2011 AP1: Prediction of Deactivation and Regeneration of DeNOx Catalyst using Simple Reaction Model - 1st Report : Model for Predicting Deactivation

Prediction of Deactivation and Regeneration of DeNOx Catalyst using Simple Reaction Model

- 1st Report : Model for Predicting Deactivation

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Selective catalytic reduction (SCR) is an effective technique to reduce nitrogen oxides (NOx) from diesel engine emissions. In this study, a simple reaction model for predicting DeNOx performance deactivation and NH3 slip on a vanadium-based commercial catalyst is developed to evaluate the effects of the gas component and temperature, and NH3/NO feed ratio. This model predicted that NOx conversion rate does not depend on the catalyst temperature when the feed ratio becomes small. The calculation results at 250 deg.C indicated that high excess air ratios and low NO and SO2 concentrations suppress the DeNOx performance deactivation. It was also shown that keeping the NH3/NO feed ratio small is necessary to avoid NH3 slip.

1. Introduction

International Maritime Organization (IMO) adopted more strict NOx emission limits, “Tier II” and “Tier III”. The “Tier III” standards require an 80 % NOx emission reduction below “Tier I” standards. In order to control NOx emission from marine diesel engines under the limit, it is necessary that not only to improve combustion performance but also to apply after-treatment system for the exhaust gas.

Selective Catalytic Reduction (SCR) is one of the most efficient after-treatment systems to reduce NOx from an exhaust gas. It has high treatment efficiency and can be operated in emissions containing SOx. However, it has two major problems; a deactivation of DeNOx performance and NH3 slip.

The “Tier III” standards apply only in Emission Control Areas (ECAs). ECAs will be designated in specific locations, such as ports and congested marine traffic areas. SCR will be operated in ECAs. Therefore, it can be important to consider the lifetime of the catalyst and the regeneration methods of deactivated DeNOx performance.

It is desirable to investigate in detail SCR systems on the study. However, there are too many parameters, such as catalyst temperature and feed gas components. Moreover it takes a long time to conduct just one experiment. For this reason, it is an effective method to predict the effect of each element on a DeNOx performance using a numerical simulation.

Many studies about a DeNOx reaction in SCR catalyst from a fundamental experiment [1-4] to a numerical analysis [5-9] have been reported. However, no these studies target a marine diesel engine; using fuel including high sulfur and performing at relatively low temperature. In addition, reaction models considering a deactivation or a regeneration of SCR catalyst have not been found, and a total reaction process has not been organized.

This paper describes a simple reaction model for deactivation of SCR, which can predict the temporal change in a NOx conversion. The model was based on outcomes obtained by experiments using macro-reactor on a commercial V2O5-TiO3 monolith catalyst. The model has been validated, and the numerical simulation has been carried out in order to investigate the effects of gas components and a feed ratio of NH3 to NO concentration (NH3 /NO) on deactivation of DeNOx performance and NH3 slip.
2. Calculation model

2.1 Calculation method

A one-dimensional simple reaction model focusing on a reaction in the catalyst was developed in this study. In this model, concentrations of each gas component in the catalyst change along the exhaust flow direction. Hydrolysis of the urea water was neglected, and the reducing agent was injected into the catalyst as NH₃. For nitrogen oxides, only NO was taken into account. The change in the gas composition (NH₃, NO, SO₂, SO₃, H₂O, N₂, O₂, NH₄HSO₄ (ammonium bisulfate)) was calculated for the hypothetical cell that was expressed by dividing the catalyst equally along the exhaust flow direction. The calculated gas composition was transported to the next computational cell, except for NH₄HSO₄. A residence time in each cell was determined by a reciprocal of a space velocity (SV). The space velocity is defined as \(SV = Q/V\) where \(Q\) is the gas flow rate \([m^3/h]\), and \(V\) is the catalyst volume \([m^3]\).

2.2 Reaction model

When a numerical analysis of the deactivation of DeNOx performance on the surface of the SCR catalyst is carried out, the following three chemical reactions are required.

