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## Abstract

A one-dimensional model was used to describe the transient heat and mass transfer as well as the hydrocarbon (HC) adsorption-desorption and the heterogeneous reactions of NOx and HC in diesel engine exhaust. The behavior of HC and NOx reactions and the HC adsorption-desorption in diesel exhaust have been simulated successfully

ディーゼルエンジン用触媒における炭化水素と

NOxの反応,炭化水素の吸脱着,物質移動および

熱移動をモデル化し,10-15モード下での選択還

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under 10-15 driving cycles. A model for DeNOx catalytic reaction which takes into consideration HC adsorption and desorption and is capable of predicting the performance of DeNOx catalyst using diesel fuel as a supplemental reductant has been successfully developed.

Keywords Modeling, NOx, Hydrocarbon, Adsorption, Desorption, Reaction, Diesel engine, Simulation

要 旨

元型NOx触媒における反応および吸脱着挙動を再 現できるモデルを構築した。

キーワード モデリング,NOx,炭化水素,吸着,脱離,反応,ディーゼルエンジン,シミュレーション

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### 1. Introduction

One approach to the reduction of NOx in leanburn engine exhaust is catalytic reduction by a supplemental hydrocarbon (HC). Problems common to conventional DeNOx catalysts in lean-burn exhaust are a narrow temperature range for maximum catalytic activity and low HC selectivity, which means that, as a reductant, the HC reacts with oxygen to a greater extent than the HC reduces NO. Thus, such DeNOx systems require improved reaction efficiency of supplemental HC for the catalytic reduction, and the temperature of the catalyst must be maintained within a narrow temperature range under generation of the reaction heat by oxidation of a supplemental HC.

In a previous study, we found that NOx was reduced more efficiently under increasing temperature, rather than under a steady state or decreasing temperature. NOx reduction by preadsorbed HC is expected to improve NOx conversion. We have developed a DeNOx catalyst having an HC adsorber in order to further improve NOx conversion. Optimization of the time and quantity required for the HC feed in automobiles diesel engines is clearly desirable from economical, practical and NOx abatement standpoints. However, experimental optimization is time-consuming and costly. One way to solve this problem is to use a computational model that can predict the performance of catalytic monolith reactors in a diesel automotive exhaust system.

Modeling studies of automotive catalytic converters have been reported and discussed based on the merits of the features of the models considered.<sup>1-10)</sup> A number of studies have focused on the transient behavior of a three-way catalyst <sup>2-4)</sup> or the oxygen storage features of three-way catalysts.<sup>5, 6)</sup> Other studies have focused on cold-start emissions,<sup>7)</sup> or the NOx reduction behavior of DeNOx catalysts.<sup>7, 8-10)</sup>

In the present study, the development of a model for lean NOx catalytic reaction by an HC is discussed with respect to HC adsorption and desorption processes, which are capable of predicting the performance of a diesel lean NOx catalyst using diesel fuel as a supplemental reductant.

### 2. Experimental

Catalytic activity measurements were performed using a diesel 2L engine run on a test bench. The engine was set up without exhaust gas recirculation (EGR). The catalyst used in this test is a Pt-based catalyst containing an amount of zeolite in monolith form ( $\phi$  103 × 150 mm at 400 cpsi). The test to determine the calculation parameters was performed at decreasing temperatures, from 325°C to 175°C, using 25°C-steps at intervals from 2 to 3 min, in order to stabilize the catalyst bed temperature. The emission measurements were performed in simulated 10-15 mode with supplemental diesel fuel injection at 1000 ppmC.

The adsorption and desorption tests were performed using a flow reactor and the abovementioned catalyst, without Pt, in order to avoid HC oxidation in small monolith form ( $\phi$  30 × 50 mm at 400 cpsi). The test protocol is as follows: starting at temperatures of 120, 150, 200, and 250°C and at a gas hourly space velocity (GHSV) of 100,000 h<sup>-1</sup> with a mixture of air and HC, which was obtained by vaporized diesel fuel using glow plug heating. The catalyst was saturated with HC at HC concentrations of 1000 and 3300 ppmC. After saturation of HC adsorption on the catalyst, HC injection was ceased, and the catalyst was then heated at a rate of 20°C/min.

