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Application of numerical modeling of selective NO_x reduction by hydrocarbon under diesel transient conditions in consideration of hydrocarbon adsorption and desorption process

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Abstract

A model of NO_x selective reduction by hydrocarbon (HC) was developed, which takes into account the adsorption and desorption of HC. The model was applied for predicting the performance of a De–NO_x catalytic reactor, working under transient conditions such as a legislative driving cycle. Diesel fuel was used as a supplemental reductant.

The behavior of HC and NO_x reactions and HC adsorption and desorption has been simulated successfully by our numerical approach under the transient conditions of the simulated Japanese 10–15 driving cycle. Our model is expected to optimize the design of selective diesel NO_x reduction systems using a diesel fuel as a supplemental reductant. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Numerical modeling; Hydrocarbon; Adsorption; Desorption; NO_x reduction; Diesel engine; Exhaust; HC-SCR

1. Introduction

A catalytic monolith reactor is widely used in automotive exhaust emission control. One of the approaches for reducing NO_x in diesel exhaust is catalytic selective reduction by a supplemental hydrocarbon (HC-SCR). The supplemental HC is required because of the lack of HC as a reductant in a typical diesel exhaust. A conventional De–NO_x catalyst has a narrow temperature range for maximum catalytic activity and low HC selectivity which means that the HC as a reductant oxidizes more rapidly than it reduces NO [1]. Thus, these De–NO_x systems are required to improve their reaction efficiency of a supplemental HC as a reductant and also to maintain the temperature of a catalyst within a narrow temperature range under the generation of the reaction heat by oxidation of a supplemental HC.

Our previous study showed that the NO_x was reduced more efficiently at an increasing temperature than that in a steady state or at a decreasing temperature [2]. NO_x reduction by the HC adsorbed in advance is expected to improve NO_x conversion. It is clearly desirable for a diesel engine automobile to optimize the time and the quantity of the HC feed from the economical, practical and NO_x abatement point of view. However, it is too time-consuming and costly to do an optimization experimentally. One way to solve this problem is to use a computational model which can predict the performance of catalytic monolith reactors in a diesel automotive exhaust system.

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Nomenclature

A_{de}	pre-exponential factor of desorption
A_{i}	pre-exponential factor
c	specific heat capacity (J/kg K)
E_{ad}	temperature dependency of adsorption equilibrium (J/mol)
E_{de}	temperature dependency of desorption rate (J/mol)
E_{i}	activation energy (J/mol)
h_{cg}	heat transfer coefficient (W/m^2 K)
$h_{\mathrm{gc}}^{\mathrm{i}}$	mass transfer coefficient (m/s)
[HC]	total HC concentration (ppm)
M_{g}	average molecular weight (kg/mol)
n	order of adsorption
[NO$_x$]	NO$_x$ concentration (ppm)
p	fraction of desorption path
q	amount of HC adsorbed (mol/m^3)
q^*	amount of HC adsorbed at equilibrium (mol/m^3)
Q_{ad}	heat of HC adsorption (J/mol)
Q_{HC}	heat of HC reaction (J/mol)
S_{i}	reaction rate (1/s)
S_{v}	specific surface area (m^2/m^3)
T	temperature (K)
u_{g}	axial velocity (m/s)

Greek letters

α	pre-exponential factor of adsorption
α_{i}	order of reaction
ε	void fraction of catalyst bed
λ_{c}	catalyst bed (solid) thermal conductivity (W/m K)
ρ	density (kg/m^3)

Subscripts and superscripts

c	catalyst bed (solid)
g	gas
i	species (HC, NO$_x$)

Many studies of the modeling of an automotive catalytic monolith reactor have been reported [3–11]. Most of the studies focused on a three-way catalyst for the gasoline exhaust [3–9]. There are few studies which focused on a De–NO$_x$ catalyst for HC-SCR in the diesel lean exhaust [1,10,11].

