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Catalytic Model on SiO_2-Based Surface and Application to Real Trajectory

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Introduction

WHEN a reentry vehicle flies at very high Mach numbers, a strong bow shock forms in front of the body, and dissociation of air takes place inside the shock layer. Some of dissociated atoms recombine according with the drop of temperature; however, if the flow is in nonequilibrium a large part of atoms remain through the boundary layer and finally recombine on the surface, which causes the increase in aerodynamic heat.

One way to protect this additional increase of heat flux is to use the thermal protection system (TPS) with materials as little catalytic as possible. SiO_2-based materials are now widely used for this purpose because of their low catalytic properties. However, even the slight catalysis of these materials increases considerable amount of heat flux around the body compared with the one with noncatalytic wall assumption.

In the design of reentry vehicles, the heat load is usually predicted through computational fluid dynamics (CFD), and two extreme assumptions are usually applied; non- or fully catalytic conditions. Designing reentry vehicles with fully catalytic condition seems to be too conservative today because it may sometimes lead to overestimation of weight of TPS and even misunderstanding of correct aerodynamic properties.[1,2] Therefore, construction of the model describing the correct physics of heterogeneous catalytic processes and being easy to incorporate into the CFD codes are now of great importance. For this purpose several models have been proposed in which the catalytic processes are treated as the combination of each elementary step.[1–4] However, more improvements in physical considerations are necessary to predict catalytic efficiencies quantitatively for various flow conditions.

In the treatment of surface catalysis in airflow, it is usually assumed that no production of NO molecules occurs. Recently, Copeland et al.[5] demonstrated that a significant concentration of NO is generated from a surface-catalyzed reaction on quartz surfaces in the room temperature range. They also pointed out that N and O atoms do not act independently and that NO may be a significant reaction product from a catalytic process.

In this Note a model describing heterogeneous catalysis on the surface of SiO_2-based materials is constructed in a new approach. The concept of the phenomenological theory proposed by Kovalev et al.[6] are generalized to describe the overall heterogeneous catalytic phenomenon including NO production in each elementary step in detail. To prove the validity of this theory and investigate the effects of NO production on the surface, this model is incorporated into the CFD codes, the flow around OREX (Orbital Reentry Experiment) is solved, and results are discussed.

Description of Heterogeneous Catalysis and Construction of Model

In this Note the following elementary steps are assumed in heterogeneous catalytic processes under the assumption that the surface temperature is not extremely high and that there are no slip effects.

1) Adsorption-desorption of atoms:

$$\mathrm{O} + (\mathrm{S}) \rightleftharpoons (\mathrm{O} - \mathrm{S}) \tag{1}$$

$$\mathrm{N} + (\mathrm{S}) \rightleftharpoons (\mathrm{N} - \mathrm{S}) \tag{2}$$

2) Recombination between gas atoms and adsorbed atoms (adatoms) [Eley–Rideal (E-R) recombination]:

$$\mathrm{O} + (\mathrm{O} - \mathrm{S}) \rightleftharpoons \mathrm{O}_2 + (\mathrm{S}) \tag{3}$$

$$\mathrm{N} + (\mathrm{N} - \mathrm{S}) \rightleftharpoons \mathrm{N}_2 + (\mathrm{S}) \tag{4}$$

$$\mathrm{O} + (\mathrm{N} - \mathrm{S}) \rightleftharpoons \mathrm{NO} + (\mathrm{S}) \tag{3$'$}$$

$$\mathrm{N} + (\mathrm{O} - \mathrm{S}) \rightleftharpoons \mathrm{NO} + (\mathrm{S}) \tag{4$'$}$$

3) Recombination between adatoms [Langmuir–Hinshelwood (L-H) recombination]:

$$(\mathrm{O} - \mathrm{S})_m + (\mathrm{O} - \mathrm{S}) \rightleftharpoons \mathrm{O}_2 + 2(\mathrm{S}) \tag{5}$$

$$(\mathrm{N} - \mathrm{S})_m + (\mathrm{N} - \mathrm{S}) \rightleftharpoons \mathrm{N}_2 + 2(\mathrm{S}) \tag{6}$$

$$(\mathrm{O} - \mathrm{S})_m + (\mathrm{N} - \mathrm{S}) \rightleftharpoons \mathrm{NO} + 2(\mathrm{S}) \tag{5$'$}$$

$$(\mathrm{N} - \mathrm{S})_m + (\mathrm{O} - \mathrm{S}) \rightleftharpoons \mathrm{NO} + 2(\mathrm{S}) \tag{6$'$}$$

Here (S) is a free active site and (Y–S) means an Y atom absorbed by the surface (adatom). The subscript m means migrating adatoms on the catalytic surface.