(1) Reaction of NOx reduction
(2) Reaction of SO₂ oxidation
(3) Deposition and decomposition of NH₄HSO₄ and deactivation of DeNOx performance

The reaction between NH₃ and NO in SCR catalyst can be expressed according to the following well-known equation:

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1)
\]

This reaction proceeds on the surface of the catalyst as follows. (1) Adsorption of NH₃, (2) Reaction of NO and NH₃, (3) Desorption of products. Figure 1 shows the schematic diagram of DeNOx reaction. The rate of the reaction is described by the following equation using the Rideal-Eley mechanism [13]:

\[
\frac{dC_{\text{NO}}}{dt} = -k_c A_p \frac{K_{\text{NH}_3} C_{\text{NO}} C_{\text{NH}_3}}{1 + K_{\text{NH}_3} C_{\text{NH}_3}} \quad (2)
\]

\[
k_c = A_{\text{NO}} \exp\left(-\frac{E_{\text{NO}}}{RT_{\text{cat}}}\right) \quad (3)
\]

where \(k_c\) is the chemical reaction rate \([m^3/m^2h]\), \(C\) is the volume concentration \([m^3/m^3]\), the subscript is the gas component, \(A_p\) is the geometric surface area per unit volume \((1044 \text{ m}^2/\text{m}^3)\), \(T_{\text{cat}}\) is the catalyst surface temperature \([K]\), and \(K_{\text{NH}_3}\) is the NH₃ adsorption constant \((0.05 \times 10^6)\). \(A_{\text{NO}}\) and \(E_{\text{NO}}\) are the pre-exponential factor \((8898 \text{ m}^3/\text{m}^2h)\) and the activation energy \((23.87 \times 10^3 \text{ J/mol})\) on the reaction of NO, respectively [10]. \(R\) is the gas constant \([\text{J/mol K}]\).

Sulfur content in fuel is oxidized to SO₂ by combustion in diesel engines. Vanadium-based SCR catalysts have the potential to oxidize SO₂ to SO₃. The oxidation reaction of SO₂ can be expressed as follows:

\[
2\text{SO}_2 + (1/2)\text{O}_2 \rightarrow \text{SO}_3 \quad (4)
\]

In a V₂O₅-TiO₂ catalyst, DeNOx and SO₂ oxidation reactions simultaneously occur on the surface of the catalyst, and SO₂ reaction proceeds more slowly than DeNOx reaction [14]. The equation of a SO₂ oxidation rate has been proposed by many researchers [14-16]. In this study, the SO₂ oxidation rate is calculated from [15]:

Figure 1. Schematic diagram of DeNOx reaction
\[ \frac{dC_{SO2}}{dt} = -k_r A_p C_{O2}^\alpha C_{H2O}^\beta (1 + k_{NO} C_{NO}) C_{SO2} \]  \hspace{1cm} (5)

where

\[ k_r = A_{so} \exp \left( -\frac{E_{SO2}}{RT_{cat}} \right) \]  \hspace{1cm} (6)

\( k_r \) is the chemical reaction rate on the reaction of \( SO_2 \), \( \alpha_{O2} \), \( \alpha_{W} \), \( k_{NO} \) and \( k_{NH3} \) are the reaction constant of \( O_2 \), \( H_2O \), \( NO \) and \( NH_3 \), respectively. \( A_{SO2} \) and \( E_{SO2} \) are the pre-exponential factor and the activation energy. \( \alpha_{O2} \) is set to the same value with the reference [15]. Other constants are determined from the experimental results of two cases at \( CSO = 800 \text{ ppm} \), \( C_{O2}=13.0 \text{ %} \), \( SV=3000 \text{ h}^{-1} \) and \( C_{H2O}=10 \text{ %} \), \( C_{NO}=1500 \text{ ppm} \) [17]. The model constants are listed in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{SO2} )</td>
<td>m³/h</td>
<td>( 20.8 \times 10^4 )</td>
</tr>
<tr>
<td>( E_{SO2} )</td>
<td>J/mol</td>
<td>( 47.7 \times 10^3 )</td>
</tr>
<tr>
<td>( \alpha_{O2} )</td>
<td>-</td>
<td>( 0.082 )</td>
</tr>
<tr>
<td>( \alpha_{W} )</td>
<td>-</td>
<td>( 0.56 )</td>
</tr>
<tr>
<td>( k_{NO} )</td>
<td>m³/m³</td>
<td>( 3.95 \times 10^3 )</td>
</tr>
<tr>
<td>( k_{NH3} )</td>
<td>m³/m³</td>
<td>( 1.04 \times 10^9 )</td>
</tr>
<tr>
<td>( E_{NH3} )</td>
<td>J/mol</td>
<td>( 58.2 \times 10^3 )</td>
</tr>
</tbody>
</table>