In this study, the application of a model of NO$_x$ selective reduction by HC which takes into account the adsorption and desorption of HC is discussed for predicting the performance of a De–NO$_x$ catalyst under transient conditions such as a legislative driving cycle using diesel fuel as a supplemental reductant.

2. Experimental

The catalytic activity measurements were performed using a diesel 2 litre engine run on a test bench in the test cycle which simulated Japanese 10–15 driving test cycle with supplemental diesel fuel injection at the concentration of 1000 ppm as a total HC. The engine was set-up without exhaust gas recirculation (EGR). The catalyst used in this test is a Pt-based catalyst with some amount of zeolite content in monolith form (ϕ103 × 150 mm).

The test for the determination of calculation parameters was performed at decreasing temperatures from 325 to 175°C at every 25°C step at intervals from 2 to 3 min to stabilize the catalyst bed temperature.

3. Modeling

3.1. Reaction mechanism and kinetics

In our model, we consider the following reaction:

$$\mathrm{HC} + \mathrm{O_2} \rightarrow \mathrm{H_2O} + \mathrm{CO_2} \tag{i}$$

$$\mathrm{NO} + \mathrm{HC} \rightarrow \mathrm{N_2} + \mathrm{H_2O} + \mathrm{CO_2} \tag{ii}$$

The contribution of CO and H_2 to NO$_x$ reduction was assumed to be neglected. CO oxidation is neglected because of its small contribution to heat balance for low CO concentration. It was also assumed that O_2 concentration is negligible in the rate expression for HC oxidation because of excessive O_2 concentration.

The rate of HC oxidation is expressed in the following:

$$S_{\mathrm{HC}} = A_{\mathrm{HC}}[\mathrm{HC}]_{\mathrm{c}}^{\alpha_{\mathrm{HC}}} \exp\left(-\frac{E_{\mathrm{HC}}}{RT_{\mathrm{c}}}\right) \tag{1}$$

Many studies of reaction kinetics and mechanisms for lean NO$_x$ reduction over noble metal catalysts have been done [8,11,12]. A simplified kinetic model for lean NO$_x$ reduction [2] was used in our study. We have assumed that on Pt surfaces the adsorbed NO dissociates into Pt–O and Pt–N, then HC reacts with an O adatom to remove the O adatom from the Pt surfaces. Based on this assumption, the rate of NO_x reduction is expressed by the following:

$$S_{NO_x} = A_{NO_x} S_{HC} [NO_x]_c^{\alpha_{NO_x}} \exp\left(\frac{E_{NO_x}}{RT_c}\right) \tag{2}$$

The term $[NO_x]_c^{\alpha_{NO_x}} \exp(E_{NO_x}/RT_c)$ expresses that the probability of NO dissociation on the Pt surface, and the term S_{HC} expresses that the probability of O adatom removal by HC. We were able to fit the experimental data to this simplified model properly [2].

3.2. HC adsorption for diesel engine exhaust

In our model, the following approximations are introduced:

1. The adsorptive consists of multi-component HC. The adsorption behavior of diesel exhaust HC can be described as that of single component HC.
2. The equilibrium relationship for the adsorbing HC is represented by the Freundlich type isotherm, and the adsorption equilibrium constant shows the exponential temperature dependence.

With these assumptions, the adsorption amount at T_c and $[HC]_c$ are described

$$q^* = \frac{\rho_g}{M_g}\left[\alpha \exp\left(\frac{E_{ad}}{RT_c}\right)\right][HC]_c^{1/n} \tag{3}$$

Adsorption and desorption rates should also be determined. The following approximations are introduced:

1. In the adsorption process ($q < q^*$), the adsorption equilibrium is established instantaneously.
2. In the desorption process ($q > q^*$), the desorption rate is expressed by two components. One is the rate for the HC desorption of the non-activated process, the other is that of the activated process.

