SIMULATION OF OXYGEN ATOM HETEROGENEOUS RECOMBINATION ON AL_2O_3 FROM *AB INITIO* APPROACH

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Abstract

To analyze the catalytic properties of heat shield materials of space vehicles the cluster model of oxygen atom adsorption on Al_2O_3 surface is constructed on the basis of density functional theory. The potential energy surface (PES) corresponding to orientation interaction of the O atom with this cluster is calculated. It was found a number of important PES features for subsequent description of heterogeneous catalytic processes with an application of molecular dynamics methods. In the framework of quasiclassical approach the modeling of heterogeneous recombination of oxygen atoms on the surface of cluster through Eley-Rideal mechanism was conducted by molecular dynamics methods. Modeling results revealed that for correct description of investigated process PES has to be calculated with taking into account internal relaxation of some top cluster layers.

Introduction

To calculate the heat loads and predict the life-time of the reusable heat shield it is necessary to have basic information on the processes of thermochemical interaction between dissociated air and heat shield materials. The most important processes are catalytic atom recombination. The heat fluxes to surfaces with different catalytic properties can differ by several times. Despite the fact that since the fifties[1] it has been well known that heterogeneous atom recombination significantly affects heat transfer at hypersonic flight velocities, the mechanisms and rates of the processes which determine the interaction between the gas and the surface have been much less closely studied than the kinetics and the homogeneous chemical reaction rates. The complexity of the problem of determining the catalytic properties of the surface is associated with the fact that even at room temperatures there are no direct methods of measuring the recombination coefficients γ_i and chemical energy accommodation β_i. These processes depend both on the external factors, namely, the degree of dissociation of the stream, diffusion and gas-phase atom recombination in the boundary layer, and on the properties of the surface itself. Therefore, the experimental data obtained by different authors differ sharply. These data can be correctly interpreted and the aerodynamic heating along the entire atmospheric re-entry trajectory investigated only if the mechanism of the heterogeneous catalytic reactions and rate coefficients of elementary steps on the heat shield coatings is taken fully into account and sufficiently complete models of the physicochemical processes in the gas phase are used.

The conventional approach used to describe and understand heterogeneous catalysis has so far relied on kinetics or phenomenological models[2]. Such models lend themselves to faster and relatively inexpensive application in the CFD codes calculating heat fluxes to space vehicles. In fact, these models are based on or depend on insufficiently accurate experimental or theoretical data. Many parameters inside phenomenological catalytic models are not well-known; as for example, the sticking coefficients, or the activation barriers of postulated surface reactions. The parameters of these models are usually derived by fitting the outcome of simulations to experimental data. The values of the parameters significantly depend on the chosen mechanism of heterogeneous recombination. For a chosen mechanism the differences in values are attributable to the fact that in the general case the solution of the multi-parameter inverse problem is non-unique In common, we don't know accurately mechanism of heterogeneous catalytic proceces and Arrhenius coefficients of elementary surface reactions.

In this context a radical suggestion is to start modelling catalysis from first principles (*ab initio* calculations), as much as practical or computational complexity will make this approach feasible.

Ab initio methods solve the quantum mechanical equations which govern the behaviour of a system. The only information which must be provided are the atomic numbers and positions of the atoms within the system. Recent years have indeed witnessed efforts to increase the accuracy of quantum mechanical calculations of chemical systems. The main reasons to address the possible study of catalysis with the *ab initio* approach are the following: uncertainty about the experimental data, making difficult to make valid test ground facility; possibility to predict every step of surface reaction pathways; it enables better understanding of unknown or previously unsuspected mechanisms; a theoretical description of reactions can minimize the large number of experiments to obtain a good catalysis description. *Ab initio* approaches are indeed promising, but there is plenty of room for further research if they must be applied to heterogeneous catalysis. For this reason, choice of an *ab initio* approach to describe realistically catalytic recombination is a major investment of resources.

Molecular dynamics (MD) models are useful to understand the surface chemical reactions from a molecular point of view. MD strategy recognizes a gas as a myriad of discrete molecules and ideally provides information on the position, velocity, and state of every molecule at all times by classical trajectory calculations. Molecular dynamics simulations predict some quantities that cannot be easily measured in experimental observations, such as : state-to-state surface coefficients (e.g, sticking coefficient) and their dependence upon the internal energy content of reactive molecule; translational and internal energy distributions of the product states; energy exchanged between the surface and the chemical system reaction mechanism and reaction pathways.

