Abstract of the dissertation

Title: Development of Numerical Model for Washcoated Honeycomb Monolith Catalyst based on Surface and Gaseous Species Measurements
（気相･表面化学種計測に基づくウォッシュコートハニカムモノリス触媒の数値モデル開発）

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Exhaust gas emission standards for automotive vehicles have become considerably stringent year by year, which has been satisfied by using catalytic systems. However, performance of conventional catalytic systems has almost reached to a limit due to the recent introduction of WLTP mode under real driving environment. Moreover, exhaust gas tends to be unsuitable conditions for catalytic conversion in modern high efficiency IC engines, i.e., exhaust gas temperature decreases drastically, and compositions are shifting to oxygen excess conditions. Optimum catalytic systems for modern and future engines, which may be out of conventional knowledge, must be explored efficiently. Computer aided development is a powerful tool to meet such demands, in which the numerous combinations of catalytic species can be simulated simultaneously. However, current numerical simulation tools are not capable of practical use. Then, in this dissertation, a numerical model which can predict the conversion behavior of catalytic converter is developed. C_2H_4 and C_3H_6 are selected as target species because both of them are contained in raw emission from I.C. engines, and further, they are key species to improve light-off performance of catalytic system because the light-off temperature of C_2H_4 is the lowest while C_3H_8 is in the middle among the unburned hydrocarbon species emitted from I.C. engines. All of the inlet / boundary conditions for numerical calculations are identified by thorough characterization. Surface reaction mechanisms are developed and validated with the experimental results of gaseous and surface species measurements

Chapter 1 presents background of the research. Recent emission regulations and the role of catalysts are introduced. Then, situation of computer aided development on the field is described by referring past research about catalytic systems for automotive cars. The major issues in the field of modelling of catalytic systems are (1) several physical properties or boundary conditions are left as fitting parameter though they must be clearly identified, and (2) chemical surface reaction mechanisms are validated only with the behavior of gaseous species. Then, we propose our concept that characterize the catalyst thoroughly, and validate the numerical results not only with gaseous but also surface species behavior.

Chapter 2 presents the experimental equipment used in this study. In this study, as for the catalytic system, Pt catalyst impregnated on γ-alumina washcoat of 0.8g/L Pt loading is used.

Experiments are conducted with two forms of catalysts, i.e., monolith honeycomb catalyst and powdered catalyst. With monolith honeycomb catalyst, conventional conversion rate examinations are conducted for various temperature conditions by Fourier Transform Infrared (FT-IR), while with the powdered catalyst, which is the fragment of monolith washcoat, characterization of catalyst are implemented, and furthermore, coverage of surface species in various adsorption regime are examined by *in-situ* FT-IR under the same conditions of inlet gas temperature and compositions as monolith honeycomb experiments. Both results of gaseous species conversion experiments and surface species coverage measurements are used to validate the surface reaction mechanisms.

Chapter 3 presents the construction of detailed surface reaction mechanism on Pt/Al_2O_3. Based reaction mechanism, i.e., CO / O_2 reaction mechanism is developed first, then, C_2H_4 and C_3H_6 decomposition / partial oxidation reaction pathways are proposed based on the recent DFT works. The point of new surface reaction mechanism is multiple surface site occupation, i.e., intermediate species of both of C_2H_4 and C_3H_6 occupies the maximum of 3 adjacent surface sites which leads to surface site limiting phenomena on their oxidation process. Rate constants of modified Arrhenius form are determined under the confinement of thermodynamic consistency.

Chapter 4 presents numerical modelling method used in this study. Monolith honeycomb catalytic converter model by BOOST^{TM} (AVL Corp.) together with equations and thermodynamic consistency method used in this study are discussed. The "after treatment model" which models a single cell of monolith honeycomb reactor is used, but almost all parts are user defined. On the model, gaseous reactants are assumed to be transferred onto the converter surface across the boundary layer, and further transported through and into the washcoat layer by pore diffusion phenomena. Equations for mass, energy and species conservation equations are solved. Pore diffusion phenomena is also treated with essential parameters, such as porosity and tortuosity which are identified by the characterization of the catalyst used in this study.

Chapter 5 presents numerical studies carried out in this study. Numerically simulated results by using numerical method and proposed developed surface reaction mechanism are discussed. Although surface reaction mechanisms for C_2H_4 and C_3H_6 are validated only for C_2H_4 / O_2 and C_3H_6 / O_2, however, it is found that the conversion behavior of complicated four components mixture ($C_2H_4 / C_3H_6 / CO / O_2$) can also be reproduced very well by the simulation.

Chapter 6 presents conclusions and suggestions for future work. In this study, new strategy of modelling of catalytic converters are proposed, and surface reaction mechanisms are developed based on the strategy. The surface reaction mechanisms developed can contribute to the drastic improvement of performance and cost of catalytic systems.