

Multiscale Analysis for Atomic Oxygen Recombination on Silica Surface

S. Shiozaki, Y. Sakiyama, S. Takagi and Y. Matsumoto

*Department of Mechanical Engineering, The University of Tokyo
7-3-1, Hongo, Bunkyo-ku, Tokyo, 113-8656, Japan*

Abstract. Many studies have been reported about the catalytic recombination of oxygen and nitrogen on silicon dioxide surface, which is quite important for the reentry of a space vehicle. But, the reaction mechanism is not fully understood. Hence, in this study, we are constructing a catalytic reaction model using the *ab initio* calculations and the Monte Carlo calculations in order to reveal the reaction mechanism. First, desorption and surface migration of oxygen atoms on the α -quartz (0001) reconstructed surface was investigated using density functional theory and transition state theory. Then simple lattice model of silica surface was constructed and kinetic Monte Carlo calculation was performed. The computational result was in good agreement with the experimental data, and Langmuir-Hinshelwood recombination mechanism was dominant at the temperature from 600 to 1100 K.

Keywords: Density Functional Theory, kinetic Monte Carlo, Transition State Theory, Reentry, Silica, Catalytic reaction
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INTRODUCTION

It is well known that the catalytic reaction plays a crucial role in the aerodynamic heating of a spacecraft reentering the atmosphere. Since experimental data is limited due to the extreme environmental conditions, numerical modeling is quite effective to understand the reaction mechanism. In general, there are two important processes for the catalytic reaction as shown in Fig.1: the Eley-Rideal (E-R) mechanism and the Langmuir-Hinshelwood (L-H) mechanism. The former is the reaction between gaseous atoms and adsorbed atoms while the latter involves two adsorbed atoms on the surface. Kurotaki has reported a catalytic model including both of them [1]. However, the model has many unknown parameters to be determined from experimental data such as adsorption energy, energetic barrier for surface migration and recombination and so on. There is no reliable data for these parameters obtained from both experiment and numerical simulation. In this study, we are constructing a catalytic reaction model based on the multiscale approach that connects various phenomena in different time/spatial scales by constructing physical models among the scales [2]. In this report, we focus on the catalytic reaction of oxygen atom on silica α -quartz (0001) reconstructed surface. First, energetic barriers were obtained from the density functional theory (DFT) calculations. These parameters are incorporated in the kinetic Monte Carlo (kMC) calculation as well as other parameters calculated by the transition state theory (TST) and estimated from literatures. Then, the temperature dependence of the catalytic efficiency and the reaction mechanism were investigated by the kMC simulation.

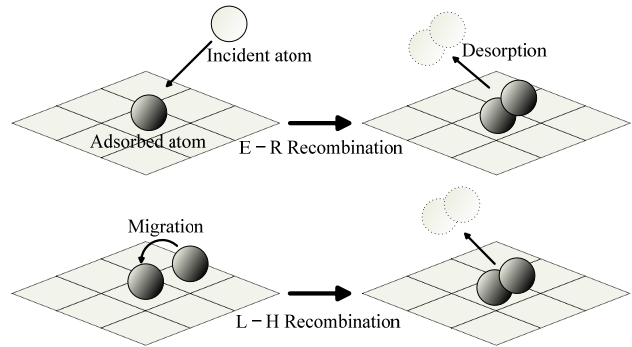


FIGURE 1. Schematic representation of E-R and L-H recombination. White squares stand for adsorption sites. White species are gaseous and grey species are adsorbed