“MD Trajectory” software complex was developed to investigate both Eley-Rideal and Langmuir-Hinshelwood mechanisms of heterogeneous recombination. “MD Trajectory” was tested on supercomputer clusters of Moscow State University and Russian Academy of Sciences and very high efficiency was achieved. Calculations of heterogeneous recombination of O atoms on the Si-based surface (SiO_2 and SiC) in Eley-Rideal reactions were conducted and satisfactory fit with other authors’ results and experimental data were obtained [3]. Thus, software complex “MD Trajectory” is rather powerful tool for investigation of chemical reaction by quasi-classical trajectory method especially for conditions hardly realized in experiment.

This paper is devoted to modelling of adsorption and heterogeneous recombination processes of oxygen atoms on the Al_2O_3 surface on the basis of the Density Functional Theory (DFT) [4, 5] and MD method.

QCT Methodology

Classical treatment was realized in the “MD Trajectory” for simulation heterogeneous recombination. In the framework of this approach atoms are divided in two groups:

1. $i = 1, \dots n$ – gas-phase atoms
2. $k = 1, \dots N$ – lattice atoms

Total hamiltonian is

$$\begin{aligned} H = \; & \sum_{i=1}^{n} \sum_{\gamma=x,y,z} \frac{1}{2M_i} P_{i\gamma}^2 + \sum_{k=1}^{N} \sum_{\gamma=x,y,z} \frac{1}{2M_k} P_{k\gamma}^2 + \\ & \sum_{i<j} V_{11}\left(R_{ij}\right) + \sum_{k<l} V_{22}\left(R_{kl}\right) + \sum_{ik} V_{12}\left(R_{ik}\right) \end{aligned} \tag{1}$$

where the first two terms are the kinetic energy of the gas-phase and surface atoms and last three terms are potential energy of interaction between gas-phase atoms – V_{11}, between lattice atoms – V_{22} and between gas-phase and surface atoms – V_{12}. R_{ij} – is interatomic distance between i-th and j-th atoms, $P_{i\gamma}$ – is γ-component (in Cartesian coordinates $\gamma = x, y$ or z) of the impulse of i-th atom.

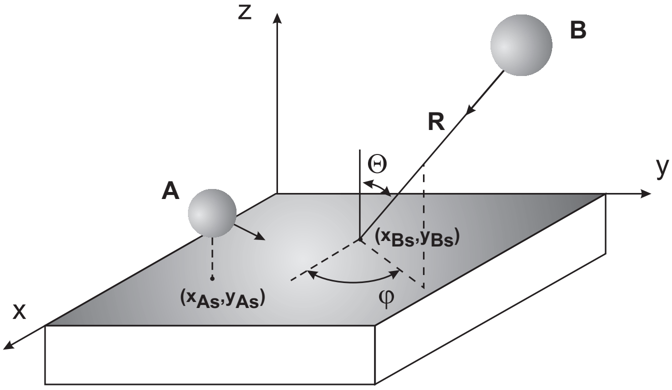


Fig. 1. Collision scheme of Eley-Rideal recombination process

Motion equations in Hamilton form are written for both gas phase and lattice atoms:

$$\begin{aligned}
\dot{\gamma_i} &= \frac{P_{i\gamma}}{M_i} \\
\dot{\gamma_k} &= \frac{P_{k\gamma}}{M_k} \\
\dot{P_{i\gamma}} &= -\frac{\partial H}{\partial \gamma_i} = -\sum_{j\neq i} \frac{\partial V_{11}}{\partial R_{ij}} \frac{\partial R_{ij}}{\partial \gamma_i} - \sum_{k} \frac{\partial V_{12}}{\partial R_{ik}} \frac{\partial R_{ik}}{\partial \gamma_i} \\
\dot{P_{k\gamma}} &= -\frac{\partial H}{\partial \gamma_k} = -\sum_{l\neq k} \frac{\partial V_{22}}{\partial R_{kl}} \frac{\partial R_{kl}}{\partial \gamma_k} - \sum_{i} \frac{\partial V_{12}}{\partial R_{ik}} \frac{\partial R_{ik}}{\partial \gamma_k}
\end{aligned} \tag{2}$$

where

$$R_{ij} = |R_i - R_j| = \sqrt{(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2} \tag{3}$$

and

$$\frac{\partial R_{ij}}{\partial \gamma_i} = -\frac{\partial R_{ij}}{\partial \gamma_j} = \frac{\gamma_i - \gamma_j}{R_{ij}} \tag{4}$$

