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Eley–Rideal reaction dynamics between O atoms on β-cristobalite (1 0 0) surface: A new interpolated potential energy surface and classical trajectory study

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ABSTRACT

We present a theoretical study of the collisions of atomic oxygen with O-precovered β-cristobalite (1 0 0) surface. We have constructed a multidimensional potential energy surface for the O_2/β-cristobalite (1 0 0) system based mainly on a dense grid of density functional theory points by using the interpolation corrugation-reducing procedure. Classical trajectories have been computed for quasithermal (100–1500 K) and state-specific (e.g., collision energies between 0.01 and 4 eV) conditions of reactants for different O incident angles (θ_v). Atomic sticking and $O_{2(\mathrm{adsorbed})}$ formation are the main processes, although atomic reflection and Eley–Rideal (ER) reaction (i.e., O_2 gas) are also significant, depending their reaction probabilities on the O incident angle. ER reaction is enhanced by temperature increase, with an activation energy derived from the atomic recombination coefficient ($\gamma_O(\theta_v = 0°, T)$) equal to 0.24 ± 0.02 eV within the 500–1500 K range, in close agreement with experimental data. Calculated $\gamma_O(\theta_v = 0°, T)$ values compare quite well with available experimental $\gamma_O(T)$ although a more accurate calculation is proposed. Chemical energy accommodation coefficient $\beta_O(T)$ is also discussed as a function of ER and other competitive contributions.

1. Introduction

Surface reactions contribute considerably to spacecraft heating during hypersonic re-entry into planetary atmospheres [1]. In the case of Earth atmosphere, atomic recombination processes involving oxygen and nitrogen in the boundary layer are catalyzed by the materials used as thermal protection systems (TPS) of these vehicles. The apparent simple elementary heterogeneous processes that occur in these conditions are difficult to study either experimentally or theoretically, even at present [2]. Along a typical re-entry trajectory the density of air changes by several orders of magnitude. Thus, there is a free molecular to continuum regime change and a laminar to turbulent flow transition. Moreover, different thermal and chemical equilibrium/non-equilibrium situations are observed at several points of the re-entry trajectory. These complex real conditions cannot be well reproduced even in sophisticated wind tunnel facilities (e.g., Von Karman Institute For Fluid Dynamics, Belgium). On the other hand, real flights (e.g., Shuttle or forthcoming EXPERT European Project [3]) can report only limited information. Standard computer fluid dynamics (CFD) simulations [2] carried out for this kind of flights give values of the aerodynamic heating with a factor two or more larger depending if a non-catalytic or a fully-catalytic model is assumed for the principal surface reactions. In these simulations two important type of coefficients are needed: (a) the atomic recombination coefficient γ_i (also called catalycity) and (b) the chemical energy accommodation coefficient β_i [4]. γ_i is defined as the probability of atomic recombination per atomic surface collision for each i species and β_i represents the amount of energy released to the TPS surface respect the maximum energy transferable per atomic recombination ($0 \leqslant \gamma_i, \beta_i \leqslant 1$). These coefficients depend on temperature and total and partial pressures (i.e., $\gamma_i(T,P)$). Hence, precise thermal or state-specific theoretical and/or experimental γ_i and β_i coefficients are necessary to simulate these severe equilibrium/non-equilibrium conditions and to improve the design of better TPSs. TPS materials should have high emissivity (to maximize the amount of energy reradiated), low surface catalycity (to minimize convective heating) and low thermal conductivity (to minimize the mass of material required to insulate the primary structure).

