

Analysis of NO_x Conversion using a Quasi 2-D NH₃-SCR Model with Detailed Reactions

Jin Kusaka Hiroyuki Shimao Hiroki Yano
Waseda University

Takanori Murasaki Naotaka Koide Hiroyasu Kawauchi Yoshifumi Kato
Toyota Industries Corporation

Copyright © 2011 Society of Automotive Engineers of Japan, Inc. and Copyright © 2011 SAE International

ABSTRACT

We have constructed a quasi-2 dimensional NH₃-SCR model with detailed surface reactions to analyze the NO_x conversion mechanism and reasons for its inhibition at low temperatures. The model consists of seven detailed surface reactions proposed by Grozzale et al., and calculates longitudinal gas flow, gas phase-catalyst phase mass transfer, and mass diffusion within the catalyst phase in the depth dimension. Using the model, we have analyzed the results of pulsed ammonia (NH₃) feed tests at various catalyst temperatures, and results show that ammonium nitrate (NH₄NO₃) is the inhibitor in NH₃-SCR reactions at low temperatures. In addition, we found that cutting the supply of NH₃ causes decomposition of NH₄NO₃, providing surface ammonia (NH₄⁺), which rapidly reacts with adjacent NO_x, leading to an instantaneous rise in nitrogen (N₂) formation. However, the decomposition rate of NH₄NO₃ depends on the catalyst temperature, hence an optimum addition of reductants, depending on the NH₄NO₃ formation/decomposition rate (and thus catalyst temperature) is required to maximize the NO_x conversion efficiency of SCR catalysts.

INTRODUCTION

In recent years, diesel engines have attracted great interest due to their high thermal efficiency, but they generate more legally restricted species, including NO_x, than gasoline engines. To reduce NO_x emissions NH₃-Selective Catalytic Reduction (SCR) catalysts are often used in commercial vehicles, partly because the associated fuel penalties are low. However, their NO_x to N₂ conversion rates are also low at exhaust gas temperatures less than 200 deg. Celsius. Thus, optimization of catalyst specifications, and the urea/water injection strategy, is required, but this is complicated by paucity of knowledge regarding the reactions involved, and their parameters. Therefore, attempts have been made to elucidate detailed NH₃-SCR surface reactions in model gas experiments by Grossale and coworkers⁽¹⁾⁽²⁾.

However, in addition to empirical data, catalyst models describing detailed surface reactions capable of analyzing phenomena such as deactivation at low temperatures can be very valuable for developing more effective catalysts.

Therefore, in the presented study we constructed an NH₃-SCR reaction model that considers the detailed reactions at the catalyst surface by utilizing the cited authors' model gas test results and the surface reactions they proposed. In addition, we examined factors affecting Fast-SCR reactions, responses of the surface species and overall NO_x conversion rates by examining the effects of injecting pulses of reducing agent (NH₃) at both low and high temperatures.

NUMERICAL METHOD

Fig. 1 presents a schematic illustration of, and equations describing, the mass transport in the gas phase and the catalyst layer. In addition to the streaming motion in one dimension (z-axis) of the NH₃-SCR catalyst, we consider mass diffusion in the catalyst depth dimension (y direction) in each computational grid point. However, mass transportation in the z direction between the grid points in the catalyst is not considered⁽⁴⁾. Hence, the model should be regarded as quasi-two dimensional.

Temperature, pressure, various components of the inlet gas, and both its temperature and pressure at the catalyst exit, are given as inputs in each time step. The temperature and pressure distribution along the z-axis are assumed to be linearly related to the pressures and temperatures at the catalyst inlet and exit. In addition, the temperature of the catalyst bed is assumed to be equal to the gas temperature in the fluid cell. The mass balance in each phase is expressed by Eqs. (1) - (3). In this model, the catalyst is regarded as having two layers, convective mass transfer occurs from the gas phase to the surface of the first catalyst layer, then species diffuse from the first to the second layer. The mass transfer

from the gas phase to the catalyst is expressed using the convective mass transfer coefficient $h_{gc}^{(3)}$, defined in Eq. (4). In addition, since pellet type catalysts were used in the experiments reported by Grossale et al., we assumed that collisions between gaseous species and the catalyst would be more frequent than in a monolithic catalyst. Thus, we set the diffusion coefficient quite high, and adopted values for the catalyst specifications that could reproduce laboratory test results in a trial calculation. The diameter of the channel was set at 6.0 mm, and we changed the length in every calculation to match the space speed (SV) and laboratory test results. We assumed that chemical reactions occur in the catalyst layer. The ordinary differential equation (ODE) system derived from species production rates is solved by the ODE solver, DVODE⁽⁵⁾.