NUMERICAL METHOD

DFT

The DFT calculations were performed with the gradient corrected periodic plane-wave using the Vienna ab initio software package (VASP)[3] to calculate the adsorption energies and energetic barriers for surface migration of adsorbed atoms. The projector augmented wave generalized gradient approximation (PAW-GGA)[4] was used to describe exchange and correlation energies. The electron-ion interactions were described using ultrasoft pseudopotentials with a cut off energy of 600 eV. The silica surface was described by a periodic supercell, which was comprised of three atomic layers along with a 15 Å vacuum layer. An additional fourth layer, which consists of hydrogen atoms, was added to terminate the dangling bonds of oxygen atoms and to make the slab charge natural. The adsorption energy E_{ad} of a single oxygen atom is evaluated as

$$E_{ad} = E_{slab} + E_{atom} - E_{total} \quad (1),$$

where E_{total} is the total energy of the unit cell containing the adsorbed atom in its equilibrium position on the silica surface and E_{slab} is the energy for the relaxed slab and E_{atom} is for the oxygen atom in vacuum. The Hessian matrix and its corresponding harmonic vibrational frequencies for the adsorbed atom were calculated keeping the slab structure fixed.

kMC

The kMC simulation [5] was performed in order to obtain statistical mechanics, which provides steady state catalytic process by considering all elementary events in atomic scale such as adsorption, desorption and surface migration. These events are determined stochastically with a probability that depends on the transition rates of the individual events at each site. Associated with each site i , three transition rates are considered: r_i^{ad} , r_i^{des} and r_i^{mig} corresponding to the probability per unit time of adsorption, desorption and surface migration, respectively. The kMC algorithm effectively simulates stochastic processes described by a Poisson distribution. The time interval between successive events Δt is given by the relation:

$$\rho_1 = \exp(-R_{total}\Delta t), \quad R_{total} = \sum_i (r_i^{ad} + r_i^{des} + r_i^{mig}) \quad (2),$$

where ρ_1 is a random number uniformly distributed between 0 and 1.

The transition rate for adsorption of atoms onto a free site i depends on the number of incident atoms per unit time and sticking coefficient S_i .

$$r_i^{ad} = S_i \frac{pA_i}{\sqrt{2\pi mk_B T}} \quad (3),$$

where p , A_i , m , k_B and T are the partial pressure of incident atom, area of site i , mass of atom, the Boltzmann constant and gas temperature, respectively.

The transition rate for desorption is determined using the TST

$$r_i^{des} = P_{des} \frac{q_i^{TS}}{q_i} \left(\frac{k_B T}{h} \right) \exp\left(-\frac{E_{ad}}{k_B T} \right) \quad (4),$$

where P_{des} is catch-all factor, q_i and q_i^{TS} are the partition function of the adsorption complex and activated adsorption complex. Assuming that the partition function of the adsorption complex can be factorized into a contribution from the surface and the adsorbed atom, equation (4) is written as follows [6]

$$r_i^{des} = P_{des} \left[\frac{1 - \exp(-\nu_{\perp} h / k_B T)}{\exp(-\nu_{\perp} h / 2k_B T)} \right] \left(\frac{k_B T}{h} \right) \exp\left(-\frac{E_{ad}}{k_B T} \right) \quad (5),$$

where ν_{\perp} is the perpendicular vibrational frequency of the adsorbed atom.

The surface migration process of adsorbed atoms from site i to nearest neighbor site can be also treated with TST like desorption process

$$r_i^{mig} = P_{mig} \left[\prod_{i=1}^3 \frac{\exp(-\nu_i^{TS} h / 2k_B T)}{1 - \exp(-\nu_i^{TS} h / k_B T)} \right] \left(\frac{k_B T}{h} \right) \exp\left(-\frac{E_{mig}}{k_B T}\right) \quad (6),$$

where E_{mig} is the energetic barrier for surface migration, ν_i and ν_i^{TS} are the vibrational frequencies of adsorbed atom and surface migrating atom at transition state.

The recombination probability R was given as follows

$$R_{ER} = P_{ER} \exp\left(-\frac{E_{ER}}{k_B T}\right), \quad R_{LH} = P_{LH} \exp\left(-\frac{E_{LH}}{k_B T}\right) \quad (7),$$

where P_{ER} and P_{LH} are the steric factor and E_{ER} and E_{LH} are the energetic barrier, respectively.