A common material used in Shuttle TPS coatings is the reaction-cured glass (RCG), a borosilicate composed by 94% of SiO_2, 4% of B_2O_3 and 2% of SiB_4. Thus, we decided to study several collision processes involving O and O_2 over silica, considering a crystalline structure, which simplifies initially the theoretical approach. Moreover, the selected structure, β-cristobalite , is the most stable polymorph at high temperatures up to the melting point of 1983 K, with very similar properties to amorphous silica (e.g., density, refractive index, band structure, etc.). We have carried out a first-principles theoretical study on several elementary processes

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involving these species. In an earlier study [5] we made a full density functional theory study (DFT) of the atomic oxygen and nitrogen interaction with a β-cristobalite (1 0 0) surface, because atomic adsorption is the first basic step for a subsequent atomic recombination reaction through an Eley–Rideal (ER), hot atom (HA) or Langmuir–Hinshelwood (LH) mechanism. We observed a large oxygen chemisorption, mainly on top a Si of the Si-ended face, which had a great influence in the atomic oxygen scattering, causing a predominant adsorption or penetration (absorption) into the SiO_2 slab [6]. In two more recent studies [7,8] we presented a dynamics study of O_2 scattering on a β-cristobalite (1 0 0) surface, which showed that reflection and sticking (absorption/adsorption) were the main processes, becoming the dissociative sticking only open at high collision energies (i.e., $E_i > 1$ eV). We have also recently reported a preliminary study on the oxygen ER reaction over β-cristobalite (1 0 0) surface [8] using the same PES and considering several state-specific initial conditions of the reactants.

There are several experimental studies about the ER oxygen recombination reaction over some silica surfaces (quartz, cristobalite, RCG, vitreosil, etc.) mainly concerned in the determination of γ and effective γ (i.e., $\gamma_{\text{eff}} = \gamma' = \gamma \cdot \beta$) coefficients (e.g., see a recent review [9]) at high temperatures (400–1800 K). These coefficients show marked temperature dependence, which increase with temperature until a critical value where the thermal desorption becomes important and then the recombination coefficient decreases. Therefore, the oxygen ER reaction over silica seems to be an activated process (e.g., $E_a = 0.29$ eV on β-cristobalite for $800 \leqslant T_s \leqslant 1830$ K or $E_a = 0.16$ eV on quartz for $850 \leqslant T_s \leqslant 1430$ K [10]. The nature of the silica material has as well a great influence on these coefficients. Only a few experimental studies have reported information on the chemical energy accommodation coefficient for oxygen over silica, indicating a strong variation with the temperature (e.g., $0.12 \leqslant \beta \leqslant 0.69$ within 1770–966 K for β-cristobalite [11]) contrary to the common assumption made in the major part of experimental γ' measurements [9], where a constant value equal to 1 is supposed.

There are scarce first principles theoretical studies on oxygen ER reactions over silica surfaces. A previous work [12] presented a semiclassical trajectory study for atomic oxygen recombination over β-cristobalite although they used a tentative empirical PES, not fully justified nor analysed. More recently, the same authors have published a very similar theoretical study over quartz [13], showing similar results as for β-cristobalite , although with a γ about three times lower.

In the current work, we present some additional DFT calculations for O_2/β-cristobalite system and we explain the construction and the properties of the new interpolated PES for this system, than can be used for both the study of molecular oxygen collisions on clean β-cristobalite (1 0 0) and for atomic oxygen collisions with O atoms preadsorbed (i.e., $O_{(ad)}$) onto the same solid surface. The dynamics of the second kind of process is studied for reactants at state-specific or thermal conditions by using classical trajectories and they are compared with available experimental data.

The present results together with our previous data on these elementary processes (i.e., atomic adsorption, molecular dissociative adsorption, etc.) involving air species and β-cristobalite are planned to be used in some kinetic models and kinetic Monte Carlo simulations to determine appropriately the γ and β coefficients as a function of partial and total pressures and temperatures.

