

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

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(Received 30 June 2016)

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.*

**2000 MSC:** 00A71

**UDC:** 533.9, 536.7

### 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  $O_2$ ) are adsorbed on a metal catalyst surface in the beginning and then between adsorbed  $CO_{ad}$  and  $O_{ad}$  under thermodynamically advantageous conditions a fusion reaction with a quick desorption process of the resultant product ( $CO_2$ ) 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  $O_2$  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  $O_2$ ) 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  $O_2$  molecule by the surface.

## 2. Problem formulation

Let us consider a motion of a diatomic molecule ( $CO$  or  $O_2$ ) 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).

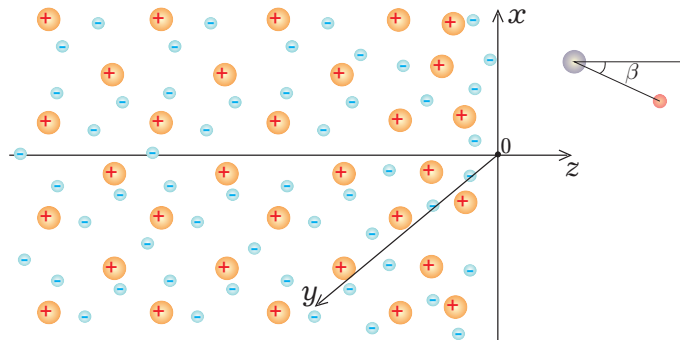


Fig. 1. Diatomic molecule near metal catalyst surface.

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

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

$$W = W_0 + \frac{1}{2} \int_V \varphi(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} - \int_V (\mathbf{d}(\mathbf{r}), \mathbf{E}(\mathbf{r})) d\mathbf{r}. \quad (1)$$

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

The diatomic molecule density of the electric field is

$$\rho(\mathbf{r}) = \rho^e(\mathbf{r}) + Q_1 e \delta(\mathbf{r} - \mathbf{R}_1) + Q_2 e \delta(\mathbf{r} - \mathbf{R}_2). \quad (2)$$

Here  $\mathbf{R}_1$  and  $\mathbf{R}_2$  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

$$\mathbf{d}(\mathbf{r}) = (d_0 + \varepsilon_0 \alpha \mathbf{E}) \delta(\mathbf{r} - \mathbf{R}^d) \mathbf{n}, \quad (3)$$

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 catalyst.

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

$$W - W_0 = \frac{1}{2} \int_V \varphi(z) \rho^e(\mathbf{r}) d\mathbf{r} - \frac{1}{2} e (Q_1 \varphi(z_1) + Q_2 \varphi(z_2)) - d_{0z} E(z_d) - \varepsilon_0 \alpha E^2(z_d), \quad (4)$$

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]:

$$\frac{d^2 \varphi(z)}{dz^2} = -4\pi en (F_1(z) - F_{ion}(z)) \quad (5)$$

or

$$\varphi(z) = \varphi(-\infty) + 4\pi en \int_{-\infty}^z dz' (z' - z) (F_1(z') - F_{ion}(z')). \quad (6)$$

Here  $F_1(z)$  is a unary distribution function of electrons,  $nF_{ion}(z) \equiv \frac{2N}{SL} e\theta(-z - m_d)$  is a unary distribution function of positive compensated charge,  $m_d > 0$  is a parameter that is determined by the electroneutrality condition:

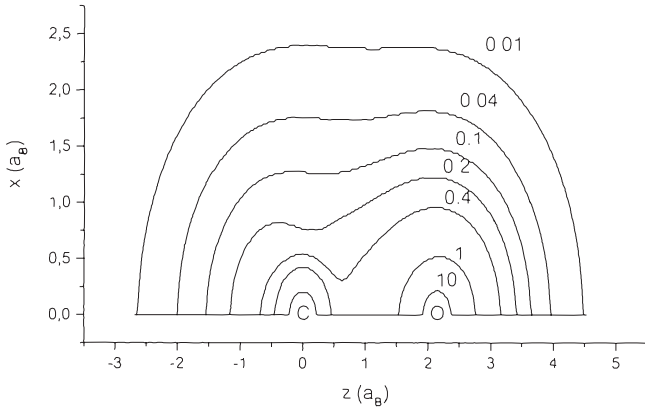
$$\int_{-\infty}^{\infty} dz (F_1(z) - F_{ion}(z)) = 0. \quad (7)$$