In L-H recombination only collisions between this migrating adatom and a "still adatom" are considered.[2] Furthermore, adsorption–desorption of molecules in the wall temperature range considered in this study is sufficiently small and can be neglected.[6] Under these assumptions the specific mass formation rates $\dot{r}_s$ per unit surface area in reactions Eqs. (1–6) and Eqs. (3′–6′) are given from the acting surface law by[6]

$$\dot{r}_1(\mathrm{O}) = -\dot{r}_1(\mathrm{O} - \mathrm{S}) = -M_O p k_1 (X_O \theta - \theta_O / p K_1), \qquad \text{etc.} \tag{7}$$

under the condition that

$$\theta + \theta_O + \theta_N = 1 \tag{8}$$

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where M_i and X_i are molecular mass and molar fraction of species i; p is pressure of mixture gas; k_n and K_n the rate constant of forward reaction and the equilibrium constant in Eq. (n), respectively; θ_i the surface fraction of the adsorbed species i; and θ the surface fraction of the free adsorption sites.

If the quasi-steady state is assumed during catalytic processes, the overall mass formation rate of adatoms should be equal to zero. Then, we obtain the following quadratic forms:

$$\theta_O/\theta = (1/A_{\theta O})(k_1 + 2k_5K_1\theta_O)X_O \tag{9}$$

$$\theta_N/\theta = (1/A_{\theta N})(k_2 + 2k_6K_2\theta_N)X_N \tag{10}$$

where

$$\begin{aligned} A_{\theta O} &= (k_3 + 2k_5K_1\theta)X_O + (k_1 + 2k_5K_1\theta_O)/pK_1 \\ &\quad + K_4^*X_N + \left(k_5^* + k_6^*\right)\theta_N/p \end{aligned} \tag{11}$$

$$\begin{aligned} A_{\theta N} &= (k_4 + 2k_6K_2\theta)X_N + (k_2 + 2k_6K_2\theta_N)/pK_2 \\ &\quad + k_3^*X_O + \left(k_5^* + k_6^*\right)\theta_O/p \end{aligned} \tag{12}$$

In this study we divide catalytic efficiency γ into two parts, for instance, for O atoms γ_{OO}, the ratio of the number of O atoms recombining into O_2 to the total numbers of atoms impinging on the surface and γ_{ON}, the ratio of the number of O atoms recombining into NO to the total numbers of atoms impinging on the surface. Then, the final expressions of catlytic efficiencies for O atoms are given by

$$\begin{aligned} \gamma_{OO} &= \left(\sqrt{8\pi M_O\bar{R}T}\big/A_{\theta O}\right)\Big\{(k_1k_3 + k_1k_5K_1\theta + k_3k_5K_1\theta_O)X_O \\ &\quad - k_5K_1\theta_O\left[k_4^*X_N + \left(k_5^* + k_6^*\right)(\theta_N/p)\right]\Big\}\theta \end{aligned} \tag{13}$$

$$\begin{aligned} \gamma_{ON} &= \sqrt{2\pi M_O\bar{R}T}\Big\{(1/A_{\theta N})\left[k_3^*(k_2 + 2k_6K_2\theta_N)X_N\right] \\ &\quad + (1/A_{\theta O})(k_1 + 2k_5K_1\theta_O)\left[k_4^*X_N + \left(k_5^* + k_6^*\right)(\theta_N/p)\right]\Big\}\theta \end{aligned} \tag{14}$$

where we use the relation $M_O pX_O = \rho\bar{R}Tc_O$, ρ is the density of mixture gas, $\bar{R}$ the universal gas constant, T the temperature of mixture gas, and c_i mass fraction of species i. For N atoms similar expressions for γ_{NN}, γ_{NO} are obtained.

The expressions of each rate constants of forward reactions and equilibrium constants can be obtained from the kinetic theory and the transition state theory.