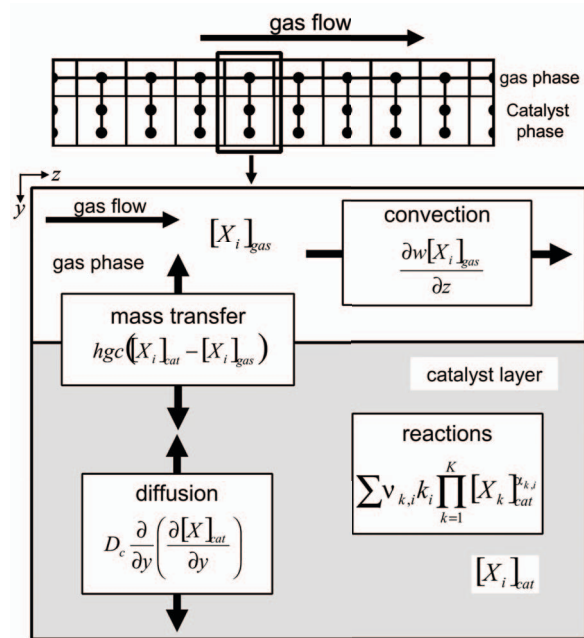


Fig. 1 Schematic Diagram of the NH₃-SCR Model

Gas phase

$$\frac{\partial [X_i]_{gas}}{\partial t} + \frac{\partial w [X_i]_{gas}}{\partial z} = h_{gc} ([X_i]_{cat,1} - [X_i]_{gas}) S_{v_{gas}} \quad (1)$$

Catalyst phase 1

$$\begin{aligned} \frac{\partial [X_i]_{cat,1}}{\partial t} = & h_{gc} ([X_i]_{gas} - [X_i]_{cat,1}) S_{v_{cat}} \\ & + D_c \frac{\partial}{\partial y} \left(\frac{\partial [X_i]_{cat}}{\partial y} \right) + \sum v_{k,j} k_i [X_i]_{cat,1}^{\alpha_{k,j}} \end{aligned} \quad (2)$$

Catalyst phase 2

$$\frac{\partial [X_i]_{cat,2}}{\partial t} = D_c \frac{\partial}{\partial y} \left(\frac{\partial [X_i]_{cat}}{\partial y} \right) + \sum v_{k,j} k_i [X_i]_{cat,1}^{\alpha_{k,j}} \quad (3)$$

$$h_{gc} = \frac{sh_i D_g}{dp} \quad (4)$$

$$Sc_i = \frac{v_g}{D_{gas}} \quad (5)$$

$$Sh_i = A \left[\text{Re} \frac{dp}{z} \right]^{0.43} Sc_i^{0.56} \quad (6)$$

$$D_c = C \frac{d}{3} \sqrt{\frac{8RT}{\pi M}} \quad (7)$$

$[X_i]$: ith species density

S_v : specific area

D_c : diffusion coefficient in catalyst layer

dp : hydraulic diameter

Re : Reynolds number

C : coefficient

h_{gc} : convective mass transfer coefficient

D_g : gas diffusion coefficient

sh_i : sherwood number

Sc_i : Schmidt Number

v_g : kinematic viscosity

DETAILED NH₃-SCR SURFACE REACTION

In the present model, the NH₃-SCR reactions⁽¹⁾ proposed by Grossale et al. are described by reactions R.1 - R.8, where σ and γ represent acid and base sites, respectively. σH^+ and σNH_4^+ are formed on the acid sites, while γOH , nitric (γNO_3^-), nitrite (γNO_2^-) and ammonium nitrate (γNH_4NO_3) groups are generated on the base sites. The Fast-SCR reaction, which occurs when $NO : NO_2 = 1 : 1$ is indicated in Eq. (8). The Fast-SCR reaction begins with reaction R.1. H₂O is absorbed and decomposed, yielding σH^+ and γOH at the acid and base sites, respectively. γOH is then decomposed to σH^+ and γO^{2-} , according to R.2. The γO^{2-} reacts with NO_2 to form γNO_2^- and γNO_3^- , occupying further base sites, as shown in R.4, and the NH_3 (reducing agent) reacts with σH^+ to form σNH_4^+ according to R.3. Then, γNO_2^- , which is an unstable surface species, reacts with σNH_4^+ in the vicinity of the γNO_2^- to form N_2 and H_2O , as shown in R.6. This is the basis of the NO_x conversion.

In contrast, the other product of the NO_2 adsorption in R.4, γNO_3^- , reacts with NO to form γNO_2^- in the reverse reaction, R.5. However, this γNO_3^- reacts with σNH_4^+ to form the stable species γNH_4NO_3 , which occupies some of the base sites according to R.7. This is thought to constrain NO_x conversion, because γNO_2^- is not formed from NO by reverse reaction of R.5. The γNH_4NO_3 formation reaction shown in R.7 is the dominant path under low temperature conditions. The reverse reaction of R.7, describing the decomposition of γNH_4NO_3 , is activated at catalyst temperatures exceeding 200 degrees Celsius. As a result, γNO_3^- is formed, then this γNO_3^- and NO generate γNO_2^- according to the reverse reaction, R. 5, thereby enhancing the NO_x conversion rate.

In the presented study, we set the rate parameters for each reaction in R.1 to R.8 using the model gas test results reported by Grossale and coworkers.