With these assumptions, the adsorption and desorption rates are described

$$\text{Adsorption rate}: \left.\frac{\partial q}{\partial t}\right|_{t=t_0} = \frac{q^*(t_0+\Delta t) - q(t_0)}{\Delta t} \tag{4}$$

$$\text{Desorption rate}: \left.\frac{\partial q}{\partial t}\right|_{t=t_0} = p\frac{q^*(t_0+\Delta t) - q(t_0)}{\Delta t} - (1-p)\frac{q^*(t_0+\Delta t) - q(t_0)}{\Delta t} A_{de} \exp\left(-\frac{E_{de}}{RT_c}\right) \tag{5}$$

3.3. Basic equations and assumptions

A one-dimensional model was used to study the dynamic behavior of catalytic monolith reactors in a diesel engine exhaust under transient conditions such as a legislated driving cycle. The model neglects the radial distributions of the temperature, concentration and flow.

The following equations describing a catalyst monolith are used [2].

Gas mass balance:

$$\frac{\partial}{\partial x}\left(\frac{\rho_g}{M_g} u_g [NO_x]_g\right) = \frac{\rho_g}{M_g} h_{gc}^{NO_x} S_v([NO_x]_c - [NO_x]_g) \tag{6}$$

$$\frac{\partial}{\partial x}\left(\frac{\rho_g}{M_g} u_g [HC]_g\right) = \frac{\rho_g}{M_g} h_{gc}^{HC} S_v([HC]_c - [HC]_g) \tag{7}$$

Gas energy balance:

$$\frac{\partial}{\partial x}(\rho_g u_g c_g T_g) = h_{cg} S_v (T_c - T_g) \tag{8}$$

Catalyst bed (wash-coat; solid) mass balance:

$$\varepsilon \frac{\partial}{\partial t}\left(\frac{\rho_g}{M_g}[HC]_c\right) = \frac{\rho_g}{M_g} h_{gc}^{HC} S_v([HC]_g - [HC]_c) + \varepsilon \frac{\rho_g}{M_g} S_{HC} - (1-\varepsilon)\frac{\partial q}{\partial t} \tag{9}$$

$$\frac{\rho_g}{M_g} h_{gc}^{NO_x} S_v([NO_x]_g - [NO_x]_c) = \varepsilon \frac{\rho_g}{M_g} S_{NO_x} \tag{10}$$

Catalyst bed (wash-coat; solid) energy balance:

$$\frac{\partial}{\partial t}(\rho_c c_c T_c) = \frac{\partial}{\partial x}\left(\lambda_c \frac{\partial}{\partial x} T_c\right) - h_{cg} S_v (T_c - T_g) + \varepsilon \frac{\rho_g}{M_g} Q_{HC} S_{HC} - (1-\varepsilon) Q_{ad} \frac{\partial q}{\partial t} \qquad (11)$$

Heat of HC oxidation and adsorption is taken into account. Heat of CO oxidation is neglected because of low CO concentration.

The following assumptions also have been made to describe the transient heat and mass transfer as well as HC adsorption–desorption and the reactions of NO_x and HC:

1. The axial heat and mass transfer from the gas phase to the catalyst bed (solid phase) are negligible.
2. NO_x and HC reactions occur in the catalyst bed, and the reaction rates depend on their concentration in the catalyst bed.
3. HC adsorption occurs inside the catalyst bed, and the adsorbed HC does not react until it desorbs.
4. The time constants of the gas-phase temperature and materials response are much smaller than that of the solid thermal response (quasi-static approximation).