2. Potential energy surface

2.1. Density functional theory calculations

We have performed extensive DFT calculations for the O_2/β-cristobalite (1 0 0) systems in order to construct a multidimensional PES for the present system, using as well previous DFT data from the O/β-cristobalite (1 0 0) [5,6] studies. The energetic calculations have been carried out by using the VASP code [14–17] to determine the O_2 and the $O/O_{(ad)}$ interactions over an Fdd2 β-cristobalite (1 0 0) surface [18,19]. We have used a similar procedure as for the previous O/β-cristobalite (1 0 0) studies [5,6]. Thus, a lattice parameter of 7.348 Å, determined for the bulk Fdd2 calculation, was used in the present work along with a slab model with six layers, ended with a silicon first layer. An extra hydrogen bottom layer was added to saturate the O dangling bonds of the inner layer. The distance between slabs (z = 17–18 Å) was large enough to prevent significant interactions between them. We carried out generalized gradient correction DFT calculations with the Perdew-Wang 91 functional (PW91). The electron–ion interactions were described by using the projector-augmented-wave technique. An energy cut-off of 400 eV for the plane wave basis set was precise enough to obtain converged properties. Integration over the Brillouin zone was made by means of a $3 \times 3 \times 1k$-points mesh by using the Monkhorst–Pack method. Spin-polarized calculations with a fixed magnetization equal to 0, 2 or 4 were carried out to consider the total possible atomic and molecular spin states (i.e., singlet, triplet or quintuplet). The final interpolated PES (see next section) will use the lowest energy for each geometry (basically singlet at short distances and triplet for longer ones), allowing the interpolation method a smoothing of the conflicting crossing regions. Thus, we assume that the evolution of the system is electronically adiabatic, which requires at least one transition between states of different spin, in the same way as for the O/β-cristobalite PES [6].

In order to make easier the search of stationary points we have considered two approaches: (a) direct DFT calculations with geometry optimization and normal mode analysis and (b) interpolation of a grid of DFT energies calculated for both parallel ($\theta = 0°$) and perpendicular ($\theta = 90°$, $\phi = 90°$ O_2 configurations over the central Si site of the unit cell (see next section); θ and φ are the polar and azimuthal angles of the molecular axis as shown in Fig. 1a. The O_2 distance (r) and the Z-coordinate of O_2 centre of mass (Z_{CM}) were changed for $1 \leqslant Z_{CM} \leqslant 4$ Å and $1 \leqslant r \leqslant 3.2$ Å (175 points), and $0.5 \leqslant Z_{CM} \leqslant 4$ Å and $1 \leqslant r \leqslant 4$ Å (216 points), respectively, with the slab geometry fixed at its most stable equilibrium configuration in absence of O_2.

We have calculated a minimum energy path for the Eley–Rideal reaction (i.e., from $O + O_{ad(\text{on top Si})}$ to $O_2(g)$) by means of the Nudged Elastic Band method (NEB) [20,21], where the four first layers of the slab have been relaxed. It is found a transition state (TS) geometry, which implies a significant reconstruction of the first layer, with the following oxygen final geometry: $X_{CM} = 5.432$ Å, $Y_{CM} = 5.472$ Å, $Z_{CM} = 3.306$ Å, $r = 1.287$ Å, $\theta = 2.7°$ and $\phi = 89.4°$. It corresponds to a triplet state and it has only one small imaginary vibrational frequency. We calculate an energy barrier $\Delta E^{\neq} = 0.78$ eV.

However, DFT calculations show the existence of two close O adsorption minima over the Si atom of the first layer, T1 (on top, $d_{OSi} = 1.525$ Å) or T1′ ($Z_O = 0.21$ Å, $d_{OSi} = 1.559$ Å and $\theta = 77.1°$). Thus, two energy barriers for the ER reaction can be derived, 0.28 eV respect T1 and 0.78 eV respect T1′, because T1′ is more stable than T1. It was impossible to ascertain if ER TS connected with T1 or T1′. Therefore, we assumed that initially T1 would be more accessible than T1′ when O gas approaches to the surface (moreover the O diffusion T1 → T1′ needs at least 0.16 eV [6]). Thus, the smaller energy barrier for ER reaction would be 0.28 eV ($\Delta E_0^{\neq} = 0.33$ eV including zero point vibrational energy), which is very close to the before mentioned experimental activation energy ($E_a = 0.28$ eV [10] derived from γ coefficient. Nevertheless, as it will be latter discussed, γ coefficient can include also contributions of another elementary heterogeneous processes (e.g., atomic adsorption, LH reaction, etc.). On the other hand, the ER process seems to be either thermo-neutral (for $O_{(ad)}$ on T1 site $\Delta E = -0.06$ eV) or