RESULTS AND DISCUSSIONS

DFT

In-plane lattice constant of α -quartz bulk structure was 5.03 Å in our DFT calculation, which is in good agreement with the experimental value of 4.91 Å [7]. The silica surface model used in this study is a slab with a hexagonal unit cell that contains one silicon layer and two oxygen layers as illustrated in Fig.2, which was the same model with Qisheng et al.[8] in their DFT study on transition-metal interaction with a silica surface. The structure corresponds to the reconstructed (0001) surface of α -quartz called “dense surface”, which was investigated from classical or first principle molecular dynamics simulation [9][10]. Four possible adsorption sites were considered as shown in Fig.2: T for the top site, B for the bridge site, H for the 3-fold site without a silicon atom underneath and H1 for the 3-fold site with a silicon atom underneath. For simplicity, only adsorbed oxygen was relaxed in the geometry optimization. Adsorption energy and vibrational frequency calculated on these adsorption sites are summarized in Table 1.

The minimum energy path (MEP) and energetic barrier for surface migration from site T to another site T was calculated using climbing image Nudged Elastic Band method (cNEB) [11]. Energetic barrier of surface migration and vibrational frequencies at transition state are shown in Table 2. The potential energy curve along the MEP is shown in Fig.3.

Transition rate for desorption and surface migration calculated from equation (5) and (6) are shown in Fig. 4. Here, the catch-all factor, which corresponds to the area ratio of the surface site to whole surface, was assumed to be 1. Surface migration and desorption is found to be dominant at extremely high temperature. This implies that adsorbed atoms mainly desorb by associative desorption and especially E-R mechanism is dominant at low temperature range.