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

$$[\mathrm{HC}]_i(0, t) = [\mathrm{HC}]_i^{\mathrm{in}} \quad (\mathrm{i} = \mathrm{g}, \mathrm{c}) \qquad (12)$$

$$[\mathrm{NO}_x]_i(0, t) = [\mathrm{NO}_x]_i^{\mathrm{in}} \quad (\mathrm{i} = \mathrm{g}, \mathrm{c}) \qquad (13)$$

$$[\mathrm{HC}]_g(x, 0) = [\mathrm{HC}]_c(x, 0) = [\mathrm{HC}]_g^{\mathrm{in}} \qquad (14)$$

$$[\mathrm{NO}_x]_g(x, 0) = [\mathrm{NO}_x]_c(x, 0) = [\mathrm{NO}_x]_c^{\mathrm{in}} \qquad (15)$$

$$T_g(x, 0) = T_c(x, 0) = T_g(0, t) = T_g^{\mathrm{in}} \qquad (16)$$

$$\left.\frac{\partial T_c}{\partial x}\right|_{x=0} = \left.\frac{\partial T_c}{\partial x}\right|_{x=\mathrm{outlet}} = 0 \qquad (17)$$

$$q(x, 0) = q_0(x) \qquad (18)$$

The values of gas/solid heat and mass transfer coefficients in Eqs. (6)–(11) were estimated based on the Nusselt and Sherwood numbers proposed by Vortuba et al. [12].

An in-house simulation code, which was written in FORTRAN language, was adopted for heat and mass transfer calculations. Eqs. (6)–(11) were solved using the finite difference method. Eqs. (6)–(8) and (10) were discretized by an upwind scheme. Eqs. (9) and (11) were discretized by a fully implicit scheme in time and the central-difference scheme in space. Parameters of the catalyst monolith (substrate and washcoat) used in the calculations are shown in Table 1.

Table 1
Parameters of the catalyst monolith (substrate and washcoat)

Monolith length (m)	0.155
Monolith cross-sectional area (m^2)	0.00833
Cell density (cell/m^2)	0.258
Density, ρ_c (kg/m^3)	2280
Thermal conductivity, λ_c (W/m K)	0.8
Specific heat capacity, c_c (J/kg K)	975

4. Results and discussion

4.1. Determination of adsorption and desorption parameters

At first, the parameters of Eq. (3) were evaluated from the results of saturated adsorption for different HC concentrations and temperatures. Eq. (3) is transformed into a natural logarithmic form

$$\ln q^* = \left(\ln \frac{\rho_g}{M_g}\alpha + \frac{1}{n}\ln[\mathrm{HC}]_g\right) + \frac{E_{ad}}{R}\frac{1}{T} \qquad (19)$$

The experimental data are plotted as (1/T)–ln q as shown in Fig. 1.

The fact that the above equation fits well at each HC concentration suggests that Eq. (3) can express the adsorbed amount of HC well. The fact that each line

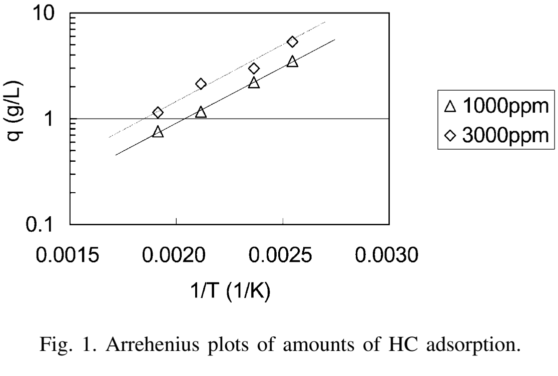


Fig. 1. Arrehenius plots of amounts of HC adsorption.

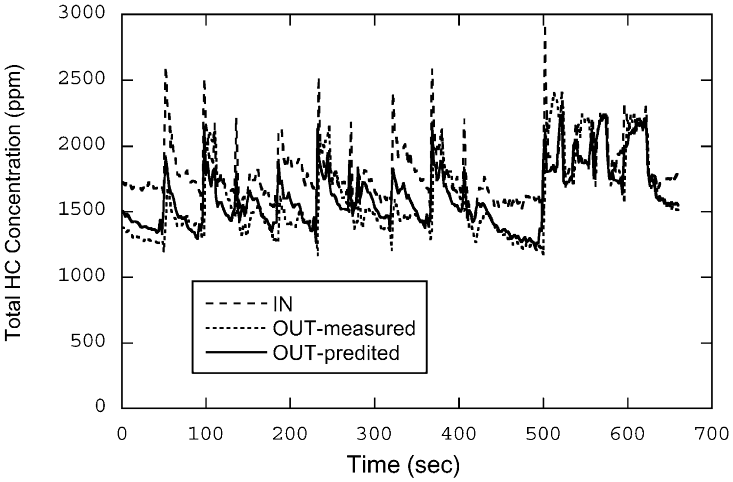


Fig. 2. Comparison between measured and predicted HC concentrations of catalyst monolith without Pt in simulated 10–15 driving cycle.