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

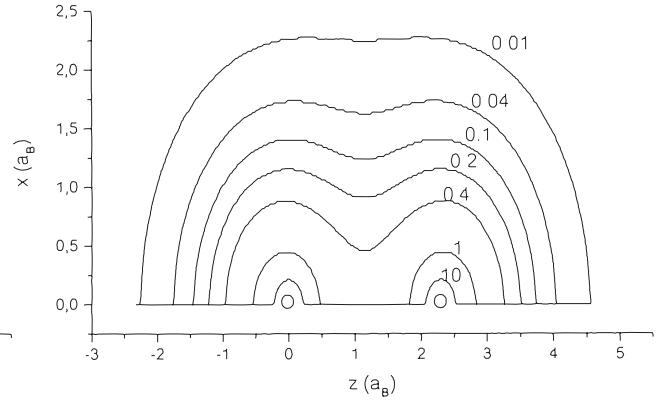
$$E(z) = -\frac{d\varphi(z)}{dz} = -4\pi en \int_{-\infty}^z dz' (n(z') - n(z)). \quad (8)$$

Here  $n(z)$  is defined according to the condition  $F_1(z) = en(z)$ .

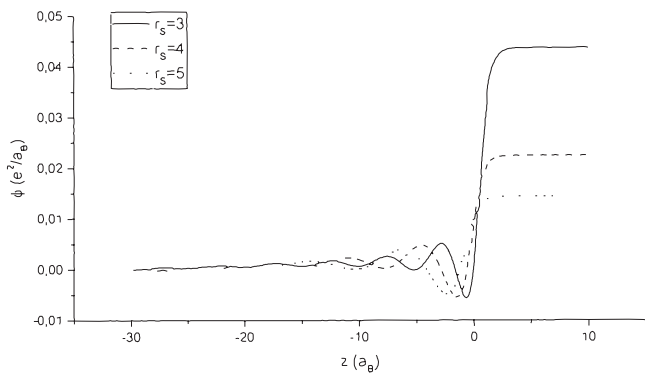
$\varphi(\mathbf{r})$  and  $E(\mathbf{r})$  were calculated using the results obtained in [17] for the unary function  $F_1(z)$ . Results of these calculations in accordance with Gell-Mann-Brueckner parameter  $r_s$  [14] are presented in Figs. 4 and 5.



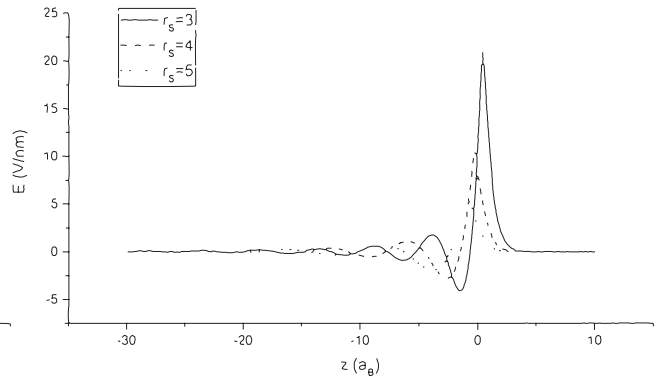
**Fig. 2.** Electronic density of  $CO$  molecule obtained by using Firefly.



**Fig. 3.** Electronic density of  $O_2$  molecule obtained by using Firefly.



**Fig. 4.** Electrostatic potential  $\varphi(z)$  for different values of  $r_s$ .



**Fig. 5.** Intensity  $E(z)$  of field for different values of  $r_s$ .

#### 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):

$$W - W_0 = \frac{1}{2} \int_V \varphi(z) \rho^e(\mathbf{r}) d\mathbf{r} - \frac{1}{2} e (Q_1 \varphi(z_1) + Q_2 \varphi(z_2)) - d_{0z} E(z_d) - \varepsilon_0 \alpha E^2(z_d),$$

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

$$\mathbf{r}' = \mathbf{r}_0 - A\mathbf{r} \quad (9)$$

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

$$A = \begin{pmatrix} \cos_{xx} & \cos_{xy} & \cos_{xz} \\ \cos_{yx} & \cos_{yy} & \cos_{yz} \\ \cos_{zx} & \cos_{zy} & \cos_{zz} \end{pmatrix}. \quad (10)$$