### 3. Results and discussion

### 3.1 Modeling

A one-dimensional model was used to describe the transient heat and mass transfer as well as the HC adsorption-desorption and the heterogeneous reactions of NOx and HC in a diesel engine exhaust. The contributions of CO and  $H_2$  to NOx reduction as well as their reaction heats were neglected. The one-dimensional model assumes the temperature, concentration and flow distribution to be uniform throughout the reactor cross section. The following assumptions were also made:

(a) Among transport processes, the heat and mass transfer from the gas phase to the catalyst bed (washcoat: solid phase) and gas-phase convection are the most important factors. 特 集 (b) NOx and HC reactions occur in the catalyst bed, and the reaction rates depend on the concentration of these compounds in the catalyst bed.

(c) HC adsorption occurs inside the catalyst bed, and the adsorbed HC does not react in the bed. Adsorption equilibrium is established instantaneously. The quantity of HC adsorption is described as a function of the HC concentration of the catalyst bed.

A schematic representation of mass and heat transfers and kinetics, which are taken into account in the present model, is shown in **Fig. 1**.

In the present study, we used the following equations describing a catalyst monolith:

Gas mass balance:  $\frac{\partial}{\partial x} \left( \frac{\rho_g}{M_g} u_g [HC]_g \right) = \frac{\rho_g}{M_g} h_{gc}^{HC} S_V \left( [HC]_c - [HC]_g \right) \cdots (1)$   $\frac{\partial}{\partial x} \left( \frac{\rho_g}{M_g} u_g [NOx]_g \right) = \frac{\rho_g}{M_g} h_{gc}^{NOx} S_V \left( [NOx]_c - [NOx]_g \right)$   $\dots \dots \dots \dots \dots (2)$ 

Gas energy balance:

$$\frac{\partial}{\partial x}(\rho_g u_g c_g T_g) = h_{cg} S_v (T_c - T_g) \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (3)$$

Catalyst bed (washcoat: solid) mass balance:

$$\frac{\rho_g}{M_g} h_{gc}^{NOx} S_V \left( [NOx]_g - [NOx]_c \right) = \varepsilon \frac{\rho_g}{M_g} S_{NOx} \quad \cdots \quad (5)$$

Catalyst bed (washcoat: solid) energy balance:

The values of the gas/solid heat and mass transfer coefficients in Eqs. (1)-(6) were estimated based on the Nusselt and Sherwood numbers proposed by Votruba et al.<sup>11</sup>:

$$h_{cg} = \frac{Nu\lambda_g}{dp} \qquad (7)$$
$$h_{gc}^m = \frac{ShD_m}{dp} \qquad (8)$$

$$Sc = \frac{V_g}{D_m}$$
 .....(11)

where the molecular diffusivity of species m,  $D_m$ , was estimated using the Slattery-Bird formula<sup>12)</sup>, and the thermal conductivity of the reaction mixture,  $\lambda_g$ , was approximated as that of air (= 0.0241 · ( $T_f$ /273.15)<sup>0.8</sup> W/m/K,  $T_f = (T_g + T_c)/2$ ). In addition, dp is the hydraulic diameter of the channel.

Using quasi-static approximation, the boundary and initial conditions are

$[HC]_g(0, t) = [HC]_g^{in} \cdots \cdots$
$[HC]_c (0, t) = [HC]_c^{in} \cdots \cdots$
$[NOx]_g(0, t) = [NOx]_g^{in} \cdots \cdots$
$[NOx]_c (0, t) = [NOx]_c^{in} \cdots \cdots$
$T_g(0, t) = T_g^{\ in} \cdots \cdots$
$\frac{\partial T_c}{\partial x}\bigg _{x=0} = 0  \cdots  \cdots  \cdots  \cdots  \cdots  \cdots  (18)$



<u>Mass balance</u>



Fig. 1 Schematic representation of mass and heat transfer aspects taken into account.

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$\frac{\partial T_c}{\partial x}\Big _{x = outlet} = 0  \dots  \dots  \dots  \dots  \dots  \dots  \dots  (19)$
$T_g(x, 0) = T_c(x, 0) = T_g^{in} \cdots \cdots$
$[HC]_{g}(x, 0) = [HC]_{c}(x, 0) = [HC]_{g}^{in} \cdots \cdots (21)$
$[NOx]_g(x, 0) = [NOx]_c(x, 0) = [NOx]_c^{in} \cdots (22)$
$q(x, 0) = q_0(x) \cdots (23)$

Equations (1) - (6) were solved using the finite difference method. Equations (1) - (3) and (5) were discretized by an upwind scheme, and Eqs. (4) and (6) were discretized by a fully implicit scheme in time and the central-difference scheme in space.

