

Numerical Simulation for Designing Next Generation TWC System with Detailed Chemistry

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ABSTRACT

A one-dimensional (1-D) micro-kinetic reaction model with considering mass transport inside porous washcoat was developed to promote an effective development of multi-functional catalysts. The validation of this model has been done successfully through the comparison with a set of basic experiments. A numerical simulation study was conducted for the various catalyst configurations of three-way catalysts under Federal Test Procedure (FTP75) condition. It was found that a double layer type had a significant advantage in the total mass emissions, especially in NO_x emissions. The reaction mechanisms in these catalysts were numerically clarified from the view point of detailed reaction dynamics. We concluded that the utilization of the numerical simulation with the detailed chemistry was effective for the optimization of catalyst design.

INTRODUCTION

Demands are growing for lower emission gasoline and diesel engine systems, which necessitate the development of highly effective after-treatment catalysts. The majority of automotive catalytic converters have a monolithic structure, which is coated with an alumina washcoat that supports the noble metal (Pt, Rh, Pd ---) and metal oxides (cerium oxide, barium oxide ---). Due to the recent advance of catalyst technology, the multi-functional catalysts (layered catalysts, zone coated catalysts, ---) are commonly adopted to improve the catalyst performance. But we have relied upon the time consuming investigations with a large number of experiments in order to modify the optimal catalyst configuration for each engine exhaust system.

We have been working on modeling of the catalytic reaction dynamics as one of the most promising approaches to accelerate the effective development of the multi-functional catalyst of the next generation. However detailed reaction mechanisms on each catalyst active site and effects of mass transport inside porous

washcoat on reaction characteristics have been not fully understood yet. Therefore it was very difficult to build the catalytic reaction model, which could predict reaction characteristics of a chemical system in a wide range of reaction conditions. In recent years, several proposals were made for the numerical simulation of catalytic converters¹⁻⁴. They adopted global reaction models in which they simplified in detailed surface chemistry occurring on the surface. These global reaction models are descriptive only in the range of conditions used for fitting of the global rate coefficients, but not predictive at the extrapolated reaction conditions.

An alternate approach is to simulate the chemical reaction by a set of "quasi-elementary" steps describing the reactions on a molecular level, so called 'micro-kinetic reaction model'. Recently several researchers proposed this kind of chemical reaction models with detailed surface chemistry⁵⁻¹⁰. These reaction models showed the potential to predict reaction characteristics of catalysts in a wide range of reaction conditions. In the previous paper⁵ we adopted a micro-kinetic surface reaction model for an automotive catalyst (a three-way catalyst and a NO_x storage-reduction catalyst) to simulate the reaction characteristics of actual after-treatment catalysts and clarified the effectiveness of the micro-kinetic reaction model under real operating conditions.

The purposes of our research are to expand the coverage of our micro-kinetic reaction model and to simulate the reaction characteristics of the multi-functional three-way catalyst under FTP75 condition by utilizing our expanded model. To achieve the above-mentioned purpose, the expansion of our micro-kinetic reaction model was made as follows: introduction of mass transport both in monolithic channel and washcoat, and addition of the surface reaction mechanisms on the active sites of Pd and Rh.

THE MICRO-KINETIC REACTION MODEL

In this study our analytical target is a honeycomb type monolithic reactor. One single channel of the monolith was modeled with one-dimensional micro-kinetic reaction model including detailed surface chemistry: adsorption & desorption on catalyst surface and chemical reactions of adsorbed species on the catalyst active sites⁵⁻¹⁰. The detailed description of the micro-kinetic model was written in the previous paper⁵. The uniform flow and the adiabatic temperature were assumed for all 1-D calculations.

