

Study of NO_x Reduction Behavior on Iron Ion-exchanged Zeolite Catalyst for ULEV50

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ABSTRACT

In response to further strengthening of emission regulations in recent years, the Urea Selective Catalytic Reduction system is gaining attention as a technology for reducing the NO_x emitted from diesel engines. The reaction between NO_x and NH₃ is known to exhibit high reduction performance (Fast-SCR) when the ratio of NO₂ to NO_x is 50%; that is to say, when the NO and NO₂ quantities are equal. On the other hand, the dynamic NO_x reduction behavior of an iron ion-exchanged zeolite (Fe-Zeolite) catalyst was analyzed in detail, and the results showed that high reduction performance can be obtained by intentionally varying the NO₂ ratio.

The behavior mentioned above is thought to occur because NO₂ adsorbs to the Fe-Zeolite catalyst and manifests a buffer function with respect to NO₂ ratio variation, so the effective NO₂ ratio near the catalyst reaction active sites is 50% even when the NO₂ ratio of the feed gas to the catalyst is not constantly maintained at 50%. Application of this intentional variation of the NO₂ ratio to vehicle control enabled clearance of the LEV-III ULEV50 standard.

1. Introduction

Recently, movements are accelerating to reduce carbon dioxide (CO₂) emissions that are said to be a cause of global warming. In addition, various regions have decided to introduce stricter emission regulations such as the LEV-III standard (California, U.S.A.) and the European Euro6 standard. Furthermore, regulations are also considered to limit the emission of nitrogen dioxide (NO₂), which is said to have an adverse effect on respiratory organs and to be a substance contributing to acid rain and photochemical smog. Moreover, European emission regulations require emission conversion technology that can adapt to a wider range of driving conditions, and European authorities have proposed and are investigating a new driving mode that adds high-load driving conditions to better represent real driving behavior of typical drivers. This new driving mode will replace the conventional New European Driving Cycle (NEDC) mode, which mainly consists of low-load driving.

Three-Way Catalyst (TWC) systems are widely used as an exhaust gas purification technology in gasoline engines, which mainly use stoichiometric air-fuel ratio control. On the other hand, TWC is not an effective exhaust gas purification technology in diesel engines, which use lean air-fuel ratio control. Carbon monoxide (CO) and hydrocarbons (HC) can be oxidized by a Diesel Oxidation Catalyst (DOC) as a method for converting exhaust gas at a lean air-fuel ratio, i.e., in an atmosphere with excess oxygen. However,

nitrogen oxides (NO_x) need to be converted by reduction, and it is a challenge to promote the reaction in a lean air-fuel ratio atmosphere, so exhaust gas conversion technology other than TWC is needed. Typically known technologies for converting NO_x in a lean air-fuel ratio atmosphere are NO_x Storage Catalyst (NSC) systems that store NO_x at lean air-fuel ratios and then reduce the stored NO_x by rich spike (varying the air-fuel ratio by increasing the fuel injection quantity), and Urea Selective Catalytic Reduction (Urea-SCR) systems that dose Urea (NH₂CONH₂) water into the exhaust gas and use the generated ammonia (NH₃) to reduce NO_x. The NSC system does not require major changes to the aftertreatment system, but the catalyst capacities and precious metal quantities need to be increased to maintain sufficient NO_x reduction performance at high NO_x concentrations, and optimum rich spike control and other technologies are required for NO_x reduction, which results in a technically challenging aftertreatment system that uses large quantities of expensive precious metals. On the other hand, due to the chemical reaction characteristics of the Urea-SCR system, high NO_x reduction performance can be expected even at high NO_x concentrations, and R&D has been promoted as a promising technology for vehicle types with high NO_x emissions that make clearing strict emission regulations a challenge.