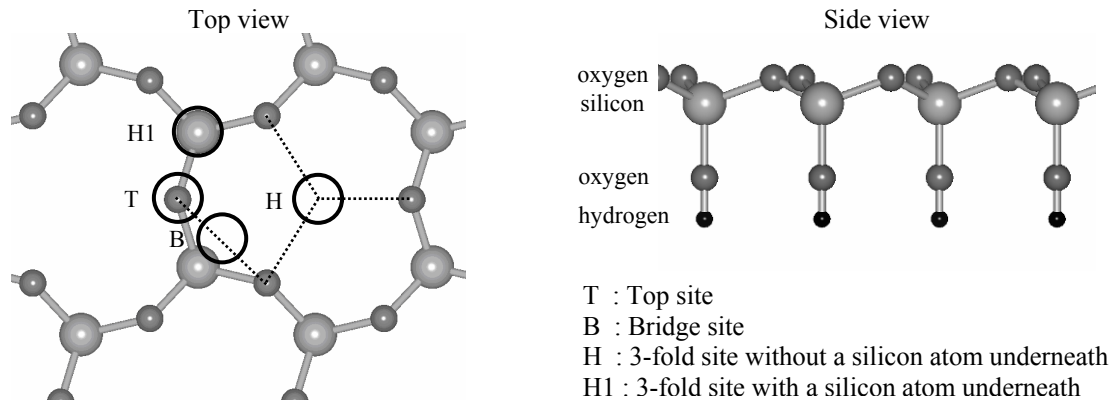


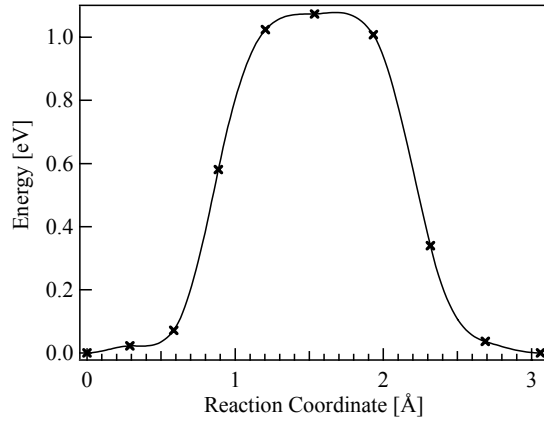
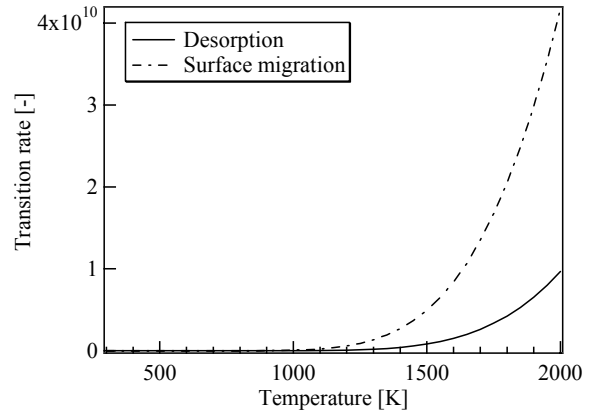
FIGURE 2. α -quartz (0001) reconstructed surface (dense surface)

TABLE 1. Adsorption energies and vibrational frequencies.

Surface site	E_{ad} [eV]	ν_{\perp} [cm^{-1}]	ν_{\parallel} [cm^{-1}]	
T	1.25	548.9	106.2	74.6
B	0.21	187.4	33.4	78.5i
H	0.14	69.2	87.1i	102.2i
H1	0.21	122.4	29.0	113.9i

TABLE 2. Energetic barrier of surface migration and vibrational frequencies at transition state.

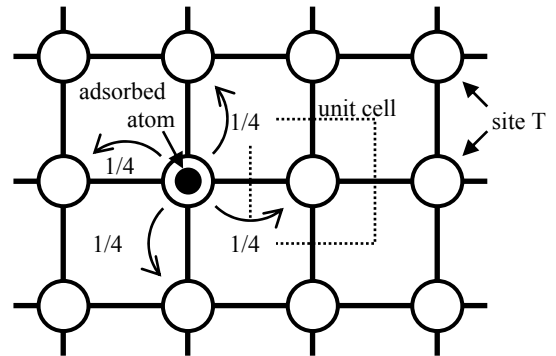
	E_{mig} [eV]	ν^{ts} [cm^{-1}]		
T-T transition state	1.07	124.5	57.6	111.1i

**FIGURE 3.** Potential energy curve along MEP for surface migration from site T to T.**FIGURE 4.** Transition rates for desorption and surface migration.

kMC

The following model was employed in our kMC simulations: the surface is described by a periodic lattice with a rectangular surface unit-cell, where each unit-cell contains only one site T as shown in Fig.5. The residence time of adsorbed atoms on the site B, H and H1 are much shorter than that on site T because of low adsorption energy on those sites. The area of single site A_i in equation (3) was obtained from the surface structure to be $7.3 \times 10^{-20} \text{ m}^2$. The adsorbed atom hops to four nearest neighbor sites. The hopping direction is selected with the probability of $1/4$ for each site. If adsorbed atom exist on the destination site, L-H recombination occurs with the probability calculated from equation(7). 100×100 sites with periodic boundary condition were considered in this kMC calculation.

Seward [12] proposed a phenomenological model fitted to the experimental data of Greaves et al. [13] at temperature from 300 to 1900 K. Although this model considers only E-R recombination mechanism, this model appears to be valid at temperature below 600 K because Fig. 4 indicates surface migration rarely occurs at low temperature. Hence, we employed this model to determine unknown parameters such as sticking coefficient S_i , steric factor P_{ER} and energetic barrier of

**FIGURE 5.** α -quartz (0001) surface model for kMC.**TABLE 3.** Values of the physiochemical parameters for catalytic recombination of oxygen on silica surface.

Parameter	Value
S_i	$0.2 \exp(-0.0027T)$
P_{ER}	$0.00013 \exp(0.0054T)$
E_{ER}	0.06 eV

recombination E_{ER} . These parameters are given in Table 3. E_{LH} was assumed to be the same with E_{ER} , and P_{LH} was varied from 0.001 to 0.7 to evaluate its sensitivity. As shown in Fig.6, we found the simulation result agreed well with experimental data by Greaves when P_{LH} was 0.3. Here, the catalytic efficiency γ was defined as

$$\gamma = \frac{\dot{n}_{rec}}{\dot{n}_{in}} \quad (8)$$

where \dot{n}_{rec} is the number flux of recombined atoms and \dot{n}_{in} is the number flux of incident atoms.