MD simulation is reduced to solving of motion equations at the various initial conditions which realize real collisions. On the Fig.1 the collision scheme for Eley-Rideal recombination process between adsorbed atom A$_s$ and gas phase atom B is represented. For this process initial conditions can be written as:

- For incident gas atom B

$$\begin{aligned}
X_B = R_B \sin\theta_B \cos\varphi_B + X_{B_s} \quad &, \quad P_{X_B} = -P_{R_B} \sin\theta_B \cos\varphi_B \\
Y_B = R_B \sin\theta_B \sin\varphi_B + Y_{B_s} \quad &, \quad P_{Y_B} = -P_{R_B} \sin\theta_B \sin\varphi_B \\
Z_B = R_B \cos\theta_B \quad &, \quad P_{Z_B} = -P_{R_B} \cos\theta_B
\end{aligned}$$

  and

$$\begin{aligned}
\theta_B &= \arccos(1 - 2\cdot\xi_1) \ \in [0, \pi] \\
\varphi_B &= 2\pi \cdot \xi_2 \ \in [0, 2\pi] \\
X_{B_s} &= X_{max} \cdot \xi_3 \ \in [0, X_{max}] \\
Y_{B_s} &= Y_{max} \cdot \xi_4 \ \in [0, Y_{max}] \\
P_{R_B} &= \sqrt{2 M_B E_{coll}}
\end{aligned}$$

  where ξ_i – random numbers uniformly distributed in the interval (0,1), M_B – mass of atom B, R_B is fixed and is taken so large as the initial interaction between atom B and lattice can be neglected, E_{coll} – relative collisional energy between atom B and lattice.

- For adsorbed gas atom A

$$\begin{aligned}
X_A = X_{A_s} &= X_{max} \cdot \xi_5 \ \in [0, X_{max}] \\
Y_A = Y_{A_s} &= Y_{max} \cdot \xi_6 \ \in [0, Y_{max}] \\
P_{X_A} &= -P_{R_A} \sin\theta_A \cos\varphi_A \\
P_{Y_A} &= -P_{R_A} \sin\theta_A \sin\varphi_A \\
P_{Z_A} &= -P_{R_A} \cos\theta_A
\end{aligned}$$

  and

$$\begin{aligned}
P_{R_A} &= \sqrt{2M_A k T_s} \\
\theta_A &= \arccos(1 - 2 \cdot \xi_7) \ \in [0, \pi] \\
\varphi_A &= 2\pi \cdot \xi_8 \ \in [0, 2\pi]
\end{aligned}$$

  where M_A – mass of atom A, k – Boltzmann constant, T_s – surface temperature, Z_A is fixed and is taken so small that potential energy of interaction between atom A and lattice is higher than kinetic energy of atom A and it cannot left the surface.

- For lattice atoms

$$R_{k\gamma} = R^0_{k\gamma} + \sqrt{2kT_s/F_k}\cos\left(\varphi^0_{k\gamma}\right), P_{k\gamma} = \sqrt{2M_k k T_s}\sin\left(\varphi^0_{k\gamma}\right)$$

  where $R^0_{k\gamma}$ – equilibrium position, F_k – force constant for k-th atom, $\varphi^0_{k\gamma}$ – phase angle, randomly distributed in $[0, 2\pi]$ (depending on random numbers ξ), M_k – mass of k-th atom.

The each trajectory calculation is stopped when the distance criterion is realized. It's easy for check during numerical integration and can be formulated as:

- $Z_A + Z_B > R_{max}$ - at least one atom leaves surface
- $Z_A + Z_B < R_{min}$ during $\tau_{calc} > \tau_{max}$ - both atoms during the long calculation period τ_{calc} are near the surface.

where $R_{min}, R_{max}, \tau_{max}$ - fixed values.
If both atoms leave surface, atomic pair AB has to be checked for bound, quasi-bound or dissociative state. If the molecule AB is in the bound or quasi-bound state, vibrational v and rotational j numbers can be determined using special iteration procedure, more details can be given in [6, 7].
Simulation is performed at the fixed parameters T_s and E_{coll} and varied other parameters, randomly distributed in the corresponding intervals. Averaging results over varied parameters the key characteristics of heterogeneous recombination $\gamma(T_s, E_{coll})$ and $\beta(T_s, E_{coll})$ can be obtain as functions of surface temperature T_s and collision energy E_{coll}.
The appropriate results with good accuracy can be obtained only if huge number of trajectories will be calculated. To use modern supercomputer cluster systems the quasi-classical trajectory (QCT) calculations code was parallelized on the basis of Message Passing Interface (MPI) technology.