The authors⁽¹⁾ proposed a combination of stoichiometric combustion and a Urea-SCR system as a low emission technology for diesel engines that require high NO_x

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reduction performance. That study indicated that high NO_x reduction in the initial stages of the driving mode is the most important factor for clearing strict emission regulations. To reduce NO_x from the initial stages of the driving mode, it is necessary to rapidly heat up the entire catalyst system to the activation temperature, and to generate an appropriate quantity of NO₂ for NO_x reduction. One rapid heat-up method is to control the engine fuel injection to emit large quantities of CO and HC, oxidize this CO and HC with a DOC and a Catalyzed Diesel Particulate Filter (cDPF) located immediately after the engine, and use that reaction heat to heat up the catalyst system⁽¹⁾. In this case it is necessary to strengthen the oxidation performance of the DOC and cDPF, but this also creates the issue that the oxidation performance is too strong in the middle of the driving mode when the system is sufficiently warmed up, so excess NO₂ is generated and the NO_x reduction performance of the Urea-SCR system is reduced.

To simultaneously address both of the above conflicting issues, this study hypothesized and verified an NO₂ ratio (percentage calculated by NO₂/NO_x) buffer concept based on NO₂ adsorption on the catalyst. As a result, it was found that the high NO_x reduction performance of the Urea-SCR system can be maintained by intentionally varying the NO₂ ratio, even under conditions where excess NO₂ is generated. In addition, prospects were obtained for clearing the LEV-III ULEV50 standard by applying the NO₂ ratio buffer concept to engine control, and those contents are also reported herein.

2. NO_x Reduction Characteristics of Urea-SCR Catalysts

2.1. Urea-SCR System

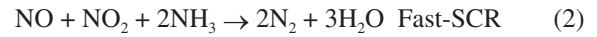
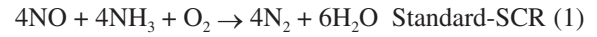
The Urea-SCR system generates NH₃ by dosing Urea water into the exhaust gas and performing hydrolysis⁽²⁾, and then uses the generated NH₃ to selectively reduce NO_x on the catalyst. Most on-board catalysts are iron (Fe) or copper (Cu) ion-exchanged zeolite catalysts. To obtain high NO_x reduction performance using a Urea-SCR catalyst, the following conditions need to be met.

2.1.1. Exhaust gas temperature

Generation of NH₃ from Urea water by hydrolysis requires an exhaust gas temperature of 180°C or more. When Urea water is dosed at less than that temperature, byproducts are generated, urea deposition occurs inside the exhaust pipe, and the Urea water cannot be effectively used as an NO_x reduction agent. However, the zeolite used in the Urea-SCR catalyst has NH₃ adsorption capability, so the adsorbed NH₃ can be used to reduce NO_x even under temperature conditions of less than 180°C. Nevertheless, the NH₃ quantity that can be adsorbed is limited, so to obtain high NO_x reduction performance, the catalyst temperature should quickly reach the Urea water hydrolysis temperature or higher.

2.1.2. NO₂ ratio in the Urea-SCR catalyst inlet gas

The following three reactions are known as NO_x reduction reactions by NH₃ in the steady state⁽³⁾.



Of the above three reactions, the reaction that proceeds from a low temperature and can be expected to exhibit high reduction performance (>95%) is the Fast-SCR reaction⁽³⁾ shown in Eq. (2). To realize high reduction performance in a Urea-SCR system, it is necessary to maintain the NO₂ ratio at the optimum ratio (NO₂ ratio = 50%).

Figure 1 shows a schematic illustration of the reaction at different NO₂ ratios. When there are equal quantities of nitrogen monoxide (NO) and NO₂ in the exhaust gas as shown in Fig. 1 (b), NO_x is reduced by the Fast-SCR reaction shown in Eq. (2). On the other hand, when there is excess NO as shown in Fig. 1 (a), a quantity of NO equal to the NO₂ quantity is reduced by the Fast-SCR reaction, and the excess NO is reduced by the Standard-SCR reaction. When there is excess NO₂ as shown in Fig. 1 (c), the excess NO₂ is reduced by the Slow-SCR reaction.