MODIFICATION OF THE MASS TRANSPORT EFFECT

A two dimensional (2-D) micro-kinetic reaction model has been developed in order to clarify the characteristics of the mass transport during catalyst reaction and to obtain the accurate mass transport parameters for constructing the 1-D micro-kinetic reaction model. A 2-D numerical simulation for a flow field and concentration field in the monolithic reactor was conducted by Lattice Boltzmann Method (LBM). The 2-D micro-kinetic model can directly predict effects of mass transport by convection and diffusion in both the monolithic channel and the disordered porous Al_2O_3 washcoat layer. Figure 1 shows an example of the results of the 2-D numerical simulation. This shows C_3H_6 concentration contours during C_3H_6 oxidation near the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst surface. In the 2-D micro-kinetic reaction model, the minimum pore size for gas phase diffusion was approximately $0.5\mu\text{m}$ and the Knudsen diffusion coefficient was adopted for the diffusion inside the micro-pores of Al_2O_3 particles. The uniform temperature was assumed for the all 2-D calculations. The 2-D micro-kinetic reaction model successfully predicted the reaction characteristics considering effects of microscopic structure of washcoat layer. In the 2-D numerical simulation, the computational domain was still limited to very small scale both in time and scale because of its huge computational cost. It means that the 2-D micro-kinetic reaction model has not been able to be directly applied to a full-size catalyst simulation yet.

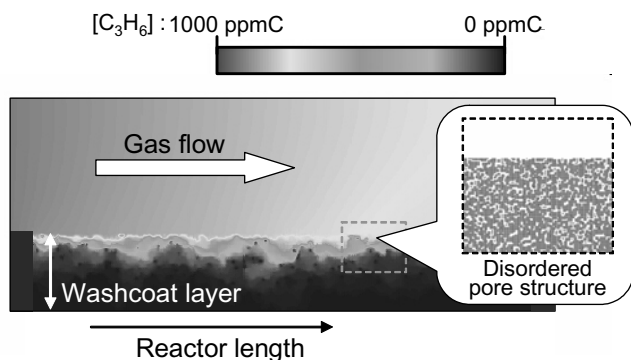


Fig.1 C_3H_6 concentration contours during C_3H_6 oxidation on $\text{Pt}/\text{Al}_2\text{O}_3$ @ $T=300^\circ\text{C}$ (the 2-D micro-kinetic model)

Parameter determination of mass transport equations

A 3-layer model has been adopted in the 1-D micro-kinetic reaction model to consider mass transport phenomena inside monolithic reactor. The 3-layer model consists of one gas phase layer for the channel flow and 2 layers for the porous washcoat. The mass balance equation between each computational domain was solved by considering convection and diffusion.

The mass transport between the gas phase layer and the upper layer of the porous washcoat was described with the film model¹¹⁻¹². The Sherwood number Sh_z as a function of reactor length z in the film model was determined by utilizing the information from the 2-D numerical simulations in various conditions (temperature, flow rate and cell density).

An effective diffusion coefficient of species i , $D_E(i)$ was adopted for the diffusive mass transport between two washcoat layers. The effective diffusion coefficient $D_E(i)$ is written in the following well-know expression.

$$D_E(i) = \frac{\varepsilon}{\tau} D_0(i)$$

where ε is a porosity, τ is a tortuosity of the porous washcoat and $D_0(i)$ is a bulk diffusion coefficient of species i respectively. These unknown parameters depending on the microstructure of each washcoat material were determined by both information from 2-D numerical simulations and experimental measurements.

SURFACE REACTION MECHANISMS

The surface reaction scheme consists of elementary reaction steps on a precious metal and a metallic oxide, e.g., dissociative and non-dissociative adsorption and desorption, and the chemical reactions steps between adsorbed species. Some activation energies are coverage-dependent due to the interactions between the adsorbed species. It was assumed that all species were adsorbed competitively onto each active site. A main part of the surface reaction mechanism has been already authorized in the literature⁸ for a numerical modeling study of the steady state three-way catalyst ($\text{Pt}/\text{Rh}/\text{Al}_2\text{O}_3$). The kinetic data of the surface reaction mechanisms for CO , H_2 , O_2 , CO_2 , H_2O , C_3H_6 and NO on the Pt/Rh active sites were mainly taken from the literature⁸. In the previous paper⁵ the reaction mechanisms for NO oxidation, O_2 storage on cerium oxide and NO_2 storage on Barium oxide were newly introduced by considering a set of basic experimental results and thermodynamics. It was confirmed that these surface reaction mechanisms successfully predicted the reaction dynamics of the three-way catalyst and NSR catalyst ($\text{Pt}/\text{Rh}/\text{Ce}/\text{Ba}$) in a wide range of reaction conditions. In this paper we additionally introduced unknown surface reaction mechanisms of $\text{Pd}/\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst and assumed that essential reaction mechanisms on Pd active sites are the same as those on Pt active sites. The surface reaction parameters were determined by considering the

thermodynamics and the basic experimental results which were conducted with the Pd/CeO₂/Al₂O₃ catalyst in various conditions (e.g. catalyst light-off experiment under the stoichiometric condition).