PES Calculation Methodology

The potential energy surface corresponding to orientational interaction of the O(^{3}P) atom with the Al_4O_6 cluster modeling the - Al_2O_3 crystal surface is calculated using the GAUSSIAN98 computer code [8]. Molecular constants of O_2, AlO and Al_2 molecules in the ground electronic state calculated by B3LYP method with various basis sets are represented in the Table . Experimental data are also included here for comparative analysis of the received results [9].

As we can see from this table, parameters of pairwise interactions of O and Al atoms are well reproduced since only valence-split basis Pople 6-31G* [10]. This basis consists from combined basis functions $[4s3p1d]_{Al}$+ $[3s2p1d]_{O}$ (quantity of basis functions of each type on the atomic centers of the molecules is indicated in square brackets).

Table 1. Properties of O_2, AlO and Al_2 molecules in the ground electronic state (including bond length (R), harmonious vibrational frequency (ω_e), dissociation energy (D_0)) calculated by B3LYP method with various basis sets.

Basis sets	Molecules								
	O_2 ($^3\Sigma_g^-$)			$AlO(^2\Sigma^+)$			Al_2 ($^3\Sigma_g^-$)		
	Properties								
	R, Å	ω_e, cm^{-1}	D_0, eV	R, Å	ω_e, cm^{-1}	D_0, eV	R, Å	ω_e, cm^{-1}	D_0, eV
6-31G	1,25	1435	4,09	1,70	853	4,21	2,58	300	1,02
6-31+G	1,26	1422	3,95	1,71	823	4,30	2,58	299	1,01
6-31G*	**1,21**	**1659**	**5,31**	**1,64**	**948**	**4,91**	**2,51**	**323**	**1,17**
6-31+G*	1,22	1642	5,13	1,65	926	4,97	2,51	322	1,15
experiment	1,21	1580	5,12	1,62	979	5,27±0,04	2,47	350	$1{,}5_5$

In the description of valence electrons the basis 6-31G* matches to two-exponential basis (on two basis functions per atomic orbital (AO)) with inclusion of external polarisation d-type functions on O and Al atoms. AO of core electrons are presented by one basis function. Basis set 6-31G* possesses more completeness in comparison with basises 6-31G and 6-31+G, which don't include polarisation d-functions. From tab. 1 follows, that calculated with basis 6-31G* equilibrium internuclear distances differ from the experimental ones no more, than on 0,04 Å, and the harmonious vibrational frequencies are agreed to their experimentally found values within 8%. The mean error for dissociation energy in system of O and Al atoms calculated with basis 6-31G* is 0,3 eV. This error can be reduced up to 0,2 eV, adding in basis set 6-31G* on one diffusive function s- and p- types per each atomic centers, i.e. transferring to basis 6-31+G*.

Difference in 0,1 eV is observed also at the description of an adsorption energy of complex $O(^3P)$-Al_4O_6 (C_{3v} - symmetry) with use of basises 6-31G* and 6-31+G* (Tab.2). However increment of calculations accuracy of PES on 0,1 eV is related to magnification of number of basis functions for system O-Al_4O_6 from 181 to 225, that increases computer time approximately in 2 times. Therefore in all our PES calculations of oxygen interaction with cluster Al_4O_6 the basis set Pople 6-31G* has been chosen as optimum between accuracy of PES description and computer time expenses.

Table 2. Calculated with different basises method B3LYP equilibrium geometric parameters and adsorption energy (E_{ads}) of complex O (^{3}P) - Al_4O_6 (C_{3v} - symmetry) (fig. 1 see). The corresponding parameters for Al_4O_6 (T_d-symmetry) are shown in the brackets.

