Simulation of Oxygen Atom Heterogeneous Recombination on Heat Shield Coatings of Space Vehicles via AB Initio Approach

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Abstract

On the basis of the density functional theory, cluster models of the adsorption of oxygen atoms on heat shield coatings are constructed and the corresponding potential-energy surface is calculated. Quantum mechanical calculations showed that it is necessary to take into account the angular dependences of the potential energy surface and the relaxation of the surface monolayers. Oxygen atom recombination on a SiO_2 or SiC or Al_2O_3 based coatings have been studied in details and all its significant characteristics including recombination and accommodation coefficients, distributions of molecules formed during recombination over vibration and rotational states have been determined. Good agreements between our results and calculations or experimental results of other authors were revealed.

1. Introduction

The design of aerospace vehicles has required the solution of radically new scientific and technological problems. One of the important problems has been to create reusable heat shield materials. 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 differ-ent 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 [2, 3]. 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 other words, we don't know accurately mechanism of heterogeneous catalytic processes and Arrhenius coefficients of elementary surface reactions.

In this context a radical suggestion is to start modeling catalysis from first principles (ab initio calculations) [4], as much as practical or computational complexity will make this approach feasible. Ab initio methods solve the quantum mechanical equations which govern the behavior of a system. The only information which must be provided is 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 Trajectory" software complex [5] 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 (SiO₂ and SiC) in Eley-Rideal reactions were conducted and satisfactory fit with other authors' results and experimental data were obtained [6]. Thus, software complex "MD Trajectory" is rather powerful tool for investigation of chemical reaction by quasi-classical trajec-tory method especially for conditions hardly realized in experiment.

This study is devoted to investigating the heterogeneous recombination of oxygen atoms on an aluminum oxide surface. Within the framework of the semi-classical approach, using the quantum mechanics methods on the basis of the density functional theory [7, 8], we find the potential energy surface (PES) corresponding to interactions of the O (3P) atoms with the cluster that models the α -Al₂O₃ surface and then use this PES in molecular dynamics calculations. The calculated recombination coefficients are in good agreement with experimental data.

2. Eley-Rideal oxygen recombination $O + O_s \rightarrow O_2$ on the Si-based surfaces

At the reentry space vehicles into the Earth atmosphere the key reactions on the surface of thermal protection systems (TPS) are heterogeneous recombination of oxygen and nitrogen atoms. There are many experimental works for investigation of this processes on the different types of silicon-based TPS (silicon carbide, silicone dioxide and etc.) on plasmatron setups. During these experiments the effective integral characteristic $\gamma \cdot \beta$ of investigated processes was measured [2, 10]. Another experimental work on the MESOX setup [11, 12] permits to split these characteristics and to obtain pure coefficient of heterogeneous recombination γ . There are very few theoretical works simulated heterogeneous recombination γ .



Figure 1: Coefficient of heterogeneous atoms recombination (a) and chemical energy accomodation (b) in Eley-Rideal process $O + O_s \rightarrow O_2$.

neous recombination by MD method. In the article [4] the semiclassical MD approach, developed by G. D. Billing [9],

was applied for study of heterogeneous recombination of oxygen atoms on the β -cristobalite. Both Eley-Rideal and Langmuir-Hinshelwood mechanisms were examined, and both coefficients γ and β were calculated. We selected the same investigated system for verification of our software complex "MD Trajectory". In our calculations we considered surface with Si atoms on the top layer and modelled Eley-Rideal recombination mechanism. Surface had dimensions 2x2 unit cells, with periodic boundary layer conditions for simulation of infinite surface. Surface temperature T_s was taken 1000K. PES for investigated system was taken from [4]. On the Fig.1 the main results of these calculations are demonstrated. Comparison between our results (curves, marked by black circles) and results of M.Cacciatore et al. (curves, marked by white squares) revealed satisfactory agreement. As the result of reaction recombination the O₂ molecules were formed in the different vibrational states. It's very important to know what part of energy goes into the internal freedom degrees. During MD calculations vibrational distributions of the formed O₂ molecules were obtained. These distributions have sharply expressed maximum and this maximum shifts to high vibrational states with growth of collision energy.