EXPERIMENTAL

TEST CATALYSTS

For this study several types of a three-way model-catalyst were prepared with a basic composition of platinum, rhodium, palladium, cerium oxide and alumina. All catalysts were the type of honeycomb monolith which had a single or double layered washcoat were degreened in a very mild condition (slightly fuel rich engine operation, 500°C x 5 hours).

ENGINE DYNAMOMETER TEST

The engine dynamometer experiments were run on a 2.4 L gasoline fueled engine. Three types of the following test experiments were conducted for the clarification of reaction dynamics in a wide range of reaction conditions.

- 1. A/F (ratio of fuel to air in the engine operation) sweep test: A/F was continuously changed from a fuel rich to a fuel lean condition at a constant inlet gas temperature.
- 2. Light-off test: the Inlet gas temperature was continuously increased at a stoichiometric A/F condition (constant engine operation) by using a heat exchanger.
- 3. A/F rich-lean switching experiment: A/F was periodically changed between fuel rich and fuel lean conditions at a constant inlet gas temperature.

The details of each experimental condition are explained in the following session.

VEHICLE TEST

A 2.4L L4 NA gasoline fueled engine vehicle (LEV2/Bin5) was used for FTP75 test. Catalysts were set in the position of regular close-coupled converter.

RESULTS AND DISCUSSION

VALIDATION OF THE 1-D MICRO-KINETIC MODEL

Validation of the mass transport model

Two Pt/Al₂O₃ model-catalysts shown in Figure 2 were prepared for the validation of the 1-D mass transport model. One was a regular Pt/Al₂O₃ catalyst and another was a Pt/Al₂O₃ catalyst covered with a dummy Al₂O₃ layer. The validation of the 1-D mass transport model was performed by the comparison between the simulation results and the experimental results for

catalyst reaction characteristics of the Pt/Al₂O₃ model catalysts. Test conditions are shown in Table 1.

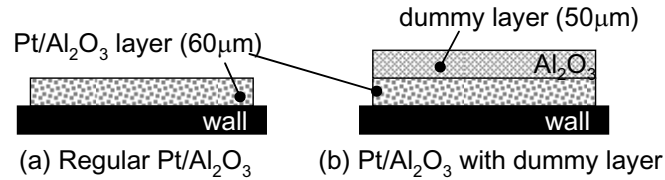


Fig.2 Schematics of the tested catalysts

Table 1 Testing conditions (A/F sweep test)

parameter	value	unit
catalyst volume	0.448	L
cell density	600	cpsi
gas flow rate	18.5	g/s
inlet gas temp.	460	°C
A/F range	13.5→15.0	-
A/F sweep rate	0.075	1/min

Figure 3 shows the relationship of between simulated emission increase factor (Predicted R_E) and experimental emission increase factor (Measured R_E). The emission increase factor (R_E) was defined in the following expression:

$$R_E = \frac{\text{[outlet conc.] of the catalyst with dummy layer (Fig.2(b))}}{\text{[outlet conc.] of the catalyst without dummy layer (Fig.2(a))}}$$

Good agreement was reached between the emission increase factor R_E in the experiment and the numerical simulation for all conditions (see Figure3). Therefore it was confirmed that the 1-D mass transport model can predict effects of diffusive mass transport inside the washcoat layer in a good accuracy.

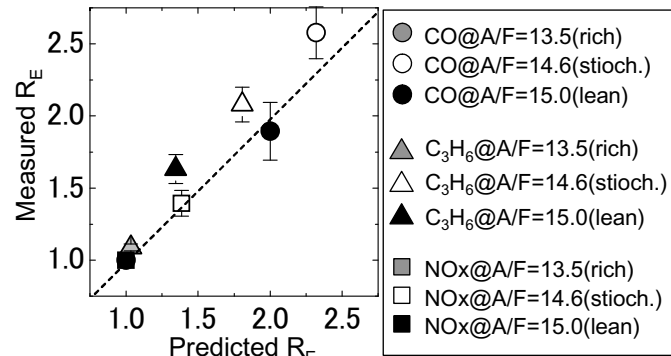


Fig.3 The effect of the dummy layer (Exp. vs. Model), R_E: The emission increase factor by the dummy layer