Properties	Basis set			
	6-31G	6-31+G	6-31G*	6-31+G*
$R(Al_2$-$O_1)$, Å	1,81	1,82	1,76	1,77
$R(Al_2$-$O_{3,4,5})$, Å	1,83 (1,78)	1,83 (1,78)	1,81 (1,74)	1,81 (1,75)
$\angle O_1$-Al_2-$O_{3,4,5}$, degrees	120 (108)	120 (108)	117 (105)	117 (106)
$R(Al_{6,7,8}$-$O_{3,4,5})$, Å	1,77 (1,78)	1,77 (1,78)	1,74 (1,74)	1,75 (1,75)
$\angle Al_2$-$O_{3,4,5}$-$Al_{6,7,8}$, degrees	120 (106)	121 (106)	114 (101)	115 (102)
$R(Al_2$-$O_{9,10,11})$, Å	3,71 (3,38)	3,71 (3,39)	3,60 (3,30)	3,61 (3,31)
$\angle O_1$-Al_2-$O_{9,10,11}$, degrees	153 (150)	153 (150)	152 (149)	152 (149)
E_{ads}, ýÂ	1,83	1,75	1,79	1,67

Results and Discussions

The chemosorption is a process of formation of chemical bonds between an adsorbate (atom, molecule) and an adsorbent (for example, a solid body surface). Cluster approaches are most effective for description of local interactions at the chemosorption due to formation of chemical bonds is determined by a short-range forces. A cluster is a rather small fragment of the crystal lattice of the solid body, including the finite number atoms of external surface layer and atoms of internal ones. In the framework of such approach due to restricted size of molecular systems the quantum mechanics methods can be used effectively.

In our case the crystal surface $\alpha - Al_2O_3$ was modelled by cluster Al_4O_6 transmitting a stoichiometry of a crystal and a valent state of surface Al atoms. The positions of oxygen atoms in

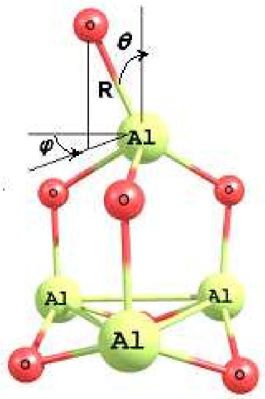


Fig. 2. Cluster model of adsorption of oxygen atom on Al_2O_3 surface.

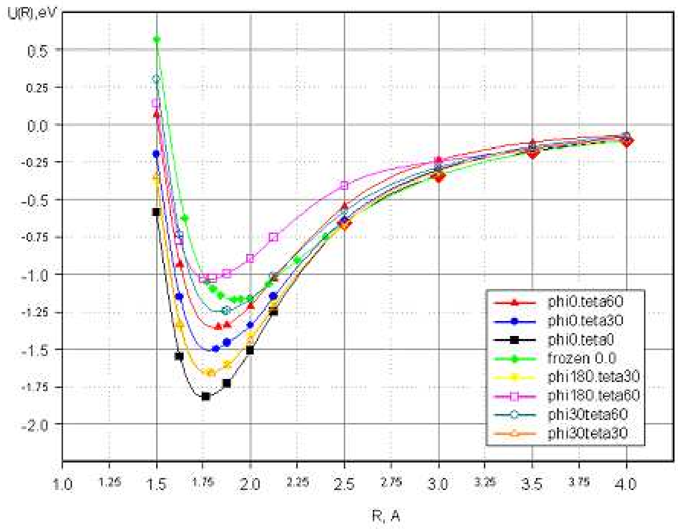
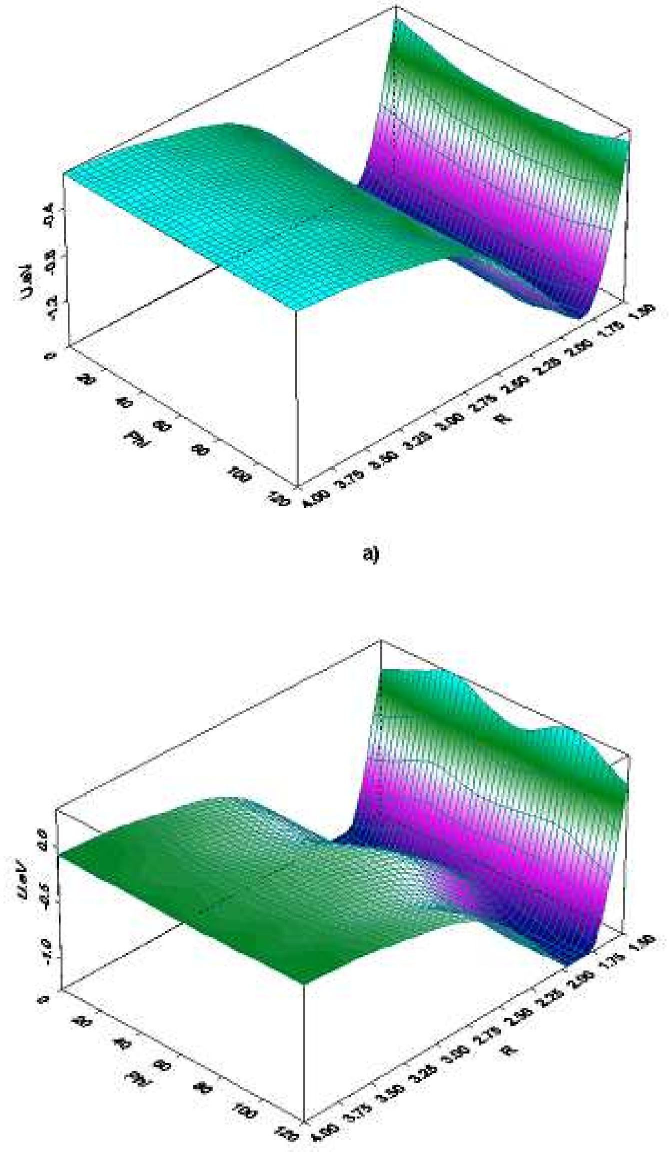