### 3.2 Reaction mechanism and kinetics

In our model, we consider the following reaction:

$$HC + O_2 \rightarrow H_2O + CO_2 \cdots \cdots \cdots \cdots \cdots (i)$$
  
NO + HC \rightarrow N\_2 + H\_2O + CO\_2 \cdots \cdots \cdots \cdots (ii)

We assumed the  $O_2$  concentration to be negligible in the rate expression of the HC oxidation due to the excessive  $O_2$  concentration.

The rate of HC oxidation is expressed as follows:  $S_{HC} = A_{HC} [HC]_c^{\alpha HC} \exp(-E_{HC}/RT_c) \cdots (24)$ 

Several studies have examined the reaction kinetics and mechanisms of lean NOx reduction over a noble metal catalyst.<sup>8, 13, 14)</sup> A simplified kinetic model for lean NOx reduction was used in the present study. We assumed that on Pt surfaces the adsorbed NO dissociates into Pt-O and Pt-N, and that HC then reacts with an O adatom to remove the O adatom from the Pt surfaces. Based on this assumption, the rate of NOx reduction is expressed by the following:

 $S_{NOx} = A_{NOx} S_{HC} [NOx]_c^{\alpha NOx} \exp(E_{NOx}/RT_c) \cdot \cdot (25)$ 

The term  $[NOx]_c^{\alpha NOx} \exp(E_{NOx}/RT_c)$  expresses the probability of NO dissociation on the Pt surface, and the term  $S_{HC}$  expresses the probability of O adatom removal by HC. The experimental data was found to agree well with this simplified model.

### 3.3 HC adsorption for diesel engine exhaust

In order to develop a model by which to describe the adsorption of HC on the catalyst emitted from a diesel engine and its fuel injection system, the following approximations are introduced:

(a) The adsorptive consists of a multi-component HC, although the adsorption behavior of diesel exhaust HC can be described as that of a single-component HC.

(b) The equilibrium relationship for adsorbing HC on the catalyst is represented by the Freundlich type

isotherm, and the adsorption equilibrium constant shows the exponential temperature dependence.

Under these assumptions, the adsorption amount at  $T_c$  and  $[HC]_c$  is described as:

$$q^* = \frac{\rho_g}{M_g} \left[ \alpha \exp\left( E_{ad} / RT_c \right) \right] \left[ HC \right]_c^{\frac{1}{n}} \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (26)$$

We next tried to fit the experimental result for saturated adsorption to the model and investigate the above equation.

Equation (26) is transformed into a natural logarithmic form:

$$lnq^* = \left(ln \frac{\rho_g}{M_g} \alpha + \frac{1}{n} ln[HC]_g\right) + \frac{E}{R} \cdot \frac{1}{T} \quad \cdots \quad \cdots \quad (27)$$

The experimental data are plotted in the form 1/Tlnq, as shown in **Fig. 2**.

The fact that the above equation fits well for each HC concentration suggests that Eq. (26) can express the adsorbed amount of HC well. The fact that the lines representing the individual concentrations has the same gradient suggests that Eq. (26) can express the adsorbed amount of HC using the same parameters for different HC concentrations and temperatures within this HC concentration range.

The parameters  $\alpha$ ,  $E_{ad}$  and n of Eq. (26) were determined to be:

 $\alpha = 0.1134, E_{ad} = 2439, n = 2.469$ 

The HC adsorption and desorption rate should be prepared before the converter simulation is performed. The following approximations are introduced

(a) In the adsorption process  $(q \le q^*)$ , the adsorption equilibrium is established instantaneously.

(b) In the desorption process  $(q>q^*)$ , the desorption rate is described by two components.



Fig. 2 Arrehenius plots for amounts of HC adsorption.

One is the desorption rate for the adsorbed HC which needs no activation energy for desorption, and the other is that which requires activation energy for desorption.