The chemical compounds (ammonium sulfate \( ((NH_4)_2SO_4) \), ammonium bisulfate etc…) are produced by a reaction of \( H_2O \), \( SO_3 \) and \( NH_3 \) in the exhaust gas is deposited on the catalyst, and the deposition of the chemical compounds deteriorates activity of the catalyst. In this case, the deactivation of catalytic performance can be modeled by the deposition of \( NH_4HSO_4 \). Deactivation of the catalyst performance is dependent on the gas and catalyst temperatures. Therefore, the reaction of \( NH_4HSO_4 \) is given by

\[ NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \]  \hspace{1cm} (7)

\[ K = \frac{p_{NH3} p_{SO3} p_{H2O}}{p_{H4SO4}} \]  \hspace{1cm} (8)

\[ log\ K = -\frac{81530}{4.574T_a} + 5.25 log\ T_a + 10.5 \]  \hspace{1cm} (9)

where \( K \) is the equilibrium constant, \( p \) is the partial pressure of each component, and \( T_a \) is the ambient gas temperature. \( NH_4HSO_4 \) is deposited if equilibrium constant of Equation (8) is greater than that of Equation (9). However, these equations express the reaction in the gas. In order to apply these equations to the catalyst, Equation (9) is modified by Kelvin equation formula [19], as defined by:

\[ ln\ \frac{P}{P_0} = -\frac{2\sigma M_{ab}}{\rho_{ab} r_{pore} T_a} \]  \hspace{1cm} (10)

Here, \( \sigma \) is the surface tension, \( M_{ab} \rho_{ab} \) is the molecular weight and density of \( NH_4HSO_4 \), and \( r_{pore} \) is the pore radius of catalyst. Surface tension and density values are used in the reference [20]. The pore radius is approximated by a Rosin-Rammler distribution function [21] obtained from the measured value.

This equation shows that the condensation is caused by the pressure \( P \) that is lower than the saturated vapor pressure \( P_0 \) of the gas in the pore. In addition, \( K \) (Eq. (9)) corresponds to \( P_0 \) (Eq. (10)).

Relationship of DeNOx reaction and deposition amount of \( NH_4HSO_4 \) on the catalyst is given by the following expression:

\[ k_r = A_{so} \exp \left( -\frac{E_{SO2}}{RT_{cat}} \right) \times \Phi = k_{o} \Phi \]  \hspace{1cm} (11)

Deactivation function \( \Phi \) is defined by the ratio of the initial reaction rate constant \( k_{o} \) and the reaction rate constant after the deactivation of the catalyst performance \( k_r \). Although it is necessary to determine the relationship between the

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deposition amount of NH₄HSO₄ and the deactivation function, the experimental results [11] shown in Fig. 2 is adopted in this study. The amount of sulfate ion per catalyst mass [mmol/gcat] on the horizontal axis of Fig. 2 is replaced by the deposition amount of NH₄HSO₄. Effect of the deactivation by NH₄HSO₄ on the SO₂ oxidation reaction expressed by Eq. (5) is not taken into account. In this calculation condition, the minimum ambient gas temperature is assumed to be 250 deg. C and the ambient gas temperature is the same value as the catalyst surface temperature, since the ambient gas temperature does not change temporarily.

3. Results and discussions

3.1 Validity of calculation model

The characteristics of the model equation were confirmed by the analysis of DeNOx reaction using only Equation (2). The effect of DeNOx performance at NH3/NO feed ratio \( \alpha \) is shown in Figure 3. Urea is used as a reducing agent in the following reference experiments. \( K_{NH3} \) is set to \( 0.05 \times 10^6 \). The calculation results are almost consistent with the experimental results. When the NH3/NO feed ratio \( \alpha \) is 1, NO reacts completely with NH3 in theory. However, NOx conversion is reduced in accordance with reduction in temperature. Considering the NH3 slip, NH3 is discharged from the catalyst at a catalyst temperature of under 300 deg. C. Thus, at the stoichiometric NH3/NO feed ratio (\( \alpha = 1 \)), complete reaction of NH3 can be achieved at the catalyst temperature over 300 deg. C. When feed ratio \( \alpha \) becomes smaller, changes in the NOx conversion does not occur with respect to the catalyst temperature. If the catalyst temperature and the feed ratio \( \alpha \) are maintained above 250 deg. C and below 0.8, it is not necessary to adjust the feed ratio in order to keep the NOx conversion. This result represents simplicity of the reducing agent injection control.