Results and Discussion

Catalytic efficiency γ for O_2-O or N_2-N binary mixture gas can be calculated if unknown surface properties are determined by the curve fit with experimental data under several conditions for partial pressure of dissociating gas.

Comparisons of catalytic efficiency γ between the present model and experimental data for O_2-O binary mixture gas are shown in Fig. 1. Two sets of experiments tabulated in Ref. 3 with different partial pressure of O atoms p_O (one is for silica with lower p_O and another for reaction-cured glass with higher p_O) are selected. In Fig. 1 it is observed that, in the lower surface temperature range less than about 500 K, E-R recombination is dominant for both cases. However, as the surface temperature increases the effect of L-H recombination appears. Figure 1 also shows that for L-H recombination in high-temperature range the partial pressure of dissociating gas has strong effects on γ and as p_O increases the value of γ decreases.

Comparisons of γ for N_2-N binary mixture gas are shown in Fig. 2. Experimental data from tabulated data in Ref. 4 and calculated results from the present model under the corresponding N partial pressure p_N are presented. Experimental results of SiC with glass sealant developed for OREX are also shown. The same tendencies as the O_2-O binary mixture cases are observed. For both cases the present model can reasonably predict γ in the wide range of both surface temperature and partial pressure of dissociating gas.

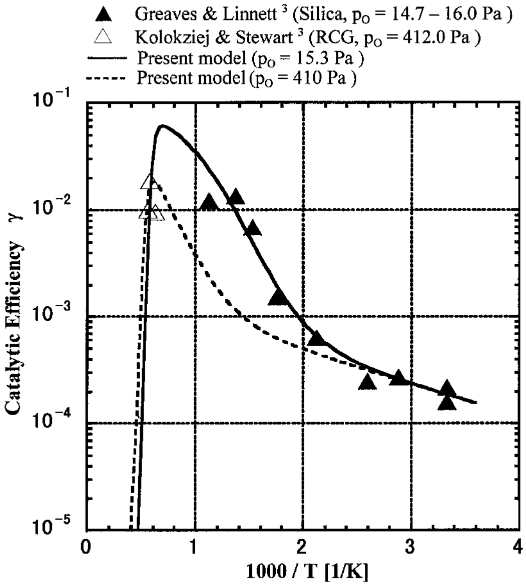

Fig. 1 Comparison of present model with experimental data for O_2-O mixtures gas.

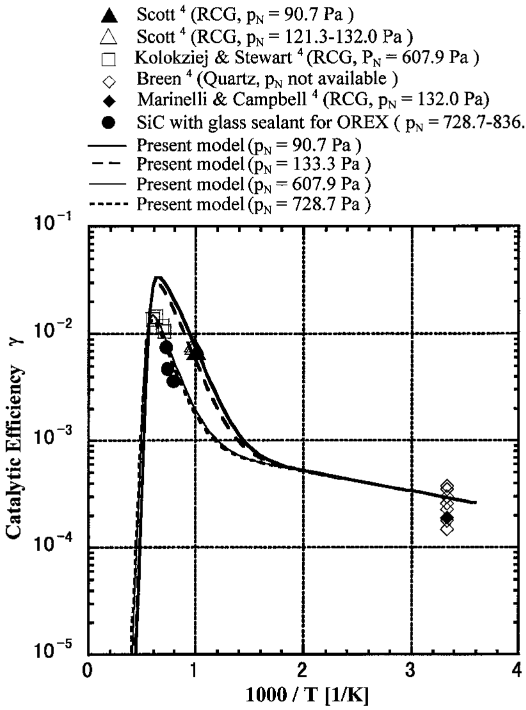

Fig. 2 Comparison of present model with experimental data for N_2-N mixtures gas.

To investigate the validity of this theory and estimate the effects of NO production in the heterogeneous catalytic processes for airflow cases, this model is incorporated into the CFD codes and is applied to a real flight trajectory of OREX. OREX was a capsule-type vehicle successfully launched in 1994 from Japan. Its shape consists of a 50-deg sphere cone with a nose radius of 1.35 m and maximum diameter was 3.4 m. Detailed data of flight history are published in Ref. 7. SiC with glass sealant was used around the stagnation region. In this study axisymmetric Navier–Stokes equations for seven-species air considering both thermally and chemically nonequilibrium are solved, and AUSM$^+$ scheme[8] is used with the second-order accuracy in space for convective terms. Only forebody is treated with 81 × 81 mesh points.