Under these assumptions, the adsorption and desorption rates are described:

Adsorption rate:  $\partial q \Big|_{-q^*(t_0 + \Delta t) - q(t_0)}$ 

Desorption rate:

Figure 3 compares the calculated HC concentrations to those measured during the adsorption-desorption test. In the adsorption phase (time< 1260 s), the catalyst was gradually saturated with HC at a temperature of  $150^{\circ}$ C. In the desorption phase (time> 1260 s), the outlet HC concentration was initially low, and reached a maximum value upon increasing the temperature. Thus, the desorption was completed. Fitting the desorption kinetic parameters allows the above behavior to be predicted well.

### 3.4 Determination of parameters

**Table 1** shows the parameter values of the catalyst and the gas used in the calculation. The physical properties of the catalyst bed were estimated as a combined material of the washcoat and substrate.



**Fig. 3** Comparison of observed HC concentration at catalyst outlet with calculated one during the adsorption and desorption test.

**Figure 4** compares the measured and calculated HC and NOx conversions as functions of inlet gas temperature. We obtained very good agreement between the measurement and calculation by fitting the reaction, adsorption and desorption parameters. In the experiment, HC conversion did not reach 100% at high temperature, as is usually observed in diesel engine exhaust. The diffusion of HC was assumed to be a rate-limiting process at high temperature. The calculation was performed based on the assumption that the observed maximum HC conversion was limited to approximately 85% by the

Table 1Parameters of the catalyst monolith (substrate<br/>and washcoat) and the gas phase.

Monolith length	0.155	m
Monolith cross sectional area	0.00833	$m^2$
Cell density	400	cell/in <sup>2</sup>
Density $(\rho_c)$	2280	kg/m <sup>3</sup>
Thermal conductivity $(\lambda_c)$	0.8	W/mK
Specific heat capacity $(c_c)$	975	J/kgK
Density of gas $(\rho_g)$	0.875	kg/m <sup>3</sup>
Specific heat capacity of gas $(c_g)$	1100	J/kgK
Average molecular weight of gas $(M_g)$	0.0290	kg/mol
Heat of HC reaction $(Q_{HC})$	6830	kJ/mol
Heat of HC adsorption $(Q_{ad})$	30000	kJ/mol



Fig. 4 Comparison of experimentally observed HC and NOx conversions with those calculated in our model.

amount of HC mass transfer between the gas phase and the solid phase. The amount of HC mass transfer is expressed by the term  $\rho_g/M_g h_{gc}^{HC}S_v$  $([HC]_g - [HC]_c)$  in Eqs. (2) and (4). The product of  $h_{gc}^{HC}$  and  $S_v$  was determined from the experimental data. In this case, the calculation was performed under the condition that  $h_{gc}^{HC}$  is a constant and  $S_{v}$  is a variable. By decreasing the temperature from 325°C, NOx conversion became a maximum and HC conversion decreased. For inlet temperatures below approximately 200°C, HC adsorption occurred and HC conversion remained above 20%. This adsorption behavior is also described as the HC adsorption occurring at 200°C and the outlet HC concentration decrease, such that HC conversion did not reach 0%. Finally, the behavior of HC and NOx reactions and HC adsorption and desorption was simulated successfully by the present numerical approach.

# 3. 5 Application for simulated japanese 10-15 mode

Figures 5 (a), (b) and (c) show a comparison between the measured and calculated results for outlet gas temperature  $(T_{g})$ , HC conversion, and NOx conversion, respectively, for the simulated 10-15 mode. The behavior of  $T_g$  was predicted successfully, as shown in Fig. 5(a). The behavior of NOx reduction peaks in Fig. 5(b) was also predicted successfully. For the case in which HC adsorption and desorption were not considered, the sharp rises in  $T_g$  due to the oxidation heat of desorbing HC and the NOx reduction peak due to DeNOx through the desorption of HC, were not predicted. The behavior of HC was predicted successfully, as shown in Fig. 5(c). We obtained very good agreement between the measurements and calculations using the present numerical approach.

### 3.6 Application for NOx reaction analysis

Based on our numerical result, we will now discuss the NOx reaction. **Figure 6** shows the HC reaction rate at each section from the inlet. **Figure 7** shows the NOx reaction rate at each section from the inlet. These results indicate that the major part of HC and NOx reacted at the front part of the catalyst converter. Figure 6 also indicates that the HC reaction rate was limited by the HC mass transfer at high temperature, as mentioned above.