Whereas these relations are linear then inverse relations can be determined identically. Let  $J$  be Jacobian matrix of the transformation from  $\mathbf{r}$  to  $\mathbf{r}'$ . Since a transformation is a rotation and does not

depend on coordinates then the determinant  $|J|$  is a constant. Hence we have that

$$\frac{1}{2} \int_V \varphi(\mathbf{r}) \rho^e(\mathbf{r}') d\mathbf{r} = \frac{1}{2} |J| \int_V \varphi(z(\mathbf{r}')) \rho^e(\mathbf{r}') d\mathbf{r}'. \quad (11)$$

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  $x$ )

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

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

$$\varphi = \varphi^* \frac{e}{a_B}, \quad \rho^e = \rho^* \frac{e}{a_B^3}, \quad d\mathbf{r}' = a_B^3 d\mathbf{r}^*. \quad (12)$$

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

$$\frac{1}{2} \int_V \varphi(z(\mathbf{r}')) \rho^e(\mathbf{r}') d\mathbf{r}' = \frac{1}{2} \frac{e^2}{a_B} \int_V \varphi^*(z^*(\mathbf{r}^*)) \rho^*(\mathbf{r}^*) d\mathbf{r}^*. \quad (13)$$

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

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

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

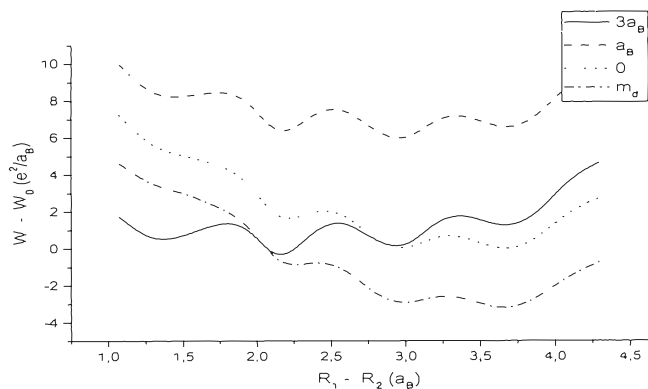
$$d_{0z} = d_0 \cos \beta,$$

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

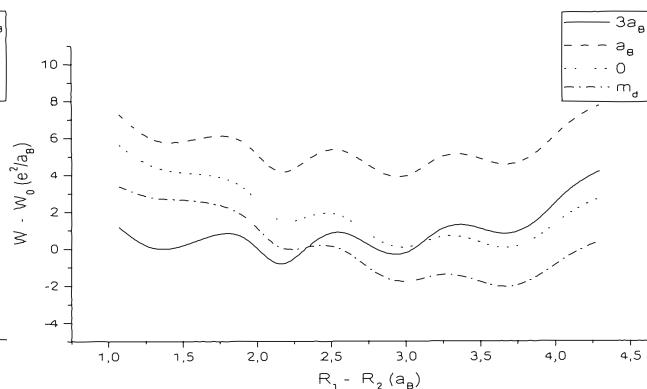
$$W - W_0 = \frac{e^2}{a_B} \left[ \frac{1}{2} \int_V \varphi^*(z^*(\mathbf{r}^*)) \rho^*(\mathbf{r}^*) d\mathbf{r}^* + \frac{1}{2} (Q_1 \varphi^*(z_1^*) + Q_2 \varphi^*(z_2^*)) - 0.00155 (d_0^* \cos \beta E(z_d^*) + 0.0026 \alpha^* E^*(z_d^*)) \right]. \quad (15)$$

Further we minimize the expression for energy (15) for different values of the internuclear distance  $|\mathbf{R}_1 - \mathbf{R}_2|$  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  $r_s = 3$   $m_d = 0.341a_B$ ; for  $r_s = 4$   $m_d = -0.3a_B$ ; for  $r_s = 5$   $m_d = -0.98a_B$ .

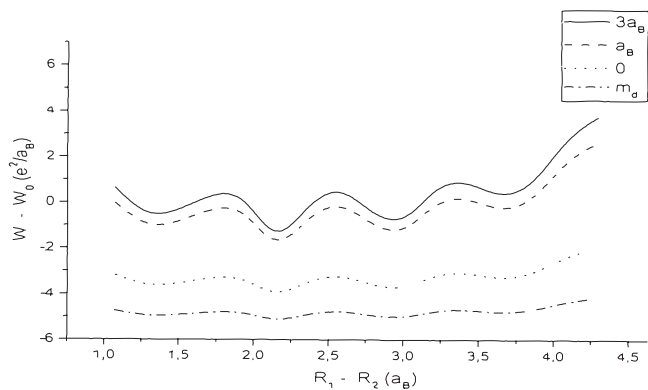
The results of numerical investigation of the proposed model show the following. For the  $O_2$  molecule, the equilibrium interatomic distance  $R_0^{O_2} = |\mathbf{R}_1 - \mathbf{R}_2|$  in the presence of electric field near the catalyst surface changes and for all the distances of the  $O_2$  molecule charge center from the catalyst