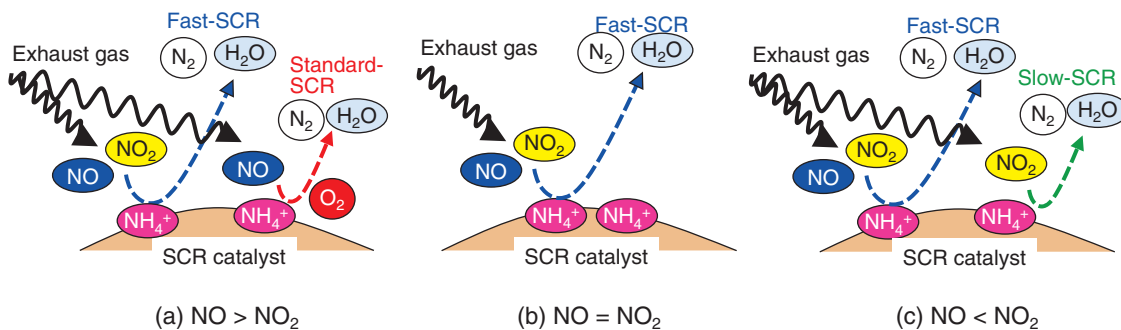


Fig. 1 Schematic illustration of NO_x reduction under various steady-state conditions, (a) NO > NO₂, (b) NO = NO₂, (c) NO < NO₂

2.2. Steady-state NO_x Reduction Characteristics of Fe-Zeolite Catalysts

The NO_x reduction performance of an iron ion-exchanged zeolite (Fe-Zeolite) catalyst at various NO₂ ratios was measured using a HORIBA model gas tester. Figure 2 shows an overview of the test apparatus. The model gas for the test was prepared by controlling the flow rates of water vapor (H₂O), oxygen (O₂) and nitrogen (N₂) gases using a Mass Flow Controller (MFC) to mix the designated quantities, passing these base gases through a heater to heat the mixture to the designated temperature, and then similarly controlling the NO, NO₂ and NH₃ component gases to the designated ratios using the MFC and mixing these component gases with the base gases. The prepared model gas was fed to the test catalyst, and the reactant gas after the test catalyst was measured using a HORIBA MEXA-6000FT that can simultaneously measure NO and NO₂. All model gas tests described hereafter measured the NO_x reduction performance using this apparatus.

The model gas was based on a gas composition simulating that of the exhaust gas during vehicle mode driving, and the gas conditions composition was set to increase the NO_x concentration in order to facilitate observation of NO_x behavior (Table 1). Figure 3 shows the NO_x reduction performance measurement results at that time.

It was confirmed that the NO_x reduction performance in the steady state shows the highest conversion rate at an NO₂ ratio of 50%, and that the Fast-SCR reaction exhibits high NO_x reduction characteristics. On the other hand, the NO_x conversion rate dropped when the NO₂ ratio deviated from 50%. The NO_x emitted from the engine is mostly NO, so in

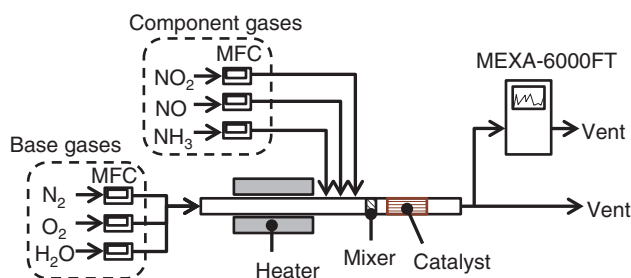


Fig. 2 Synthetic gas bench

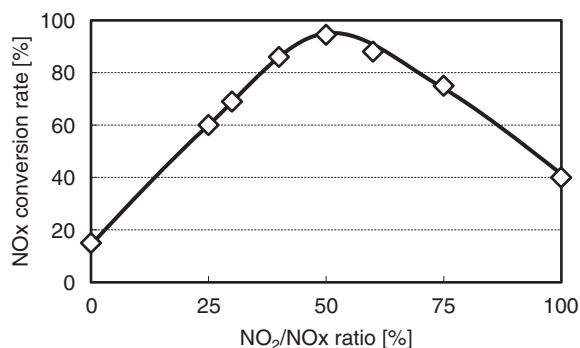


Fig. 3 NO_x conversion rate at each NO₂/NO_x ratio

Table 1 Gas conditions for various NO₂/NO_x ratios

NO _x [ppm]	200
NO ₂ /NO _x ratio [%]	0, 25, 30, 50, 60, 75, 100
NH ₃ [ppm]	200
O ₂ [%]	6
H ₂ O [%]	7
N ₂	Balanced
Space velocity [1/h]	37500
Temperature [°C]	250

order to control the NO₂ ratio fed to the Fe-Zeolite catalyst to 50%, it is important to appropriately oxidize the NO to NO₂ using an oxidation catalyst located upstream of the Fe-Zeolite catalyst.