Figure 4 shows the relationship between NOx conversion and the feed ratio \( \alpha \) as function of \( SV \). The catalyst temperature is set at 200, 250 deg. C. Effect of the residence time in the catalyst is examined by the change in \( SV \). Because residence time becomes longer as \( SV \) decreases, NOx conversion can be improved. In addition, a linear relationship between NOx conversion and feed ratio \( \alpha \) can be maintained at smaller \( SV \). The NOx conversion tends to be independent of feed ratio \( \alpha \) with the increase of feed ratio under all conditions. Ammonia slip is occurred at this time. Hence, it is important to perform the injection
control of the reducing agent in the range of the linear relationship of the feed ratio and NOx conversion.

In the presence of SO2, SO2 can be oxidized to SO3 over monolithic SCR catalyst containing V2O5-TiO2. Catalyst performance is deactivated by NH4HSO4 produced from SO3, NH3, and H2O. In order to confirm the capability of this model to predict the deactivation of the catalyst performance, the calculation results were compared with the deactivation tests for 100 hours [11]. Figure 5 shows an example of a temporal change in the NOx conversion. The catalyst temperature is 200, 230 and 250 deg. C, and the SO2 concentration is 30 and 80 ppm, respectively. The decomposition of NH4HSO4 is dependent on various conditions, such as ambient gas components and temperature. Predicted and experimental results are almost consistent with all conditions. This consistency shows that this deactivation model is able to reproduce the reaction behavior of this catalyst.

Figure 5 shows that DeNOx performance is gradually reduced with the increase of time during the long operation as the amount of NH4HSO4 deposition on the catalyst surface is increased. Since the deactivation of DeNOx performance is affected by the catalyst temperature and SO2 concentration, relation between the deposition temperature of NH4HSO4 and the sulfur content in the fuel is investigated. The maximum deposition temperature in this model is compared with the deposition temperature for the sulfur contained in the fuel in the MAN's literature [22]. The comparison between maximum deposition temperatures of NH4HSO4 in this model and reference [22] is shown in Figure 6. The pore radius r_pore of Eq. (10) is set at 0.4 nm, which is defined as 1 % passing diameter of the Rosin-Rammler distribution function. Relationship between the sulfur content in the fuel and SO2 concentration was determined from the following chemical reaction expression:

\[
C_a H_b S_c + \lambda (a + b/4)(O_2 + 3.773N_2) \rightarrow \alpha a CO_2 + (b/2)H_2O + cS\bar{O}_2 + \lambda (a + b/4)3.773N_2 + \{a + b/4(\lambda - I) - c\}O_2
\]

\( C_a H_b S_c \) is the fuel, and \( \lambda \) is the excess air ratio (\( \lambda = 2.5 \)). Complete combustion is assumed. Number of atoms of carbon and hydrogen in the fuel are \( a = 13 \) and \( b = 28 \), respectively. In Figure 6, it can be confirmed that the SO2 concentration in the exhaust gas is about 800 ppm at approximately 3.3 % sulfur in the fuel. The low sulfur component in the fuel inhibits NH4HSO4 deposition, which obtained from this model and the reference [22]. When NH3 has been changed to 1500, 1000, 500 ppm at SO2 = 800 ppm and \( \alpha = 1 \), the maximum temperature in NH4HSO4 deposition is not affected at 325, 323, 319 deg. C, respectively.

### 3.2 Effect of feed gas concentration on deactivation of catalyst performance

Feed H2O and O2 concentrations in Figures 3 and 5 are 10 % and 13 %, respectively. Concentrations of H2O and O2 in the exhaust gas from diesel engines consist of 7.07~3.60 % and 10.1~15.4 % in the excess air ratio at 2.0~4.0. Therefore, effect of DeNOx performance on H2O and O2 concentrations is examined by the change in the excess air ratio. The effect of the excess air ratio \( \lambda \) on the deactivation rate is shown in Figure 7. NOx conversion oscillates up to around 3 hours after the start of NOx reduction. This is because that NH3 concentration varies depending on the NH4HSO4 deposition in each computational cell.