Another surface where Eley-Rideal oxygen recombination was simulated is silicon carbide. There are many different polytypes of SiC - 3C, 2H, 4H, 6H and etc. In our calculations we modelled 3C-SiC with Si atoms on the top layer. Potential energy surface was taken in many-body Tersoff form [13]. Comparison of calculation results for two types of



Figure 2: Coefficient of heterogeneous atoms recombination (a) and chemical energy accomodation (b). Comparison of QCT calculations results for Eley-Rideal recombination reaction $O + O_s \rightarrow O_2$ on the different type of surfaces.

surfaces are shown on the Fig.2. Recombination coefficient for so called sintered silicon carbide (SSiC) (black square on the Fig.2 was taken from paper [10]. We can see that at low collision energy $E_{coll} < 0.04$ eV recombination process is more effective on the SiC surface than on the SiO₂ one, but at more high energies the situation is reversed. Since $E_{coll} = 1$ eV the value γ becomes almost zero for both surfaces. Surface SiC will be heated more effective due to oxygen recombination than SiO₂ one because chemical energy accommodation coefficient for this surface is higher than last one on the full range of collision energy (see Fig.2b). We can reject data at $E_{coll} = 1$ eV because there are very few trajectories to lead to recombination and there is very large statistical uncertainty.

3. Simulation of Oxygen Atom Heterogeneous Recombination on Al₂O₃

3.1 PES calculation methodology

The potential energy surface corresponding to the orientationally interaction dependence of the $O({}^{3}P)$ atom with the Al₄O₆ cluster modeling the α – Al₂O₃ crystal surface is calculated using the GAUSSIAN98 computer code [14]. Molecular constants of O₂, AlO and Al₂ molecules in the ground electronic state calculated by the B3LYP method with various basis sets are represented in the Table 3.1. Experimental data are also included here for comparative analysis with the results obtained [15].

As we can see from this table, parameters of the pairwise interactions of O and Al atoms are well reproduced by valence-split basis Pople 6-31G* [16]. This basis consists of combined basis functions $[4s_3p_1d]_{Al} + [3s_2p_1d]_O$ (the quantity of basis functions of each type on the atomic centers of the molecules is indicated in square brackets).

In the description of valence electrons, the basis $6-31G^*$ matches the two-exponential basis (two basis functions per atomic orbital (AO)) with the inclusion of the external polarisation *d*-type functions on O and Al atoms. AO

	Molecules									
Basis	$O_2 (^3\Sigma_g^-)$			$AlO(^{2}\Sigma^{+})$			$\operatorname{Al}_2({}^3\Sigma_g^-)$			
sets	Properties									
	R, Å	ω_e ,	D ₀ ,	R, Å	ω_e ,	D ₀ ,	R, Å	ω_e ,	D ₀ ,	
		cm ⁻¹	eV		cm ⁻¹	eV		cm ⁻¹	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	$5,27\pm0,04$	2,47	350	1,55	

Table 1: Properties of O₂, AlO and Al₂ molecules in the ground electronic state (including bond length (*R*), harmonic vibrational frequency (ω_e), dissociation energy (D_0)) calculated by B3LYP method with various basis sets.

of the each core electron is presented by one basis function. The basis set $6-31G^*$ possesses more completeness in comparison with basis sets 6-31G and 6-31+G, which do not include the polarisation *d*-functions. From Table 1 it follows the equilibrium internuclear distances, calculated with the $6-31G^*$ basis set differ from the experimental values by no more, than on 0.04 Å, and the harmonic vibrational frequencies agree with their experimental values within 8%. The mean error for the dissociation energy in the AlO molecule is calculated with the basis set $6-31G^*$ to be 0.3 eV. This error can be reduced to 0.2 eV, by adding to basis set $6-31G^*$ one diffusive function of s- and p- types per each atomic centers, i.e. transforming to the basis set $6-31+G^*$.

The difference in 0.1 eV is observed also for the adsorption energy of the $O({}^{3}P)-Al_4O_6$ complex ($C_{3\nu}$ - symmetry) with the use of basis sets 6-31G* and 6-31+G* (Tab.2). However the increase in computer time to achieve a more accurate PES is about a factor of two because the number of basis functions for the O-Al_4O_6 system increases from 181 to 225. Therefore in all our PES calculations of oxygen interaction with Al_4O_6 cluster the Pople 6-31G* basis set has been chosen as the optimum tradeoff between the accuracy of the PES description and computer time expenses.

Table 2: Equilibrium geometric parameters and adsorption energy (E_{ads}) of complex O (³P) - Al₄O₆ (C_{3v} - symmetry) (fig. 1 see) calculated with different basis sets using B3LYP method. The corresponding parameters for Al₄O₆ (T_d -symmetry) are shown in the brackets.