Fig. 3. Potential energy curves U(R) corresponding to interaction of atomic oxygen O (^{3}P) with the Al_4O_6 cluster. R is the distance between O (^{3}P) atom and Al atom lying on surface of solid Al_2O_3 during the O (^{3}P) atom approach the surface in different directions determined by θ and φ angles. Symbols R, θ and φ are given in Fig.2

the bottom plane of Al_4O_6 cluster were fixed at the modelling of adsorption of an oxygen atom on Al_2O_3 surface. The positions of remaining atoms were optimized at the given R, θ è φ coordinates of adsorbed atom O (^{3}P) (Fig.2). Such model takes account of surface monolayers relaxation caused by their interaction with adsorbate. The performed calculations show the importance of the structural relaxation processes for surface atoms. As the O (^{3}P) atom approaches the surface up to the equilibrium distance $R_e = 1.77$Å in normal direction ($\theta = 0^{\hat{1}}$) (Fig.3), the distance between upper planes of atoms O and Al (Fig.2) increases more than 70% and the relaxation energy contribution to adsorption energy $E_a = 1.8$ eV is of 30% in comparison with the model that does not take into account the relaxation of structure parameters (upper curve in Fig.3). Similar effects of structural relaxation for Al_2O_3 surface are revealed during study of the H_2O [11, 12] and O_2 [12] molecule adsorption on this surface. Note that according to paper [12] the adsorption energy of molecular oxygen on Al_2O_3 surface is 0.6 eV at equilibrium distance 1.98Å counted off from lower O atom in the O_2 molecule.

As follows from Fig.3, the potential energy curves corresponding to orientational interaction of the O (^{3}P) atom with the Al_4O_6cluster have a smooth and binding character that means the absence



a)

б)

Fig. 4. PES of oxygen atom interaction with Al_4O_6 cluster in co-ordinates R and φ at $\theta = 30$(a), and $\theta = 60$(b)

of activation barriers in process of atomic oxygen adsorption on Al_2O_3 surface. As the angle θ of the O (^{3}P) atom attack of Al_2O_3 surface is risen, the depth of adsorption minimum at PES decreases while the equilibrium distance R_e increases.

At $\theta = 30$ with increasing φ there is an interaction energy stabilization in system O (^{3}P) - Al_4O_6 whereas at $\theta = 60$ the opposite trend in behavior of potential curves occurs. Both at $\varphi = 0$, and at $\varphi = 60$ the kernel configuration of the adsorptive complex O-Al_4O_6 has a unique symmetry - a plane transiting through formed bond O ... Al and corresponding bond Al - O in Al_4O_6 cluster, i.e. the complex is characterized by C_S symmetry (see Fig.2). The additional examinations executed at $\varphi = 60$, have shown, that downturn of symmetry does not change interaction potential energy of atom O(^{3}P) with Al_4O_6. The highest position of curve $U(R)$ at $\varphi = 60$, $\theta = 60$ among curves on the Fig.3 can be explained by mutual repulsion between an adsorbed oxygen atom and oxygen atom of cluster Al_4O_6 due to their convergence in a symmetry plane of Al_4O_6 complex.

As a result of the executed calculations it was obtained that PES is periodical through φ with period 120^o (Fig.4). At the attack angle $\theta = 30$ the angular dependence has slowly expressed character (Fig.4a), whereas at $\theta = 60$ PES angular dependence becomes more essential(Fig.4b).