2.3. Issues for Using a Urea-SCR Catalyst System in a Vehicle

The previous section described the features of the Urea-SCR catalyst system and the NO_x reduction behavior on an Fe-Zeolite catalyst in the steady state. However, the exhaust gas temperature, flow rate, NO_x concentration and other factors related to the Urea-SCR reaction vary greatly in the vehicle condition, making it a challenge to keep a stable NO_x reduction reaction such as in steady state. With regards to this issue, Tokui et al.⁽³⁾ and Murata et al.⁽⁴⁾ conducted studies based on the mechanism in an Fe-Zeolite catalyst whereby ammonium nitrate (NH₄NO₃) is generated from NO₂ and NH₃ at a high NO₂ ratio and the generated NH₄NO₃ and NO react at a low NO₂ ratio⁽⁵⁾. These studies confirmed that keeping the NO₂ ratio during the driving mode within the range of 50 ± 10% leads to high NO_x reduction performance, and reported the need to select oxidation catalysts with appropriate oxidation performance.

On the other hand, a recent trend in emission regulations is to emphasize test methods that are more deeply based on actual driving, and demands are increasing for low emissions during driving with a wider range of engine loads than current driving modes. In addition, as emission regulation values become stricter, high NO_x reduction performance is required from the initial stages of each mode. This means that it is necessary to enhance oxidation catalyst performance to generate NO₂ from lower temperatures, which makes it a challenge to select an oxidation catalyst that achieves an appropriate NO₂ ratio (50 ± 10%) after warm-up. These demands for conflicting catalyst characteristics are a major issue facing the Urea-SCR catalyst system.

2.4. SCR Catalysts Concept for Optimized NO_x Reduction at Transient Vehicle Operation

To develop emissions technology that better conforms to the vehicle condition, it is considered necessary to understand dynamic NO_x reduction behavior in which the NO₂ ratio varies, unlike the steady state shown in Fig. 1.

Regarding the dynamic NO_x reduction characteristics of SCR catalysts, NO₂ adsorption behavior on an Fe-Zeolite catalyst has been reported⁽⁶⁾, which suggests the existence of NO_x reduction behavior via NO₂ adsorption.

Therefore, as a result of examining the phenomenon of NO₂ adsorption to an Fe-Zeolite catalyst in conjunction with NO_x reduction behavior, it is thought that the adsorbed NO₂ acts as a buffer for the varying NO₂ ratio. Figure 4 shows a schematic illustration of the NO_x reduction behavior due to adsorbed NO₂. This concept is noted hereafter as the NO₂ ratio buffer concept.

When the NO₂ ratio is more than 50% as shown in Fig. 4 (a), the excess NO₂ is adsorbed near the catalyst active sites. Conversely, when the NO₂ ratio is less than 50% as shown in Fig. 4 (b), the excess NO contacts the adsorbed NO₂ and reacts by Fast-SCR. Therefore, a high NO_x conversion rate can be obtained without limiting the NO₂ ratio variation width by alternately repeating the states in Fig. 4 (a) and Fig. 4(b). In this manner, the NO₂ ratio buffer concept is a new approach that establishes local Fast-SCR on the catalyst via adsorbed NO₂ by intentionally repeating the high and low NO₂ ratio conditions, attaining high NO_x reduction performance even when the NO₂ ratio varies.

