

BASIC REACTION MODEL OF AUTOMOBILE EXHAUST GAS TREATMENT OVER Pt-Rh CATALYST

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Summary

A reaction model, which is comprehensive and simple enough to be a base of the dynamic model, of the after-treatment of automobile exhaust gas was proposed. For attaining a short residence time, a small reactor having the 2–73 mm long honeycomb catalyst with Pt and Rh supported alumina washcoated was employed. To formulate the reaction rate, the subsets of reactions such as CO oxidation, C₃H₆ oxidation, N₂O and NO reduction by CO or C₃H₆ were carried out over wide range of gas composition at 140–340 °C. The results calculated with the proposed model well represented the experimental results.

Keywords

Reaction Path Analysis

Introduction

The after-treatment of automobile exhaust gas is a complex reaction system. Moreover, the reaction conditions including the inlet gas composition are changed over time greatly and rapidly according to a driver's operation. For estimating the behavior of the catalytic converter, a dynamic model is desired. In this study, a steady-state reaction model, which is comprehensive and simple enough to be a base of the dynamic model, was developed based on a wide range of experimental results.

Experimental

The commercial catalytic converter is a monolith reactor. Pt and Rh supported Al₂O₃ is washcoated to the inner wall of the cordierite honeycomb. In order to attain the uniform temperature distribution and to lower the reactant conversion, a small reactor was employed. The 1 mm pitch honeycomb catalyst was 2–73 mm long and 10 mm in diameter, cut out of a commercial catalyst. A 90 kg/m³ precious metal/alumina layer is coated; the amount of Pt is 0.7 kg/m³ and Pt/Rh = 3 : 1. The space velocity was 10⁴–7×10⁵ h⁻¹. To formulate the reaction rate, the subsets of reactions such as CO oxidation, HC oxidation, NO reduction by CO or HC, and N₂O reduction by CO were carried out at 140–340 °C. The gas composition was ranged over four orders of magnitude. As the light-off easily takes place in the oxidation reactions, only the reduction experiments were carried out over 190 °C. A

micro gas chromatograph and a mass spectrometer were used for gas analysis. The reaction rate was calculated as a rate of the increase in the molar flow rate of a component per unit mass of the washcoated layer of the catalyst.

Results and Discussion

CO oxidation— CO oxidation was carried out below the light-off temperature, where temperature in the reactor was uniform. The measured CO oxidation rate is plotted against the CO partial pressure in Fig. 1. The O₂ dissociative adsorption model¹ cannot represent the CO oxidation rate dependency on the CO partial pressure and the slow molecular adsorption model² cannot account for the rate dependency on the O₂ pressure.⁴ The model, in which rapid molecular adsorption of O₂ and rate-controlling O₂σ dissociation are assumed,³ represented the experimental data excellently as shown in Fig. 1.

C₃H₆ oxidation— Since the catalytic hydrocarbon

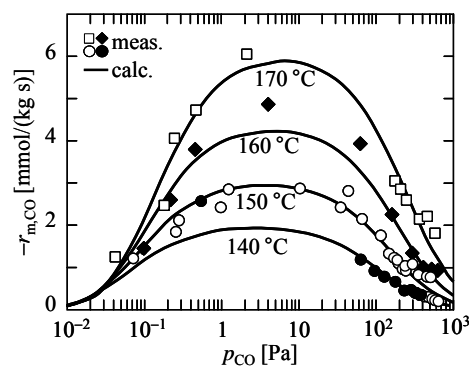


Fig. 1 Dependency of CO oxidation rate on CO partial pressure ($p_{O_2} = 500$ Pa)

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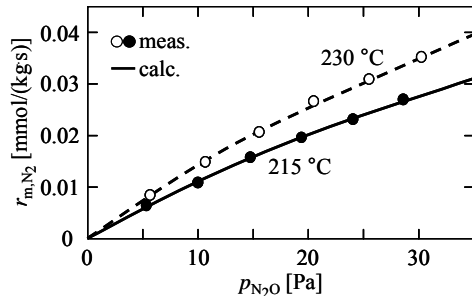


Fig. 2 Dependency of N_2 formation rate on N_2O partial pressure ($p_{CO} = 10$ Pa)

oxidation is too complicated, it was approximated with assumption that the first dissociation step of adsorbed propylene is rate-controlling and leading rapidly to CO_2 and H_2O . Slow O_2 molecular adsorption kinetics reproduced the experimental results as well as the CO oxidation case.

