

Numerical Computational Fluid Dynamics Analysis of Pd-based Three-way Catalysts Considering Detailed Surface Reactions

- Effects of Mass Transport in the Catalyst Layer -

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Improving the thermal efficiency of internal combustion engines lowers exhaust gas temperatures, requiring three-way catalysts (TWCs) to achieve high conversion performance at low temperatures. Catalyst-layer structures must also reduce precious-metal usage while maintaining performance. This requires quantitative evaluation of gas diffusion and surface reactions within catalyst layers. Although inactive layers have been used to distinguish reaction and mass-transfer effects, multilayer catalyst design requires diffusion models based on actual pore structures. In this study, pore properties were obtained by mercury intrusion porosimetry and scanning electron microscopy (SEM), and a gas diffusion model was developed for a layered Pd three-way catalyst. Light-off tests and calculations were compared to investigate rate-limiting processes.

A honeycomb-supported Pd three-way catalyst was used. To evaluate intralayer diffusion, inactive alumina layers of 0, 60, and 120 g/L were coated above the active layer, producing Pd/A, Pd/A+A60, and Pd/A+A120, respectively. CO-O₂ light-off tests were conducted with simulated exhaust gas. The inlet temperature was increased from 150 to 500°C at 20°C/min at a space velocity of $1.5 \times 10^5 \text{ h}^{-1}$. CO conversion was calculated from upstream and downstream concentrations.

A quasi-two-dimensional model was developed by extending an existing Pd/A reaction model to include diffusion through the catalyst-layer thickness. The model considered channel-flow convection, gas-to-layer mass transfer, intralayer diffusion, and surface reactions. Effective diffusivities were calculated using a parallel-pore model incorporating molecular and Knudsen diffusion, together with pore diameter, porosity, and tortuosity. Surface reactions on Pd sites were described using the Langmuir-Hinshelwood mechanism, with rate constants calculated using the Arrhenius equation.

Figure 1 compares the experimental and calculated CO light-off characteristics. Average inlet CO and O₂ concentrations and the corresponding air excess ratio, λ , are also shown. Differences in the temperature required for 50% CO conversion were small. However, the inactive-layer effect increased at higher conversion levels, and the temperature required for 95% conversion of Pd/A+A120 was approximately 146°C higher than that of Pd/A. The gradual conversion increase above 250°C was attributed to enhanced gas transport as diffusivity increased with temperature. Using measured layer thicknesses and porosity, the representative pore diameter and tortuosity were identified as 2.1 μm and 3.4, respectively. With common reaction and diffusion parameters, the model reproduced the effect of inactive-layer thickness on light-off behavior. These results indicate that surface reactions dominate at low temperatures, whereas diffusion resistance increasingly limits CO transport to the active layer at high conversion levels.

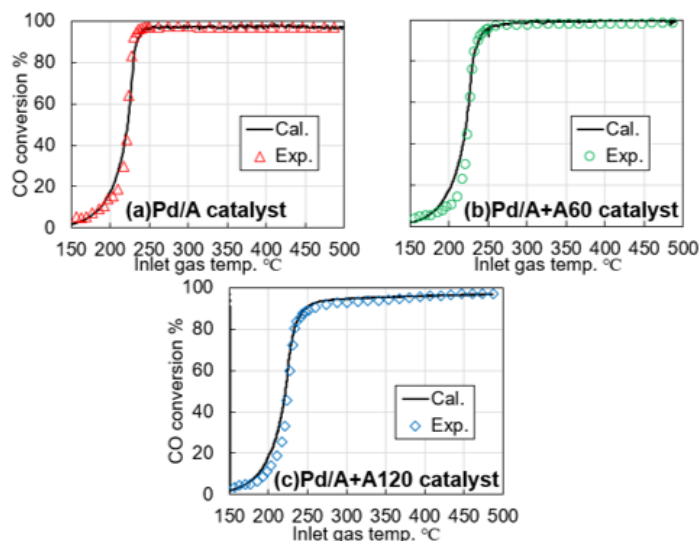


Fig.1 Comparison and validation of experimental results and 1+1D model predictions for light-off behavior
Pd/A (λ :0.987, CO:6021ppm, O₂:2929ppm)
Pd/A+A60 (λ :0.999, CO:5871ppm, O₂:2929ppm)
Pd/A+A120 (λ :1.006, CO:5847ppm, O₂:2961ppm)