has the same gradient for the different concentrations suggests that Eq. (3) can express the adsorbed amount of HC using the same parameters for different HC concentrations and temperatures. The parameters α, E_{ad} and n of Eq. (3) were determined: $\alpha = 0.1134$; $E_{\mathrm{ad}} = 2439$; $n = 2.469$.

Fig. 2 presents the comparison between the measured and calculated HC concentration of the catalyst monolith without Pt to avoid the reaction of HC during the 10–15 driving cycle. The desorption kinetic parameters were determined by fitting the experimental result. It is found that we can obtain a good prediction of adsorption and desorption behavior from results of the fitting.

4.2. Determination of reaction parameters

Fig. 3 shows the comparison between the measured and calculated HC and NO_x conversions as a function of inlet gas temperature programmed from 325°C at −10°C/min. We obtained a very good agreement between the measurements and calculations by fitting the reaction, adsorption and desorption parameters. In the experiment, HC conversion did not reach 100% at high temperature as usually observed in the diesel engine exhaust. It is assumed that the diffusion of HC was a rate-limiting process at high temperature. The calculation was done on the assumption that the observed maximum HC conversion was limited up to about 85% by the amount of HC mass transfer between the gas phase and the solid phase. The amount of HC mass transfer is expressed by the term $(\rho_{\mathrm{g}}/M_{\mathrm{g}})\, h_{\mathrm{gc}}^{\mathrm{HC}} S_{\mathrm{v}}([\mathrm{HC}]_{\mathrm{g}} - [\mathrm{HC}]_{\mathrm{c}})$ in Eqs. (7) and (9). The product of $h_{\mathrm{gc}}^{\mathrm{HC}}$ and S_{v} was determined from the experimental data. In this case, the calculation was done where $h_{\mathrm{gc}}^{\mathrm{HC}}$ is a constant and S_{v} is a parameter. For inlet temperatures below about 200°C, the HC adsorption made the outlet HC concentration decreasing, so that the apparent HC conversion remained above 20%.

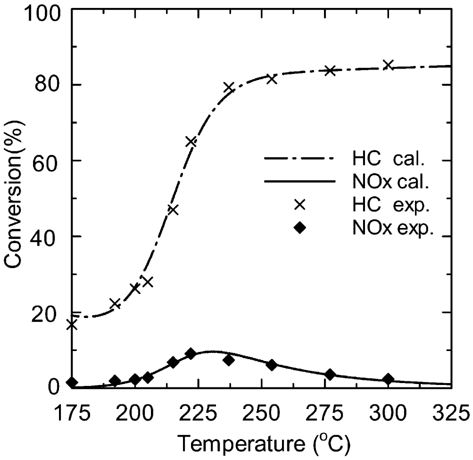


Fig. 3. Comparison of experimentally observed HC and NO_x conversions with those calculated.

