



Molecular dynamics study of the effects of adsorbed molecules on reaction probability and energy transfer

Masahiko Shibahara^{a,*}, Masashi Katsuki^b

^a *Science and Technology Center for Atoms, Molecules and Ions Control, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

^b *Department of Mechanical Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

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Abstract

To understand the processes involved in nanoscale fabrication or nanoscale catalytic combustion, it is useful to establish a fundamental numerical method for simulating heat transfer and chemical reactions on surfaces at real molecular scales. To comprehend and model the fundamental mechanisms of deterioration of a catalytic surface, this study employed a molecular dynamics simulation of the effects of adsorbates on surface reactions and energy transfer. The simulation system chosen was the process of collision of oxygen molecules with a silver surface; we expressed the molecule–surface interaction, including the effects of surface temperature, by a London–Eyring–Polanyi–Sato potential energy surface. Argon, krypton, xenon, and oxygen molecules constituted the typical adsorbates and their potential energies were modeled by Lennard–Jones functions. We discuss the effects of surface temperature and the characteristics of the adsorbates with regard to the statistically averaged values of the surface reaction probability and energy transfer under varying initial conditions for an oxygen molecule and its target position on a silver surface. Even though the coverage of the adsorbates on the surface on a real molecular scale remained the same, the surface reaction probability and the average energy transfer changed, depending on the characteristics of the adherent molecules. When the adsorbates were highly mobile, absorbing much of the kinetic energy of a colliding oxygen molecule, their dynamic behavior enhanced the surface reaction probability and surface energy transfer in reflection.

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Keywords: Surface reaction; Molecular dynamics method; Adsorbates; Heat transfer; Surface contamination

1. Introduction

To make progress in nanoscale fabrication or nanoscale catalytic combustion, it is now important to understand how molecules behave in reactive ther-

mal flow in the vicinity of surfaces. For example, actual industrial systems use a “direct heating process without oxidation of surfaces” [1] and “a dry-type degreasing method by flames” [2]. On a molecular scale, it is not easy to analyze and elucidate the mechanisms of surface oxidation processes and surface cleaning processes that employ burning gas containing various chemical species. So far, we have developed a molecular dynamics method to analyze chemical reactions and the energy transfer of oxygen molecules which

* Corresponding author. Fax: +81 6 6879 7254.
E-mail address: siba@mech.eng.osaka-u.ac.jp
(M. Shibahara).

collide with metallic surfaces [3]. However, the question of how numerical simulations can connect the gas, surface temperature, and surface adsorbates with molecular states on the surfaces is unresolved. Hence, they cannot determine how the growth rate of oxidized layers or reaction rate may depend on surface temperature. Moreover, molecular dynamics simulations require so much computer time that the largest computer in the world can calculate the properties of molecular systems only over distances less than 1 μm and over time periods less than 1 μs .

In the present study we have carried out a molecular dynamics simulation to investigate the effects of adsorbates on surface reaction probability and energy transfer at a real molecular scale. We utilize such reaction probability and energy transfer values in a Monte Carlo simulation to analyze the surface state within a realistic treatment period so as to connect the macroscopic properties of a thermal fluid to molecular-scale phenomena. As simulated systems, our study focuses on the collision processes of oxygen molecules with a silver surface. To elucidate one of the fundamental steps in the catalytic partial oxidation of ethane, we chose this focus because a reliable potential energy surface between the molecules is available [4] and many experimental studies [5,6] and numerical simulations [4,7–9] of the interaction between gas molecules and a silver surface exist.

A full determination of the effects of surface contamination and surface adsorption on surface reactions and energy transfers is very important to elucidate the fundamental mechanism of deterioration of a catalytic surface. However, such effects have never been elucidated from a molecular dynamics point of view or as a real molecular-scale phenomenon. In the present study, we have calculated the surface reaction probability and energy transfer to the surface under varying molecular conditions, such as the surface coverage of the adsorbed molecules, the kinds of adsorbates, the internal energy of the oxygen molecules, the surface temperature, and the incident angles of the oxygen molecules onto the surface. We have adopted a molecular dynamics point of view to discuss the dynamic effects of the adsorbates on surface reactions and surface energy transfers. Our final objectives here are to elucidate and model adsorbate effects on surface reaction probability and energy transfer and to employ surface nanoscale structures and appropriate surface temperatures to control surface contamination.

2. Numerical method

Fig. 1 shows the logical structure of the computational analysis scheme of the present study, including

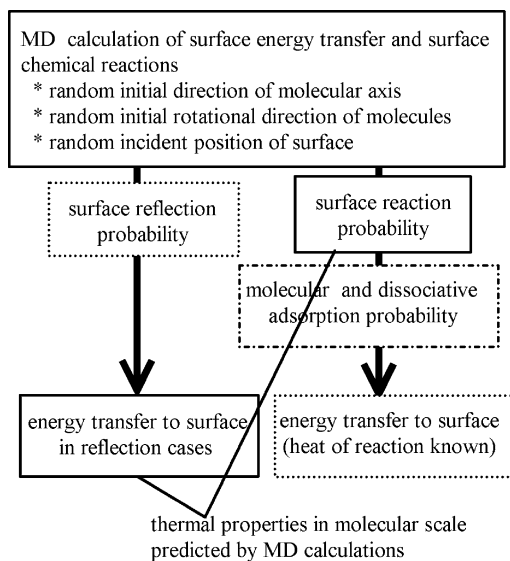


Fig. 1. Molecular dynamics (MD) calculation procedure of the surface reaction probability and the average energy transfer to the surface.

Table 1
Calculation conditions

E_{trans} (10^{-19} J)	0–3.2
T_{rot} (K)	0, 1053.01, 3412.93
T_{vib} (K)	1132.54, 3371.58
θ_{in}	0° – 60°
T_{s} (K)	100–500

the procedures used to calculate the surface reaction probability and the average energy transfer to the surface. The molecular dynamics calculations of surface energy transfer and surface chemical reactions were conducted with a random initial direction of the molecular axis and a random initial rotational direction of the oxygen molecules. The target collision positions on the silver surface were also determined randomly by the Monte Carlo method. The reaction probability and the average energy transfer to the surface in reflection were calculated with changing initial conditions such as the translational, rotational, and vibrational energy of the oxygen molecules, the initial surface adsorption state, and the surface temperature. These physical parameters are shown in Table 1. We used more than 500 trials for the same initial condition with different initial directions of the molecular axis, the rotational directions of the oxygen molecules, and the target positions on the surface. The number of trials was determined by checking convergence of the reaction probability and the average energy transfer. The surface reflection probability can be evaluated by a subtraction of the surface reaction probability from unity. The energy transfer in a re-

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