Durantian	Basis set						
Properties	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}, eV	1,83	1,75	1,79	1,67			

3.2 Results and Discussions

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

In our case the crystal surface $\alpha - Al_2O_3$ was modelled by an Al_4O_6 cluster reproducing a stoichiometry of a crystal and a valent state of surface Al atoms. The positions of oxygen atoms in the bottom plane of the Al_4O_6 cluster were fixed when modelling the adsorption of an oxygen atom on the Al_2O_3 surface.



Fig. 3: Cluster model of adsorption of oxygen atom on Al_2O_3 surface (a) and extended cluster model $O(^3P) - Al_8O_{12}$ (b).

The positions of the remaining atoms were optimized at the given R, θ and φ coordinates of adsorbed atom O (³P) (Fig.3a). Such a model takes account the relaxation caused by the interaction of the surface monolayers with the adsorbate. Our calculations show the importance of the structural relaxation processes for surface atoms. As the O (³P) atom approaches the surface up to the equilibrium distance R_e = 1.77Å in the normal direction ($\theta = 0^{\circ}$) (Fig.4), the distance between the upper planes of O and Al atoms (Fig.3a) increases more than 70% and the relaxation energy contribution to the adsorption energy, E_a = 1.8 eV, is 30% compared with the model that does not take into account the relaxation of structure parameters (upper curve in Fig.4). Similar effects of structural relaxation for an Al₂O₃ surface were revealed during the study of the H₂O [17, 18] and O₂ [18] molecular adsorption on this surface. Note that according to Ref. [18] the adsorption energy of molecular oxygen on an Al₂O₃ surface is 0.6 eV at an equilibrium



Fig. 4: Potential energy curves U(R) corresponding to interaction of atomic oxygen O (³P) with the Al₄O₆ cluster. R is the distance between O (³P) atom and Al atom lying on surface of solid Al₂O₃ during the O (³P) atom approach the surface in different directions determined by θ and φ angles. Symbols R, θ and φ are given in Fig.3a

distance 1.98Å from the lower O atom in the O₂ molecule.

As follows from Fig. 4, the potential energy curves for different orientations of the O (³P) atom with the Al₄O₆ cluster have a smooth and binding character that signifies the absence of activation barriers in the process of atomic oxygen adsorption on an Al₂O₃ surface. As the angle θ of the O (³P) atom attack of Al₂O₃ surface increases, the depth of the adsorption minimum in the PES decreases while the equilibrium distance R_e increases.

At $\theta = 30^{\circ}$ with increasing φ there is an interaction energy stabilization in the O (³P) - Al₄O₆ system whereas at $\theta = 60^{\circ}$ the opposite trend in the behavior of the potential curves occurs. Both at $\varphi = 0^{\circ}$ and 60° the kernel configuration of the adsorptive complex O-Al₄O₆ has a unique symmetry - a plane passing through the O ... Al bond formed and the corresponding Al - O bond in the Al₄O₆ cluster, i.e. the complex is characterized by C_S symmetry (see Fig.3). The additional cases at $\varphi = 60^{\circ}$ show that the downturn of symmetry does not change the interaction potential energy of O(³P) with Al₄O₆. The highest energy of the curve U(R) at $\varphi = 60^{\circ}$, $\theta = 60^{\circ}$ on the Fig. 4 can be explained by the mutual repulsion between an adsorbed oxygen atom and oxygen atom of the Al₄O₆ cluster due to their approach in the symmetry plane of the Al₄O₆ complex.



Fig. 5: PES of oxygen atom interaction with Al₄O₆ cluster in co-ordinates R and φ at $\theta = 30^{\circ}(a)$, and $\theta = 60^{\circ}(b)$

Moreover, from the analysis of Fig. 4 it follows that the potential curves U(R) constructed at different θ and φ with the structural relaxation taken into account, mainly lie between the two curves corresponding the O(³P) approach in a normal line direction to a surface ($\theta = 0^{\circ}$), 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 Al₂O₃, but also the angular dependencies of the calculated PES.

As a result of the calculations it was found that PES is periodical in φ with a period of 120° (Fig. 5). At the attack angle of $\theta = 30^\circ$, the angular dependence has slowly expressed character (Fig. 5a), whereas at $\theta = 60^\circ$ PES angular dependence becomes more essential (Fig. 5b).