The effect of O2 and H2O concentrations on the deactivation of DeNOx performance is taken into account by H2O and O2 in Equation (5) and the H2O partial pressure in Equation (8). With the increase of the excess air ratio, the H2O concentration decreases and the O2 concentration increases. Accordingly, NH4HSO4 deposition is reduced with low H2O concentration and the inhibition of SO2 oxidation. This result indicates that DeNOx performance can be maintained by the increase of the excess air ratio. The increase in excess air ratio can be achieved by reducing fuel consumption rate or improving the performance of
In this model, SO2 and NO concentrations affect the deactivation of DeNOx performance. Figure 8 shows the influence of SO2 and NO concentrations on DeNOx performance at 8 hours after the start of NOx reduction. Ammonia concentration is determined by NO concentration, because the overall NH3/NO feed ratio remains stoichiometric. It appears that the deactivation of DeNOx performance is enhanced in the presence of SO2 and NO. This effect is confirmed by Equation (5) and (8).

These results suggest that the long catalyst lifetime can be achieved by fuel desulfurization or NOx reduction technologies in diesel engines. NOx reduction in diesel engines is effective to reduce the consumption of the reducing agent and to maintain DeNOx performance.

### 3.3 Relation between NH3/NO feed ratio \( \alpha \) and NH3 slip

Ammonia slip is caused by low DeNOx reaction rate. When the high catalyst temperature is maintained and a substoichiometric feed ratio (\( \alpha < 1 \)) is employed with the injection control of the reducing agent, NH3 slip does not occur. In this model, because Equation (2) represents the reaction rate after NH3 adsorption equilibrium, unreacted NH3 is discharged from the catalyst without adsorbed on the catalyst. Ammonia slip is dependent on NH3 feed amount and deactivation of DeNOx performance. Relationship between NH3 slip and \( \alpha \) was investigated. As the initial condition of the calculation, \( \alpha \) and feed NO concentrations are changed so that NO concentration of the catalyst outlet is fixed at 300 ppm. \( \alpha \) was set to six types.
of $0.5$, $0.66$, $0.75$, $0.8$, $0.825$ and $0.85$.

Figure 9 shows the change in the NO concentration at 8 hours after the start of NOx reduction. The temporal change of NH$_3$ slip is shown in Figure 10. Deactivation of DeNOx performance proceeds faster in large $\alpha$. NOx conversion is aggravated rapidly in $\alpha \geq 0.8$. Therefore, it is necessary to regenerate the catalytic performance. On the other hand, NH$_3$ slip does not occur in $\alpha < 0.8$. Thereby, NH$_3$ slip can be prevented by keeping the small feed ratio $\alpha$ without reaching the maximum catalyst potential. It is necessary to reduce NOx in an engine from the results of NH$_3$ slip.

4. Conclusions

Modeling of a vanadium-based commercial SCR catalyst reaction was carried out to predict the effect of DeNOx performance on feed gas component, NH$_3$/NO feed ratio and catalyst temperature. This model is based on the experimental results by the micro-reactor. The following conclusions were deduced.

(1) NOx conversion does not depend on the catalyst temperature in the high temperature region, when NH$_3$/NO feed ratio becomes smaller. If the catalyst temperature and the feed ratio $\alpha$ are maintained above 250 deg. C and below 0.8, it is not necessary to adjust the feed ratio in order to keep the NOx conversion. Thereby, the catalyst temperature is excluded from the factor to control the catalytic performance. In addition, the injection control of the reducing agent must be performed in the linear range of the relationship between the NH$_3$/NO feed ratio and the NOx conversion.

(2) High excess air ratios and low NO and SO$_2$ concentrations suppress the DeNOx performance deactivation. In diesel engines, improvement of fuel consumption rate and NOx reduction is required in order to maintain DeNOx performance.

(3) For avoidance of NH$_3$ slip, it is important to keeping the small NH$_3$/NO feed ratio without reaching the maximum catalyst potential. Therefore, NOx reduction by combustion technologies in diesel engines is one of the most effective methods.

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References


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