In Fig. 3 flight history of heat flux q_w and CFD results with noncatalytic, fully catalytic, and finite rate catalytic boundary conditions at the stagnation point are shown. A parameter α represents the degree

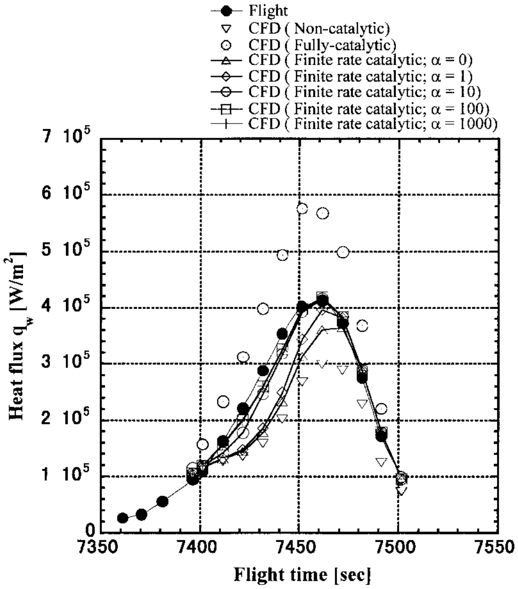

Fig. 3 Flight history of stagnation point heat flux and corresponding CFD results in OREX trajectory.

of NO production in L-H recombination compared with the one of corresponding N_2 or O_2 production. For instance, $\alpha = 0$ corresponds to no NO production and $\alpha = 1$ means NO production is in the same degree with N_2 or O_2 production.

Except for a very high altitude, more than about 80 km around at the flight time of 7400 s where slip conditions should be considered, flight data of heat flux exist between two extreme noncatalytic and fully catalytic cases. Therefore, the finite rate catalytic treatments in real flight cases are very important in a practical sense.

From CFD results with various α, which represents the degree of NO production in L-H recombination, Fig. 3 also indicates that the NO production in the heterogeneous catalytic processes has great effects for the heat flux. If the production of NO molecules in L-H recombination is totally ignored ($\alpha = 0$) or underestimated ($\alpha = 1, 10$), it is difficult to evaluate heat flux correctly.

The reason for the increase of heat flux according with α can be explained from the following reaction:

$$NO + N \rightleftharpoons N_2 + O + 76.4 \text{ Kcal/mol} \qquad (15)$$

Because the forward reaction rate of Eq. (15) is very high in the temperature range near the surface, NO molecules produced in the heterogeneous catalytic processes immediately react with dissociating N atoms near the surface with the amount of heat release. Furthermore, newly produced O atoms collide with the surface and contribute to the increase of heat flux through the catalysis on the surface again. These synergy effects should be very high in the medium range of altitudes between 60 and 80 km (corresponding to flight time of 7420–7470 s) because in this range the flow is strongly in nonequilibrium, and, therefore, there are enough dissociating N atoms inside the boundary layer as a resource to react with NO molecules.

Only from this OREX case the specific value of α cannot be determined; however, the appropriate range of it can be estimated as

$$\alpha \gtrsim 100 \qquad (16)$$

For this range the agreement between flight data and CFD predictions is excellent as can be seen in Fig. 3. This result indicates that in L-H recombination N and O adatoms reacts to each other more preferentially than among the same species of adatoms.

These discussions strongly support the experimental results of NO formation from a surface-catalyzed reaction on quartz surfaces by Copeland et al.,[5] although NO formation in the OREX case is observed in more higher surface temperature range where the L-H recombination is dominant.

Conclusions

In this Note a new model describing heterogeneous catalysis on the surface of SiO_2-based materials is constructed. Especially, NO production in each elementary step during heterogeneous catalytic processes is treated in detail. The overall phenomenon is formulated with phenomenological theory, and expressions for catalytic efficiencies are derived. Each unknown variable in them is evaluated in terms of kinetic theory and the transition state theory.

To investigate the validity of this theory, it is applied to a real flight trajectory of OREX and compared with the stagnation heat flux data. CFD results indicate that NO production in L-H recombination has great effects for the heat flux. For the appropriate degree of NO production estimated in this study, this model can reasonably predict the heat flux throughout the flight trajectory.

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