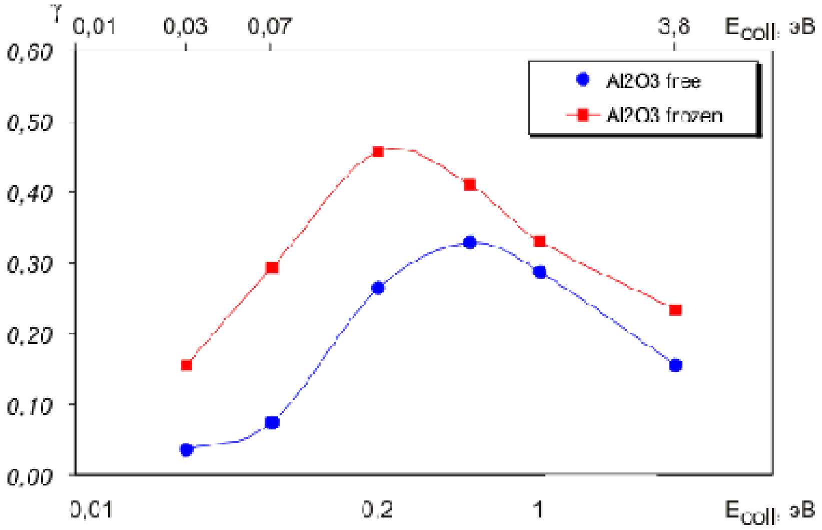


Fig. 5. Coefficients of heterogeneous recombination of oxygen atoms on Al_2O_3 surface calculated for collinear arrangement of atoms ($\theta = 0$), with the account (Al_2O_3 free) and without the account (Al_2O_3 frozen) an internal relaxation of Al_4O_6 cluster.

The represented PES of the oxygen atom adsorption on Al_2O_3 surface was used for further molecular dynamics study of the processes of heterogeneous recombination of oxygen atoms via the Eley-Rideal mechanism [13] $O_{gas} + O_{ad}S \rightarrow O_2 + S$, where O_{ad} is the oxygen ad-atom on the surface S of aluminium oxide, O_{gas} is the gas phase oxygen atom. The probability values of atoms recombination are calculated at different gas and surface temperatures. Their sensitivity to parameters of PES of the O (^{3}P) atom adsorption on Al_2O_3 surface is investigated.

On the Fig.5 the calculations results are represented for coefficient of heterogeneous recombination γ at a collinear arrangement of atoms ($\theta = 0$) for two potential curves, one of which considers internal relaxation Al_4O_6 (phi0.teta0 on Fig.3) - approach of free bonds, and another is received in the assumption of the frozen bonds (frozen 0.0 on Fig.3).

The horizontal axis on the Fig.5 corresponds to relative collision energy E_{coll} which was varied over the range from 0,03 to 3,8 eV. The upper curve on the Fig.5, marked by small squares, corresponds to approach of the frozen bonds, the lower curve marked by circles - to approach of free bonds. As follows from Fig.5, both curves have equal qualitative character of dependencies - area of monotonic increase, maximum, and area of the monotonous decrease, however, their quantitative performances essentially differ. The maximum of recombination probability for approach of the frozen bonds achieves value $\gamma = 0,457$ at $E_{coll} = 0,2$ eV, in approach of free bonds does not exceed value 0,329. The given comparison has shown, that for the correct description of heterogeneous recombination of oxygen atoms on the surface of Al_4O_6 cluster it is necessary to use PES, received with taking into

Fig. 6. Extended cluster model $O(^3P) - Al_8O_{12}$ adsorption of oxygen atom on Al_2O_3 surface account a relaxation of the top surface layers.

Moreover, from the analysis of Fig.3 follows, that potential curves U (R), constructed at different θ and φ with the structural relaxation account, mainly lie between two curves of convergence of O(^{3}P) atom in a normal line direction to a surface ($\theta = 0$), obtained in models of the free and frozen bonds. Therefore for the subsequent description of heterogeneous catalytic processes by methods of molecular dynamics it is necessary to consider not only structural relaxation of surface Al_2O_3, but also angular dependencies of calculated PES.

