that the scalar surfaces of the electronic density for CO coincide with results of analogical calculations given in [16].

The electrostatic potential \( \varphi (z) \) in our model (Fig. 1) is a solution of Poisson’s equation [15]:

\[
\frac{d^2 \varphi (z)}{dz^2} = -4\pi e n (F_1 (z) - F_{\text{ion}} (z))
\]

or

\[
\varphi (z) = \varphi (-\infty) + 4\pi e n \int_{-\infty}^{z} dz' \left( F_1 (z') - F_{\text{ion}} (z') \right).
\]

(5)

(6)

Here \( F_1 (z) \) is a unary distribution function of electrons, \( n F_{\text{ion}} (z) \equiv \frac{2r}{\pi^2} e \theta (-z - m_d) \) is a unary distribution function of positive compensated charge, \( m_d > 0 \) is a parameter that is determined by the electroneutrality condition:

\[
\int_{-\infty}^{\infty} dz (F_1 (z) - F_{\text{ion}} (z)) = 0.
\]

(7)

The unary distribution function \( F_1 (z) \) was calculated in the research [17]. Knowing \( F_1 (z) \) it is possible to write the intensity of induced electrostatic field as follows

\[
E(z) = -\frac{d\varphi (z)}{dz} = -4\pi e n \int_{-\infty}^{z} dz' \left( n (z') - n (z) \right).
\]

(8)

Here \( n (z) \) is defined according to the condition \( F_1 (z) = e n (z) \).

\( \varphi (\mathbf{r}) \) and \( E (\mathbf{r}) \) were calculated using the results obtained in [17] for the unary function \( F_1 (z) \). Results of these calculations in accordance with Gell-Mann-Brueckner parameter \( r_s \) [14] are presented in Figs. 4 and 5.
4. Calculation of flue gas and oxygen molecules energy near the catalyst surface

Let us go back to the expression for the energy of diatomic molecule in an electric field (4):

\[ W - W_0 = \frac{1}{2} \int \varphi(z) \rho(e) \, dr - \frac{1}{2} e (Q_1 \varphi(z_1) + Q_2 \varphi(z_2)) - d_0 E(z_d) - \varepsilon_0 \alpha E^2(z_d), \]

In the first term, let us make a transformation from coordinate system of catalyst to coordinate system of the diatomic molecule (Fig. 1). Let \( r = (x, y, z) \) be coordinates in the catalyst coordinate system, \( r' = (x', y', z') \) are coordinates in the molecule coordinate system. These coordinate systems are related by the correlations:

\[ r' = r_0 - Ar \]  \hspace{1cm} (9)

where \( r'_0 = (x'_0, y'_0, z'_0) \) is a coordinate origin of molecule in catalyst coordinates, \( A \) is a rotation matrix, which contains direction cosines between the axes.

\[ A = \begin{pmatrix}
\cos_{xx} & \cos_{xy} & \cos_{xz} \\
\cos_{yx} & \cos_{yy} & \cos_{yz} \\
\cos_{zx} & \cos_{zy} & \cos_{zz}
\end{pmatrix}. \]  \hspace{1cm} (10)

Whereas these relations are linear then inverse relations can be determined identically. Let \( J \) be Jacobian matrix of the transformation from \( r \) to \( r' \). Since a transformation is a rotation and does not
depend on coordinates then the determinant $|J|$ is a constant. Hence we have that

$$\frac{1}{2} \int_{V} \varphi(r) \rho^*(r')dr = \frac{1}{2} |J| \int_{V} \varphi(z(r')) \rho^*(r')dr'.$$  \hspace{1cm} (11)

Note, since in the explored model only the angle $\beta$ of the slope of the axis $z$ plays a role then one of the axes $x$ or $y$ is going to be unchangeable. Thus, the matrix (10) can be expressed as follows (for the unchangeable axis $x$)

$$A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \beta & -\sin \beta \\ 0 & \sin \beta & \cos \beta \end{pmatrix}. \hspace{1cm}$$

The determinant of this matrix is equal to 1. Nondimensionalize the expression (11). Let

$$\varphi = \varphi^* \frac{e}{a_B}, \quad \rho^* = \rho^* \frac{e}{a_B^2}, \quad dr' = a_B^3 dr^*.$$  \hspace{1cm} (12)

Then, including that $|J| = 1$,

$$\frac{1}{2} \int_{V} \varphi(z(r')) \rho^*(r')dr' = \frac{e^2}{2 a_B} \int_{V} \varphi^*(z^*(r^*)) \rho^*(r^*)dr^*.$$  \hspace{1cm} (13)

In a similar way to (11), let us nondimensionalize the second term related to nucleus:

$$\frac{1}{2} e(Q_1 \varphi(z_1) + Q_2 \varphi(z_2)) = \frac{e^2}{2 a_B} (Q_1 \varphi^*(z_1^*) + Q_2 \varphi^*(z_2^*)).$$  \hspace{1cm} (14)