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In order to provide an example in which NOx conversion was improved by the exploitation of HC adsorption, a comparison of the predicted NOx conversion between the results taking into account HC adsorption and those not taking into account the HC adsorption under an increase in temperature is shown in **Fig. 8**. The maximum NOx conversion with increasing temperature is twice that with decreasing temperature. The difference between the results taking into account HC adsorption and those



**Fig. 5** Comparison between measured and calculated results: (a) HC conversion, (b) NOx conversion, (c) Outlet gas temperature.



Fig. 6 HC reaction rate at each section from the inlet.



Fig. 7 NOx reaction rate at each section from the inlet.



**Fig. 8** Comparison of the predicted NOx conversion between the results with consideration of HC adsorption and without it.

not taking into account HC adsorption indicates the improvement provided by the exploitation of HC adsorption. The increased amount of reacted HC and the catalyst bed temperature of the backward section of a catalyst monolith improves NOx conversion. This predicted improvement of NOx reduction is very synergistic for the NOx reduction of automotive exhaust emissions. Under driving conditions, a large part of the NOx is emitted during acceleration, at which time the temperature is increasing. If a proper amount of HC is preadsorbed before acceleration, then upon acceleration, NOx can be greatly reduced by desorbing HC. We confirmed the effective use of the HC adsorbent, and supplemental HC is expected to improve NOx reduction under transient conditions.

### 4. Conclusions

We attempted to express the adsorption of diesel exhaust HCs by the Frendlich type isotherm, which has the adsorption equilibrium constant of the exponential temperature dependence. In addition, we attempted to express the NOx reaction using our simplified kinetic equations. The behavior of HC and NOx reactions and HC adsorption and desorption has been simulated successfully by our numerical approach. A model for lean NOx catalytic reaction, taking into account HC adsorption and desorption, which is capable of predicting the performance of diesel lean NOx catalyst using diesel fuel as a supplemental reductant, has been successfully developed. This model was also applied to the optimization of the HC supply using the evolutionary programming method and was found to be useful. In addition, the proposed model was used to estimate NOx reduction on DeNOx catalysts.

### Acknowledgments

This research was supported by Mr. Y. Harada and Dr. T. Fukuma at Toyota Motor Corporation, and Messrs. A. Asano, Y. Sakakibara, T. Kondo, K. Banno, K. Yokota and Dr. H. Shinjoh at Toyota Central R&D Labs., Inc.

## 5. Nomenclature

 $u_g = axial velocity (m/s)$ 

 $\rho = \text{density} (\text{kg/m}^3)$ 

 $M_g$  = average molecular weight (kg/mol)

- $S_v = \text{specific surface area } (\text{m}^2/\text{m}^3)$
- [HC] = HC concentration (ppmC)
- [NOx] = NOx concentration (ppm)
- $h_{gc}^{i}$  = mass transfer coefficient (m/s)
- $h_{cg}$  = heat transfer coefficient (W/m<sup>2</sup>K)
- c = specific heat capacity (J/kgK)
- T = temperature (K)
- $\lambda_c$  = catalyst bed (solid) thermal conductivity (W/mK)
- $Q_{HC}$  = heat of HC reaction (J/mol)
- $Q_{ad}$  = heat of HC adsorption (J/mol)
- $\varepsilon$  = void fraction of catalyst bed
- $q^*$  = amount of HC adsorbed at equilibrium (mol/m<sup>3</sup>)
- q = amount of HC adsorbed (mol/m<sup>3</sup>)
- $E_{ad}$  = temperature dependency of adsorption equilibrium (J/mol)
- $S_i$  = reaction rate (1/s)
- $E_i$  = activation energy (J/mol)
- $A_i$  = pre-exponential factor
- $\alpha_i$  = order of reaction
- $\alpha$  = pre-exponential factor of adsorption
- n =order of adsorption
- $\alpha_{de}$  = order of reaction
- $E_{de}$  = temperature dependency of desorption rate (J/mol)
- p = fraction of desorption path

Subscripts and superscripts

g = gas

### c = catalyst bed (solid)

i =species (HC, NOx)

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(Report received on July 19, 2002)



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