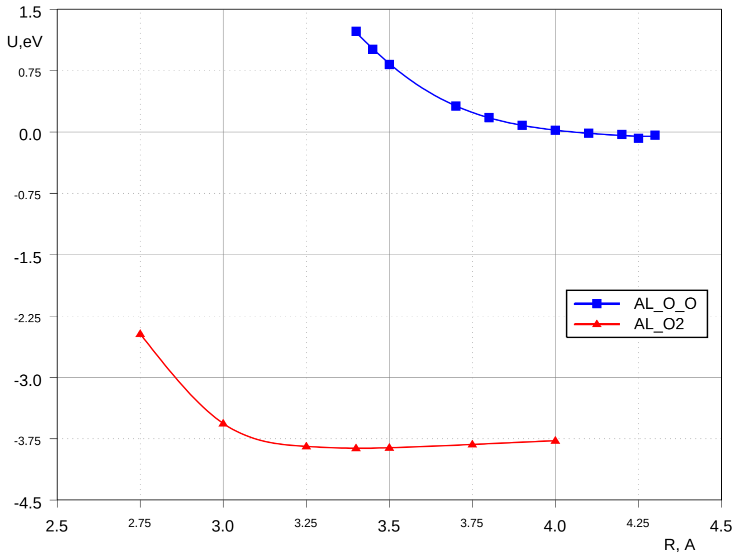


Fig. 7. PES for interaction of Al_4O_6 cluster with oxygen molecule (red curve) and two separated oxygen atoms (blue curve).

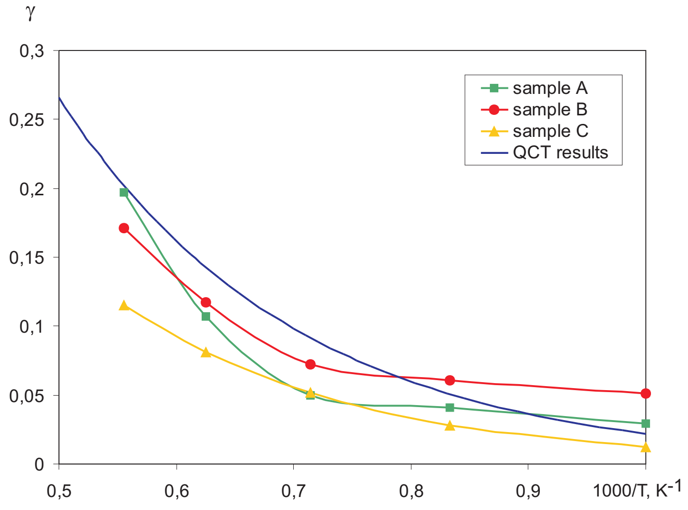


Fig. 8. Coefficient of heterogeneous recombination of oxygen atoms on the Al_2O_3: experimental data (samples A,B,C from [14]) and calculated QCT results.

Accurate definition of PES parametres, answering of adsorption of O (^{3}P) atom on the $\alpha - Al_2O_3$ surface, were performed on the basis of extended cluster model O(^{3}P) $-$ Al_8O_{12} (Fig.6). In approach of the frozen bonds cluster Al_8O_{12} the adsorption energy of O(^{3}P) atom equals 1,24 eV at $\theta = 0$ against the corresponding value 1,17 eV for cluster Al_4O_6. Equilibrium distance R_e equals 1,89Å between upper atom Al of cluster Al_8O_{12} and atom O(^{3}P) against analogous distance R_e = 1,91Å in complex O(^{3}P) - Al_4O_6 (T_d - symmetry) (see minimum on the potential curve marked by rhombus on the Fig.3). Practical agreement of PES parameters allows to hope for their convergence to a size of the cluster modelling surface Al_2O_3. However for final definition of sensitivity of PES parameters to size of cluster models Al_2O_3 it is necessary further calculations with structural relaxation of Al_2O_3 surface within the limits of its extended cluster model Al_8O_{12}

For detailed study of heterogeneous recombination the PES for interaction of Al_4O_6 cluster with oxygen molecule and two separated oxygen atoms (adsorbed and gas-phase) at the different internuclear distances were calculated (Fig.7). Transition from upper curve to bottom describes process of heterogeneous recombination. Available experimental data was taken into account at the calculation of reaction barrier. Comparison of calculated results in the present work with experimental data [14] on coefficient of heterogeneous recombination of oxygen atoms on the Al_2O_3 surface is shown on the Fig.8 for temperature T from 1000 to 2000K.The rather good agreement was obtained for reaction barrier $E_a = 0.43$eV. The maximum difference between calculated and experimental data achieves at the temperature T $\simeq$ 1400 K which can be explained by change of recombination mechanism from Eley-Rideal to Langmuir-Hinshelwood. The authors want to thank the Russian Foundation for Basic Research (projects 01-08-00230) for financial support of this work.

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