Let us analyze a contribution related to the presence of a dipole moment in a molecule. The dipole moment is directed towards the field by $OZ$ axis of catalyst coordinate system. Then

$$d_{0z} = d_0 \cos \beta,$$

where $d_0$ is the value of the dipole moment of the molecule (for CO molecule experimental value of $d_0$ is equal to 0.112 Debye, for $O_2$ molecule it is equal to 0). Nondimensionalizing the last term in (4), we obtain

$$W - W_0 = \frac{e^2}{a_B} \left[ \int_{V} \varphi^*(z^*(r^*)) \rho^*(r^*)dr^* + \frac{1}{2} (Q_1 \varphi^*(z_1^*) + Q_2 \varphi^*(z_2^*)) 
- 0.00155 (d_0^* \cos \beta E(z_d^*) + 0.0026 \alpha \ E^*(z_d^*)) \right].$$  \hspace{1cm} (15)

Further we minimize the expression for energy (15) for different values of the internuclear distance $|R_1 - R_2|$ and for the angle $\beta$. In Figs. 6–11, there are represented numerical results of investigations of catalyst electric field influence on energy of flue gas and oxygen molecules in the distances $3a_B, a_B, 0$ with the minimal possible distance of $m_d$ and $m_d-0.5a_B$ (condition (7)) and the angles $\beta = 0^\circ, 45^\circ, 90^\circ$. The Gell-Mann-Brueckner parameter is chosen specific to platinum ($r_s = 4$). Below the surface $z = m_d$, a positive charge lays and a molecule with respect to strong Coulomb repulsion in our model cannot enter. For $r_s = 3 \ m_d = 0.341 a_B$; for $r_s = 4 \ m_d = -0.3a_B$; for $r_s = 5 \ m_d = -0.98a_B$.

The results of numerical investigation of the proposed model show the following. For the $O_2$ molecule, the equilibrium interatomic distance $R_0^{O_2} = |R_1 - R_2|$ in the presence of electric field near the catalyst surface changes and for all the distances of the $O_2$ molecule charge center from the catalyst
Fig. 6. Dependence of the energy (15) on internuclear distance of CO for different distances to the surface for the angle of $\beta = 0^\circ$.

Fig. 7. Dependence of the energy (15) on internuclear distance of CO for different distances to the surface for the angle of $\beta = 45^\circ$.

Fig. 8. Dependence of the energy (15) on internuclear distance of CO for different distances to the surface for the angle of $\beta = 90^\circ$.

Fig. 9. Dependence of the energy (15) on internuclear distance of O$_2$ for different distances to the surface for the angle of $\beta = 0^\circ$.

Fig. 10. Dependence of the energy (15) on internuclear distance of CO for different distances to the surface for the angle of $\beta = 45^\circ$.

Fig. 11. Dependence of the energy (15) on internuclear distance of CO for different distances to the surface for the angle of $\beta = 90^\circ$. 

surface \( R_{0}^{O_2} = 2.22943a_B \). It is 130\% of the equilibrium distance \( R_{0}^{O_2} \) when the electric field of catalyst is absent: \( R_{0}^{O_2} = 2.147a_B \).

The energy change \( \Delta E = E_{\min}(E \neq 0) - \varepsilon_{\min}(E = 0) \) depends on the angle \( \beta \) and is the following:

\[
\begin{align*}
\beta = 0^\circ: & \quad \Delta E = -\frac{e^2}{2a_B}, \quad R_{0}^{O_2} = 2.2942, \\
\beta = 45^\circ: & \quad \Delta E = -0.5\frac{e^2}{a_B}, \quad R_{0}^{O_2} = 2.2942, \\
\beta = 90^\circ: & \quad \Delta E = -3\frac{e^2}{a_B}, \quad R_{0}^{O_2} = 2.2942.
\end{align*}
\]

These results testify that the shown dipole moment \( d_{O_2} \) of the molecule \( O_2 \) when it is approaching the catalyst surface becomes parallel to the surface and the molecule becomes \( O_2 \) asymmetric.

For the \( CO \) molecule, the location of energy minimum \( (R_{0}^{CO}) \) depends on the angle \( \beta \) of the dipole moment and on the distance \( r_0 \) of the \( CO \) molecule charge center from the surface of catalyst, namely

<table>
<thead>
<tr>
<th>( r_0 ) or ( \beta )</th>
<th>0° ± 50°</th>
<th>50° ± 70°</th>
<th>70° ± 90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta = 0^\circ )</td>
<td>2.147</td>
<td>2.147</td>
<td>2.147</td>
</tr>
<tr>
<td>( \beta = 45^\circ )</td>
<td>3.650</td>
<td>3.00</td>
<td>2.147</td>
</tr>
</tbody>
</table>

This table demonstrates that when the \( CO \) molecule approaches the catalyst surface, it does not tend to decay into atoms (in contrast to \( O_2 \) molecule).

5. Conclusions

A simple mathematical model of diatomic molecule (\( CO \) or \( O_2 \)) behavior description near the Pt-catalyst surface is suggested and investigated. It is shown that a near-surface electric field has a significant influence on the change (or appearance) of dipole moment of molecules and changes the equilibrium interatomic distance. The changes of these characteristics for the molecules \( CO \) and \( O_2 \) are evaluated.


Моделювання впливу поверхні Pt-каталізатора на характеристики молекул кисню і окису вуглецю

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Розглянуто просту математичну модель впливу поверхні Pt-каталізатора на поведінку молекул чадного газу та кисню. Показано, що електричне поле, локалізоване в приповерхневому шарі Pt-каталізатора, призводить до значної зміни дипольного моменту та рівноважної міжатомної відстані.

Ключові слова: двоатомні молекули в електричному полі, явище каталizu, півобмежений метал.

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