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INVESTIGATION OF HETEROGENEOUS RECOMBINATION OF OXYGEN ATOMS ON THE SI-BASED SURFACES

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Abstract. Using molecular dynamics approach the elementary catalytic heterogeneous reactions on SiO₂ or SiC based coatings can be studied in details and all its significant characteristics including both γ and β coefficients, distributions of molecules formed during recombination over vibrational and rotational states can be determined. Good agreement between our results and calculations or experimental results of other authors were revealed.

1. 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 fifties¹ 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 processes 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. In fact, the available ab initio tools are still too limited, therefore if we are willing to use them in investigating and understanding catalytic recombination, the main effort should focus on developing new tools.

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. 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.

2. Classical molecular dynamics

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

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

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.

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

$$\begin{aligned} \dot{\gamma}_i &= \frac{P_{i\gamma}}{M_i} \\ \dot{\gamma}_k &= \frac{P_{k\gamma}}{M_k} \\ \dot{P}_{i\gamma} &= -\frac{\partial H}{\partial \gamma_i} = -\sum_{j \neq i} \frac{\partial V_{11}}{\partial R_{ij}} \frac{\partial R_{ij}}{\partial \gamma_i} - \sum_k \frac{\partial V_{12}}{\partial R_{ik}} \frac{\partial R_{ik}}{\partial \gamma_i} \\ \dot{P}_{k\gamma} &= -\frac{\partial H}{\partial \gamma_k} = -\sum_{l \neq k} \frac{\partial V_{22}}{\partial R_{kl}} \frac{\partial R_{kl}}{\partial \gamma_k} - \sum_i \frac{\partial V_{12}}{\partial R_{ik}} \frac{\partial R_{ik}}{\partial \gamma_k} \end{aligned} \quad (2)$$

where

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

and

$$\frac{\partial R_{ij}}{\partial \gamma_i} = -\frac{\partial R_{ij}}{\partial \gamma_j} = \frac{\gamma_i - \gamma_j}{R_{ij}} \quad (4)$$

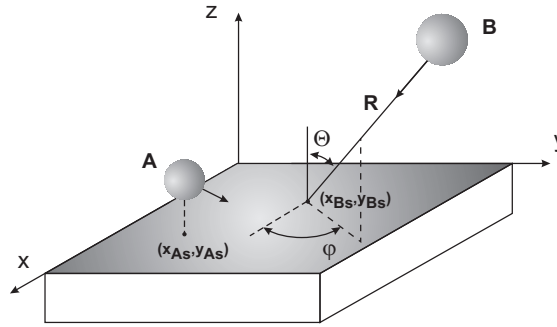


Figure 1: Collision scheme of Eley-Rideal recombination process

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, and gas phase atom B is represented. For this process initial conditions can be written as:

- For incident gas atom B

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

and

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

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

$$\begin{aligned}
 R_{k\gamma} &= R_{k\gamma}^0 + \sqrt{2kT_s/F_k} \cos(\varphi_{k\gamma}^0) \\
 P_{k\gamma} &= \sqrt{2M_k k T_s} \sin(\varphi_{k\gamma}^0)
 \end{aligned}$$

where $R_{k\gamma}^0$ – equilibrium position, F_k – force constant for k-th atom, $\varphi_{k\gamma}^0$ – 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 ν and rotational j numbers can be determined using special iteration procedure, more details can be given in.^{3,4}

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.

3. 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.^{2,5} Another experimental work on the MESOX setup^{6,7} permits to split these characteristics and to obtain pure coefficient of heterogeneous recombination γ .

There are very few theoretical works simulated heterogeneous recombination by MD method. In the article⁸ the semiclassical MD approach, developed by G. D. Billing,³ 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 veri-

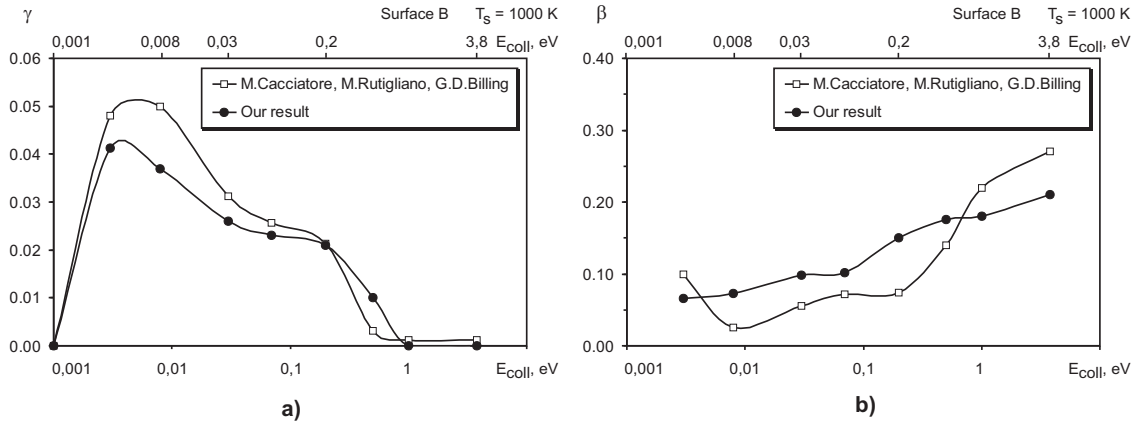


Figure 2: Eley-Rideal process $O + O_s \rightarrow O_2$. a) Coefficient of heterogeneous atoms recombination and b) Chemical energy accomodation coefficient

fication 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. Potential energy surface (PES) for investigated system was taken from.⁸