Fig.7 shows the contribution of the L-H mechanism to the catalytic efficiency. At temperature below 600 K, the surface migration of adsorbed atoms is inactive due to the relatively high diffusion barrier. Hence, the E-R mechanism is dominant. At temperature between 600 and 1100 K, the surface migration becomes significant and the L-H mechanism is dominant. At the temperature over 1100 K, the surface coverage decreases drastically because of the thermal desorption, which reduces the number of collision between adsorbed atoms. Then, the E-R mechanism becomes dominant again.

In equation (5) and (6), we assumed that the partition functions of the surface and the adsorption atom are independent on each other. However, the vibrational model of the surface can be altered by the adsorbed atoms. Hence, we need to evaluate more accurate expression for the partition functions. In addition, the recombination model for the E-R and the L-H mechanism must be constructed by the DFT and the TST instead of using the classical collision model. These are focused on our future work.

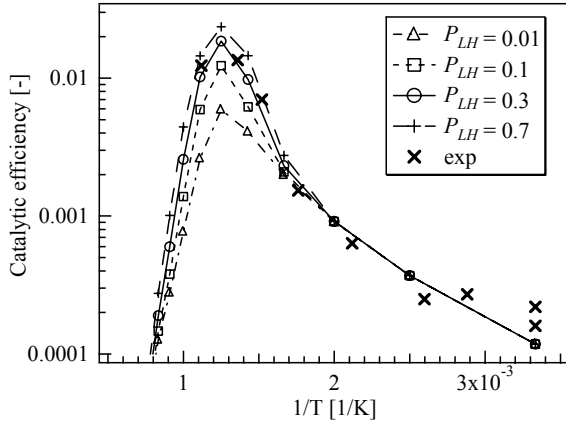


FIGURE 6. Effect of modifying the P_{LH} on the catalytic efficiency. $E_{LH} = 0.06$ eV/atom

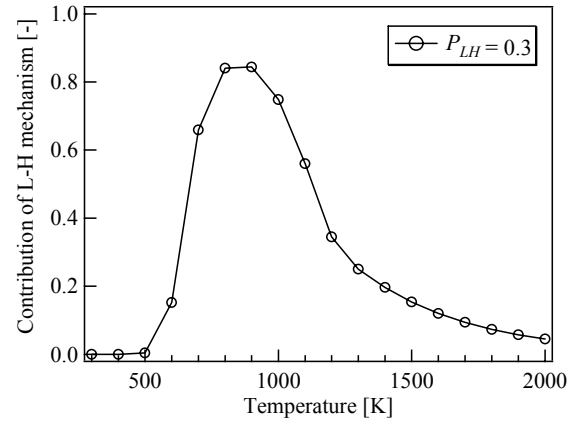


FIGURE 7. Contribution of L-H recombination to catalytic efficiency.

CONCLUSIONS

The periodic DFT study was performed to investigate the desorption and migration of atomic oxygen on the α -quartz (0001) reconstructed surface. The adsorption energies and the vibrational frequencies were obtained for the four different adsorption sites. The site T was the most stable site and the adsorption energy was 1.25 eV. The energetic barrier of the surface migration was found to be 1.07 eV using the cNEB method.

Then, the lattice model of the site T was constructed and the kMC calculation was performed for the various steric factors of the L-H recombination mechanism. The simulation result was in good agreement with the experimental data when $P_{LH}=0.3$. Our results showed the L-H mechanism was dominant at the temperature from 600 to 1100 K.

We will construct the E-R and the L-H recombination model using the DFT and the TST, and eventually non-empirical model for catalytic reaction process.

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