Accurate definition of the PES parameters, corresponding to the adsorption of O (³P) atom on the α – Al₂O₃ surface, were performed on an extended cluster model O(³P) – Al₈O₁₂ (Fig. 3b). Using an approach that considers the Al₈O₁₂ cluster bonds frozen, the adsorption energy of an O(³P) atom equals 1.24 eV at θ = 0° compared with the corresponding value 1.17 eV for cluster Al₄O₆. The equilibrium distance R_e between the upper atom Al of the Al₈O₁₂ cluster and O(³P) was found to be 1.89Å compared with the analogous distance 1,91Å of R_e in the O(³P) - Al₄O₆ complex (T_d - symmetry) (see the minimum on the potential curve marked by the rhombus symbols in Fig. 4). This good agreement between the PES parameters to the size of the Al₂O₃ cluster model still requires further calculations using structural relaxation of the Al₂O₃ surface with the extended cluster model of Al₈O₁₂.

For molecular dynamics studies of the processes of heterogeneous recombination of oxygen atoms via the Eley-Rideal mechanism

$$O_{gas} + O_{ad}S \to O_2 + S \tag{1}$$

(O_{ad} is the oxygen ad-atom on the surface S of aluminium oxide, O_{gas} is the gas phase oxygen atom) one needs for calculate the PES, curves corresponding to the interaction of the reagents (curves 1 and 4) and products (curves 2 and



Fig. 6: (a)PES for interaction of Al_4O_6 cluster with oxygen molecule and two separated oxygen atoms and (b) Coefficient of heterogeneous recombination of oxygen atoms on the Al_2O_3 : experimental data (samples A,B,C from [19]) and calculated QCT results

3) of reaction (1) without and with structural relaxation of the Al_2O_3 surface, respectively as shown in Fig.6a. The proximity of curves 2 and 3 indicates that the role of the effects of structural relaxation of the Al_2O_3 surface in its interaction with the O_2 molecule is insignificant, whereas taking structural relaxation of the surface into account in describing the reagent interaction in process (1) crucially changes the behavior of the potential curves. The transition from the upper curve 1 to the lower curve 2 describes the process of heterogeneous recombination accounting for the structural relaxation of the Al_2O_3 surface. We note that without the Al_2O_3 surface relaxation, the interaction $O_{gas}+O_{ads}$ does not have a barrier (curve 4), whereas, with relaxation of the surface monolayers reaction (1) displays an activation barrier (curve 1). Note that curve 1 has a deeper minimum than the lower curve 4 in Fig.4 as compared with the minimum of curve 3 which does not account for the relaxation of the structural parameters. The calculations showed that the barrier of reaction E_a can be taken as the value 0.43 eV (curve 5).

The calculated PES was used for further molecular dynamics studies of reaction (1). The probability values of atomic recombination, γ , on the Al₂O₃ surface are calculated at different gas and surface temperatures and shown in Fig.6b (curves 1 and 2). Since it is assumed that the cluster is frozen, the calculated γ values (curve 1) are substantially higher than the experimental data obtained in [19] (curves 3, 4, and 5) with a difference of up to an order of magnitude. The recombination probabilities taking into account the structural relaxation of the Al₄O₆ cluster (curve 2) are in good agreement with the experimental data over a wide surface temperature range (from 1000 to 2000K).

4. Conclusion

An efficient method of investigating the processes of interaction between gas mixtures and catalytic surfaces is developed within the framework of classical molecular dynamics and quantum mechanics. Oxygen atom recombination on a SiO₂ and SiC based coatings have been studied in details and all its significant characteristics including recombination and accommodation coefficients, distributions of molecules formed during recombination over vibration and rotational states have been determined. Good agreements between our results and calculations or experimental results of other authors were revealed.

On the basis of quantum-mechanical calculations, the potential energy surface of the crystal represented aluminum oxide surface is found and its characteristics, including the dependence on atom relaxation in the crystal lattice, are studied. The data obtained were used in the molecular dynamics simulation of heterogeneous oxygen atom recombination on an Al_2O_3 surface. It was revealed that for the correct description of heterogeneous recombination of oxygen atoms on the surface of an Al_4O_6 cluster it is necessary to use a PES, obtained that takes into account the relaxation of the top surface layers. For a surface temperature range of 1000 to 2000 K the calculated recombination probabilities were found to be in good agreement with experimental data.

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