3. Investigation of Dynamic NO_x Reduction Behavior of Urea-SCR Catalysts

3.1. Verification of NO_x Reduction Behavior when the NO₂ Ratio Varies

The dynamic NO_x reduction behavior when the NO₂ ratio varies was measured using a model gas tester to verify the NO₂ ratio buffer concept. Test conditions (NO₂ ratio variation cycle test) were set that simulate NO₂ ratio variation in the vehicle condition, and the NO_x reduction characteristics were confirmed. When accelerating in the vehicle condition, the NO_x quantity increases and the NO₂ ratio drops, so the NO₂ ratio variation method in the cycle test was set to increase the NO gas concentration. In consideration of the Urea dosing control delay due to rapid acceleration, the NH₃ concentration was maintained at the high NO₂ ratio side condition. The NO₂ ratio variation time

Table 2 Synthetic gas conditions for cycle test (Mode 1)

	High NO ₂ /NO _x ratio	Low NO ₂ /NO _x ratio
NO [ppm]	50	350
NO ₂ [ppm]	150	150
NO ₂ /NO _x ratio [%]	75	30
NH ₃ [ppm]	200	200
O ₂ [%]	6	6
H ₂ O [%]	7	7
N ₂	Balanced	Balanced
Time [s]	30	10
Space velocity [1/h]	37500	
Temperature [°C]	250	

was set to a cycle with a high NO₂ ratio for 30 s and a low NO₂ ratio for 10 s in reference to the vehicle driving mode pattern. Table 2 and Fig. 5 show the test conditions, and Fig. 6 shows the test results.

The NO_x conversion rate when the NO₂ ratio was varied between 75% and 30% was between 80% and 100%, and indicated an average conversion rate of 90% (red line in Fig. 6). The average conversion rate for the NO₂ ratios of 75% and 30% obtained from the steady-state test results was 73% (blue dotted line in Fig. 6), so a 17% increase in the conversion rate was confirmed. That is to say, higher NO_x reduction performance than that in the steady state is exhibited by varying the NO₂ ratio, which suggests that the

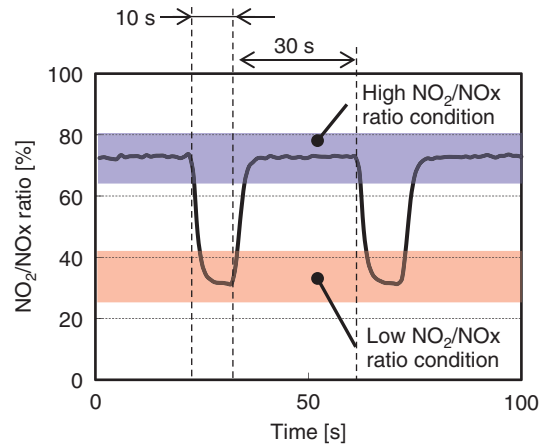


Fig. 5 Cyclic curve of NO₂ ratio (Mode 1)

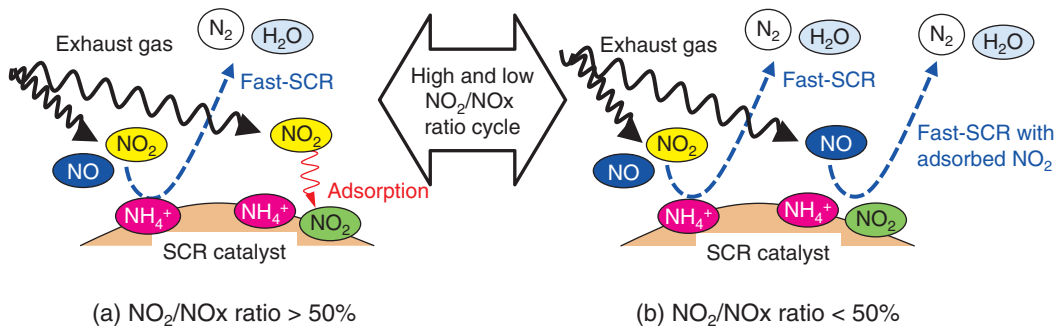


Fig. 4 Schematic illustration of NO_x reduction behavior during NO₂/NO_x ratio cycle, (a) high NO₂/NO_x ratio, (b) low NO₂/NO_x ratio

inferred NO_2 ratio buffer concept is manifesting.