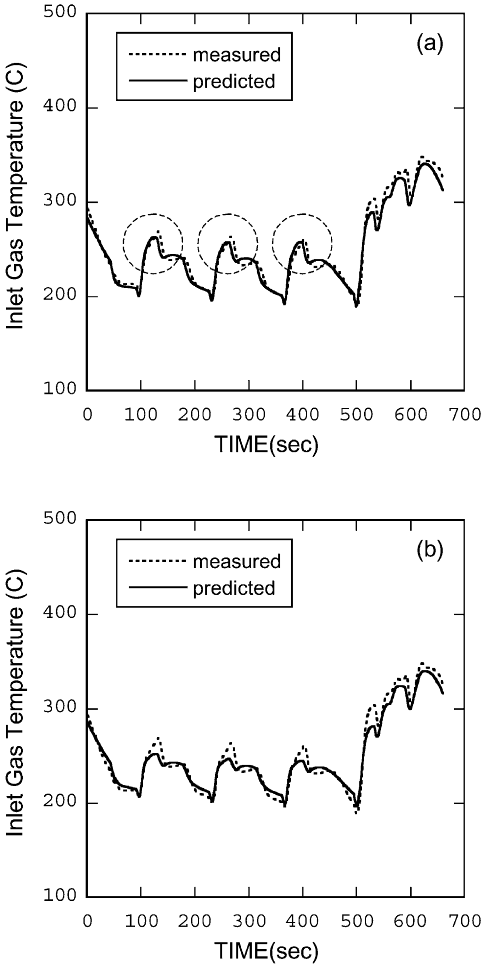


Fig. 4. Comparison between measured and predicted outlet gas temperatures (T_g out) in simulated 10–15 driving test cycle: (a) with adsorption and desorption; (b) without adsorption and desorption.

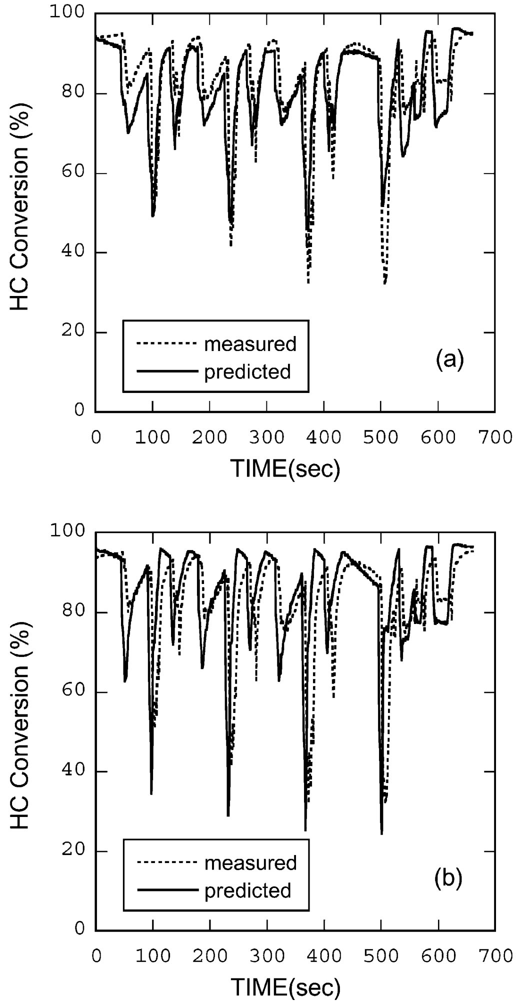
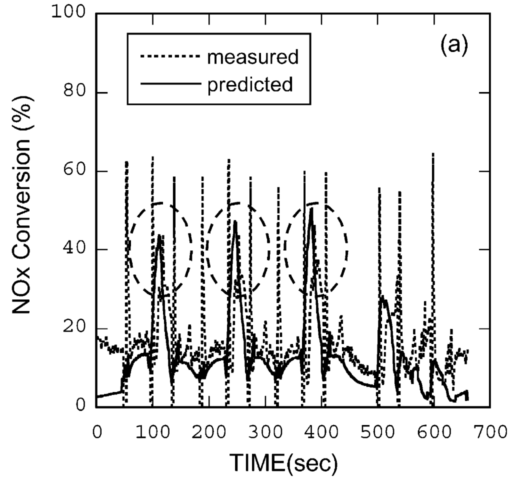


Fig. 5. Comparison between measured and predicted HC conversion in simulated 10–15 driving test cycle: (a) with adsorption and desorption, (b) without adsorption and desorption.