N_2O reduction by CO— N_2 formation rate in N_2O reduction by CO is shown in Fig. 2. Good linearity was observed in the Langmuir plot, $p_{N_2O} / r_{m,N_2}$ vs. p_{N_2O} , of these experimental data. This indicates that N_2 is formed from a single adsorbed species; it should be adsorbed N_2O . *NO reduction by CO*— N_2 and N_2O formation rates were measured. A model which consists of N_2 formation from adsorbed NO and N adatom and N_2O formation from adsorbed NO well represented the experimental results. It is consistent with the previous results reported for NO reduction with C_3H_6 .⁵

Reaction model— Based on the results shown above, a reaction model illustrated in Fig. 3 is proposed. With the steady-state approximation for O adatom and N adatom, the following overall rate equations are derived:

$$-r_{m,CO} = k_{m2} K_{CO} p_{CO} \theta_O \theta_v, \quad (1)$$

$$-r_{m,C_3H_6} = k_{m7} K_{C_3H_6} p_{C_3H_6} \theta_O \theta_v, \quad (2)$$

$$r_{m,N_2O} = k_{m5} K_{NO}^2 p_{NO}^2 \theta_v^2 - k_{m6} K_{N_2O} p_{N_2O} \theta_v, \quad (3)$$

$$r_{m,N_2} = k_{m3} K_{NO} p_{NO} \theta_v^2 + k_{m6} K_{N_2O} p_{N_2O} \theta_v, \quad (4)$$

$$\text{where } \theta_O = \frac{2k_{m1}K_{O_2}p_{O_2} + 2k_{m3}K_{NO}p_{NO} + k_{m5}K_{NO}^2p_{NO}^2}{k_{m2}K_{CO}p_{CO} + 9k_{m7}K_{C_3H_6}p_{C_3H_6}} \theta_v, \quad (5)$$

$$\theta_v = \frac{1 - \frac{k_{m6}K_{N_2O}p_{N_2O}}{k_{m2}K_{CO}p_{CO} + 9k_{m7}K_{C_3H_6}p_{C_3H_6}}}{1 + \frac{k_{m3}}{k_{m4}} + \sum K_j p_j + \frac{2k_{m1}K_{O_2}p_{O_2} + 2k_{m3}K_{NO}p_{NO} + k_{m5}K_{NO}^2p_{NO}^2}{k_{m2}K_{CO}p_{CO} + 9k_{m7}K_{C_3H_6}p_{C_3H_6}}}. \quad (6)$$

The determined parameters are shown in the Arrhenius plot in Fig. 4 with symbols different for the reactions used for analysis. The values below and above 190 °C were determined respectively from the oxidation experiments and the reduction experiments. Even though the parameters were determined from different reactions, the recalculated values are in fairly good agreement with the experimental results. The values determined from C_3H_6

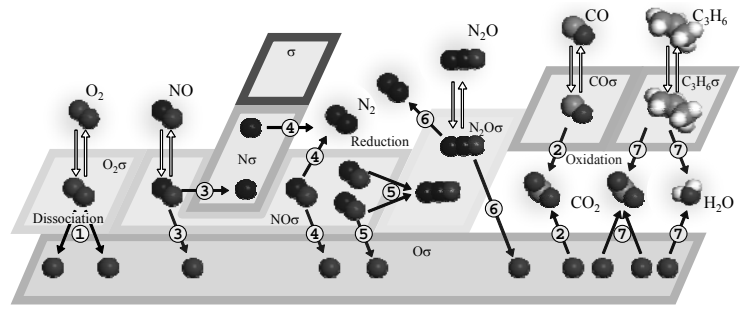


Fig. 3 Proposed reaction model

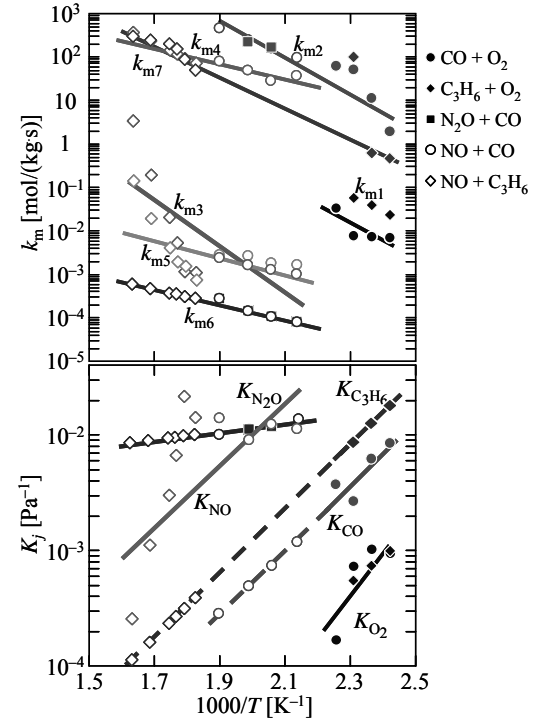


Fig. 4 Determined kinetic parameters

reactions seem to be inaccurate compared with the other values. For further refinement, detailed analysis of hydrocarbon reactions is necessary.

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