On the Fig.2 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 re-

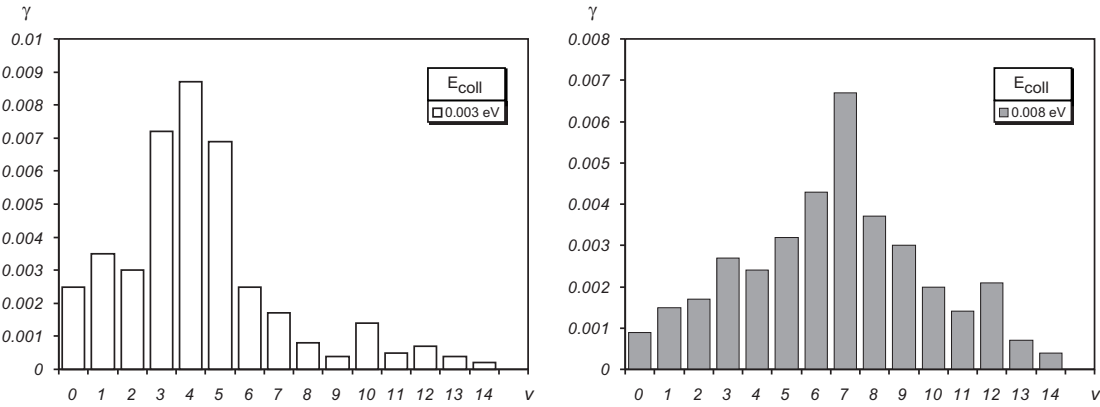


Figure 3: Vibrational distribution of the formed O_2 molecules in the Eley-Rideal recombination reaction on the β -cristobalite at the different collision energy E_{coll}

combination the O_2 molecules were formed in the different vibrational states. It’s very important to know what part of energy goes into the internal freedom degrees. On the Fig.3 vibrational distributions of the formed O_2 molecules are demonstrated for two collision energies $E_{coll}= 0.003\text{eV}$ and 0.008 eV where reaction probabilities are maximum. We can see that both of 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.¹⁰ Comparison of calculation results for two types of

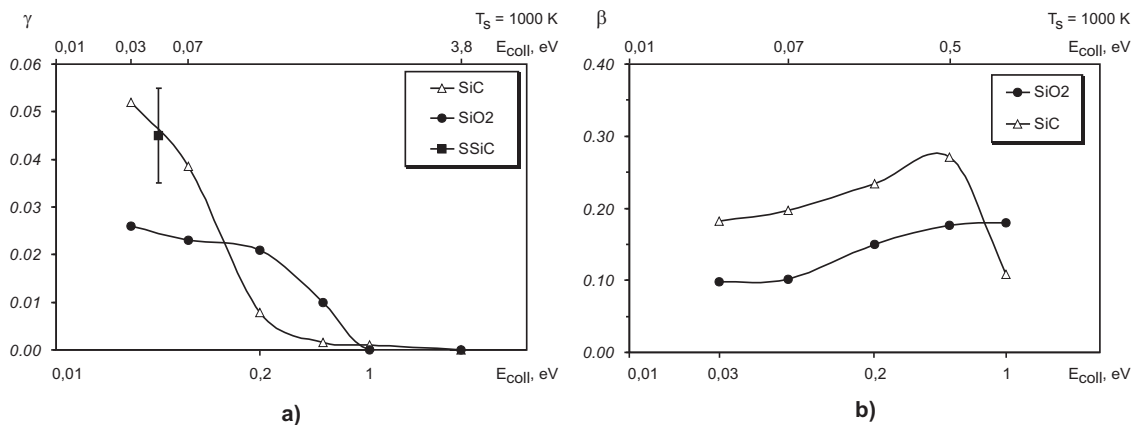


Figure 4: Comparison of QCT calculations results for Eley-Rideal recombination reaction $O + O_s \rightarrow O_2$ on the different type of surfaces. a) Coefficient of heterogeneous atoms recombination and b) Chemical energy accomodation coefficient

surfaces are shown on the Fig.4. Recombination coefficient for so called sintered silicon carbide (SSiC) (black square on the Fig.4a) was taken from paper.⁵ 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.4b). 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.

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