4.3. Application for simulated Japanese 10–15 *driving cycle testing*

Figs. 4–6 show the comparison between the measured and calculated results of outlet gas temperature (T_g), HC conversion and NO_x conversion, respectively, in the simulated 10–15 driving test cycle. We obtained very good agreement between the measurements and calculations by fitting the reaction, adsorption and desorption parameters. The behavior of increasing T_g around the peak temperature as shown in the circles in Fig. 4(a) was simulated successfully by the present numerical approach. These sharp rises in T_g were due to the oxidation heat of desorbing HC which was adsorbed on the catalyst at lower temperature. The behavior of HC was also predicted successfully as shown in Fig. 5. The behavior of NO_x reduction peaks as shown in the circle in Fig. 6(a) was also predicted successfully, but it was not as shown in Fig. 6(b) in the case where HC adsorption and desorption were not considered. It can be considered that



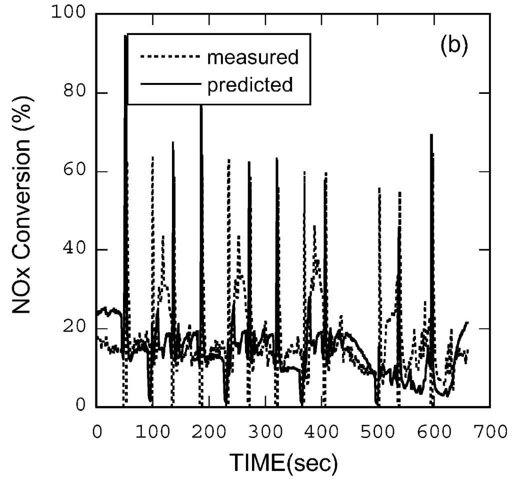


Fig. 6. Comparison between measured and predicted NO_x conversion in simulated 10–15 driving test cycle: (a) with adsorption and desorption, (b) without adsorption and desorption.

these NO_x reduction peaks are due to the reduction by desorbing HC from the comparison of these results.

Fig. 7 shows the comparison between the measured and predicted cumulative NO_x emissions in the simulated 10–15 driving cycle test with various concentrations of supplemental HC. The results show good agreement in the measured and predicted amounts at each concentration of supplemental HC. The consideration of HC adsorption is assumed to be necessary for good prediction of the performance of De–NO_x catalytic monolith reactor as a comparison of predicted results between with and without consideration of HC adsorption. In this case, we showed the results at constant HC concentration. It may be expected that the effective supply of HC improves the NO_x emission more than a constant supply does especially under transient condition such as a usual driving condition which have the alternating patterns of accelerations and decelerations.

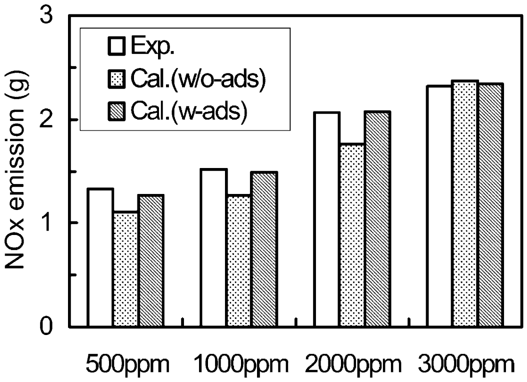


Fig. 7. Comparison between the measured and predicted cumulative NO_x emissions in the simulated 10–15 driving cycle test with various concentrations of supplemental HC.

5. Conclusions

The behavior of HC and NO_x reactions and HC adsorption and desorption under transient conditions has been simulated successfully by our numerical approach. Our model for lean NO_x catalytic reaction with consideration of HC adsorption and desorption was found to be capable of predicting the performance of diesel lean NO_x catalyst using diesel fuel as a supplemental reductant. It is clear that such a model is expected to optimize the design of selective diesel NO_x reduction systems with a supplemental HC.

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