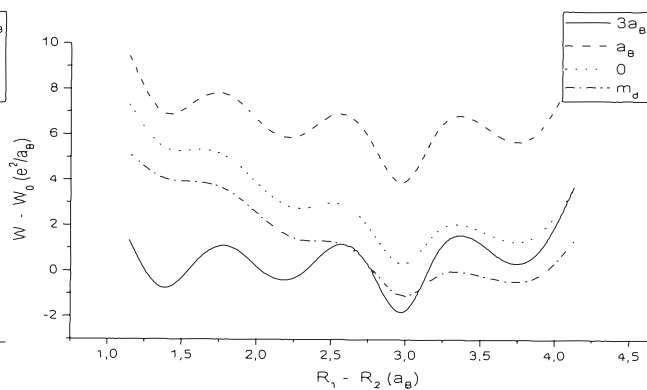
**Fig. 6.** Dependence of the energy (15) on internuclear distance of  $CO$  for different distances to the surface for the angle of  $\beta = 0^\circ$ .



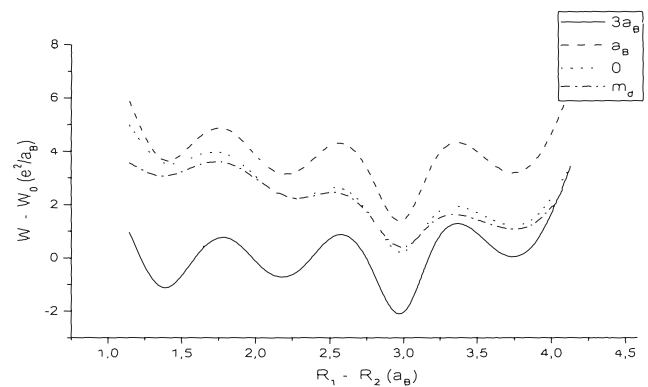
**Fig. 7.** Dependence of the energy (15) on internuclear distance of  $CO$  for different distances to the surface for the angle of  $\beta = 45^\circ$ .



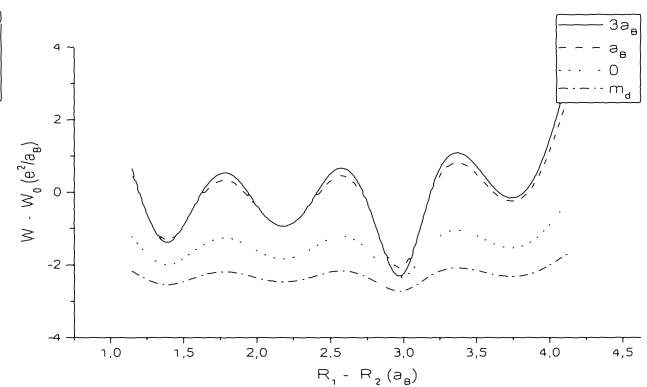
**Fig. 8.** Dependence of the energy (15) on internuclear distance of  $CO$  for different distances to the surface for the angle of  $\beta = 90^\circ$ .



**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:

$$\beta = 0^\circ: \Delta E = -1 \frac{e^2}{2a_B}, \quad R_0^{O_2} = 2.2942,$$

$$\beta = 45^\circ: \Delta E = -0.5 \frac{e^2}{2a_B}, \quad R_0^{O_2} = 2.2942,$$

$$\beta = 90^\circ: \Delta E = -3 \frac{e^2}{a_B}, \quad R_0^{O_2} = 2.2942.$$

These results testify that the shown dipole moment  $\mathbf{d}_{O_2}$  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 1.** Dependence of  $CO$  molecule energy minimum location on model parameters.

$r_0/\beta$	$0^\circ \div 50^\circ$	$50^\circ \div 70^\circ$	$70^\circ \div 90^\circ$
$1 \div 3$	2.147	2.147	2.147
$0 \div m_d$	3.650	3.00	2.147

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.

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## 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 каталізу, пів-обмежений метал.*

**2000 MSC:** 00A71

**UDC:** 533.9, 536.7