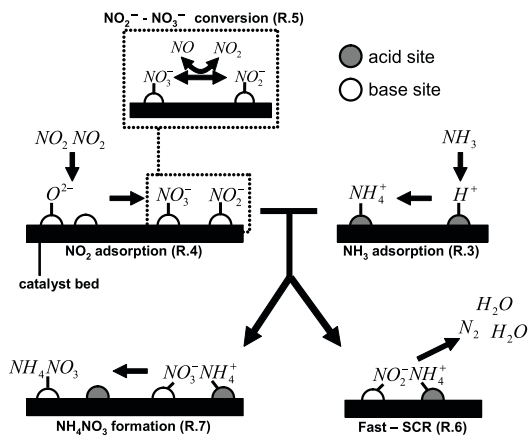
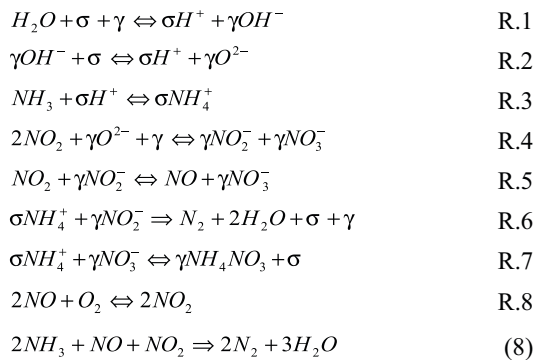


Fig. 2 The model's SCR reaction scheme

RESULTS AND DISCUSSION

NH₃ ADSORPTION REACTION

The reaction parameters and acid site density were set using the NH_3 saturation adsorption test results⁽¹⁾ and adsorption curve⁽²⁾ presented by Grossale et al. We also set the catalyst specifications, including porosity, using this curve. The test and calculation conditions are summarized in Table 1.

Table 1 Exp. & Cal. Conditions for NH_3 Adsorption Analysis

Catalyst temp. deg. C	150, 180, 200	
SCR inlet gas	NH_3 ppm	1000
	H_2O vol%	1.0
	O_2 vol%	2.0
	He	Balance
SV 1/h	23000	
Catalyst weight g	0.08	

Fig. 3 compares calculated time courses of NH_3 absorption at 180 deg. C (obtained using the fitted parameters) and corresponding laboratory test results⁽²⁾. The point at which the rate of increase of the absorption begins to decline is believed to mark the point at which adsorption starts to occur inside the catalyst, rather than on its surface. In addition, no discharge of NH_3 was observed during the first 200 sec.

in the experiments, probably due to its physical adsorption on the catalyst. It is not possible to reproduce these phenomena using our model, in which adsorption of the NH_3 is expressed solely by the chemical reactions in R.3. However, as shown in Fig. 4, the consequences of this underestimation of adsorption, at each tested temperature, are minor, indicating that the model generally reproduces the experimental NH_3 adsorption profiles robustly.

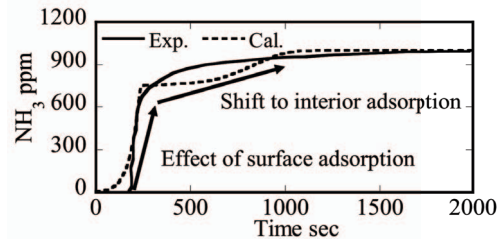


Fig. 3 Exp.⁽²⁾ and Cal. NH_3 Adsorption Curves (Cat. Temp. 180 deg. C.)

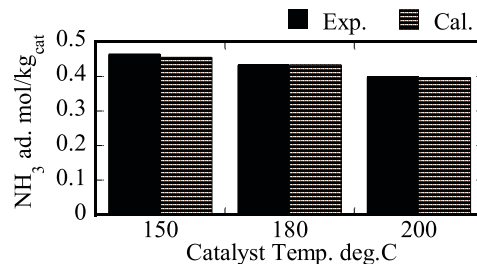


Fig. 4 Exp. and Cal. NH_3 Adsorption Results⁽¹⁾

NO₂ adsorption reaction

In the next step, we selected parameters for reactions R.4 and R.5, and compared results calculated using them (under conditions listed in Table 2) to experimental results⁽¹⁾.

Table 2 Exp. & Cal. Conditions for NO₂ Adsorption

Catalyst temp. deg. C	50, 150, 200	
SCR inlet gas	NO_2 ppm	1000
	H_2O vol%	1.0
	O_2 vol%	2.0
	He	Balance
SV 1/h	18800	
Catalyst weight g	0.16	

As shown in Fig. 5, these numerical results generally reproduce the experimental results well. At a catalyst temperature of 50 deg. Celsius, no NO_2 discharge was observed during the first 100 sec. experimentally, due to physical absorption (as mentioned for NH_3 earlier). Our model does not display this delay, since it does not consider physical adsorption. However, discharge of NO_2 was observed almost immediately after experiments started at about 150 and 200 deg. Celsius. Thus, physical adsorption appears to have little influence, and our model appears to generate results that are highly consistent