Examination of the NO_x reduction behavior in Fig. 6 reveals that there is a time difference between the NO_2 ratio behavior and the NO_x conversion rate behavior. That is to say, when the NO_2 ratio changes from a higher state to a lower state, the NO_x conversion rate shifts accordingly to a higher conversion rate. However, when the NO_2 ratio changes from a lower state to a higher state, the NO_x conversion rate does not change immediately, and instead exhibits behavior to shift to a lower conversion rate after a delay. This is thought to indicate the following behavior: at a low NO_2 ratio, the NO_2 adsorbed to the Fe-Zeolite catalyst is consumed by local Fast-SCR on the catalyst, and at a high NO_2 ratio, the excess NO_2 is adsorbed to the Fe-Zeolite catalyst and the NO_x conversion rate then gradually drops to the same level as that in the steady state as the adsorption sites on the Fe-Zeolite catalyst become filled with NO_2 .

In order to verify the inferred dynamic NO_x reduction behavior described above, that is to say NO_2 adsorption at a high NO_2 ratio and local Fast-SCR on the catalyst at a low NO_2 ratio, NO_2 ratio variation cycle tests were performed with different conditions to confirm the effects on NO_x reduction performance.

3.2. Verification of NO_2 Ratio Variation Buffering Effects of Adsorbed NO_2

The effects on reduction performance when the NO_2

Table 3 Synthetic gas conditions for cycle test (Mode 2)

	High NO_2/NO_x ratio	Low NO_2/NO_x ratio
NO [ppm]	50	150
NO_2 [ppm]	150	150
NO_2/NO_x ratio [%]	75	50
NH_3 [ppm]	200	200
O_2 [%]	6	6
H_2O [%]	7	7
N_2	Balanced	Balanced
Time [s]	30	10
Space velocity [1/h]	37500	
Temperature [°C]	250	

ratio was set to vary between 75% and 50% were verified as conditions under which excess NO is not generated at a low NO_2 ratio. Table 3 lists the test conditions, and Fig. 7 shows the test results and compares them with the results of the steady-state test.

In the Mode 2 test, the NO_2 ratio variation width was changed to between 75% and 50%. This mode exhibited almost the same NO_x conversion rate performance as that in the steady state shown in Fig. 3 at both a high NO_2 ratio and low NO_2 ratio, and it was confirmed that the high NO_x reduction performance at a high NO_2 ratio described in section 3.1 above was not exhibited. That is to say, it is thought that high reduction performance could not be manifested because the conditions were such that excess NO was not generated

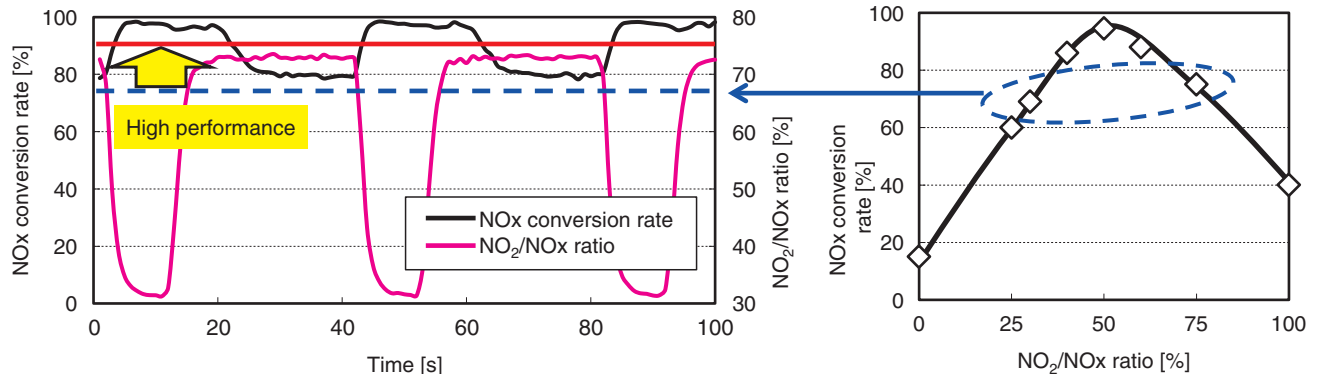


Fig. 6 Results of synthetic cycle gas test (Mode 1)

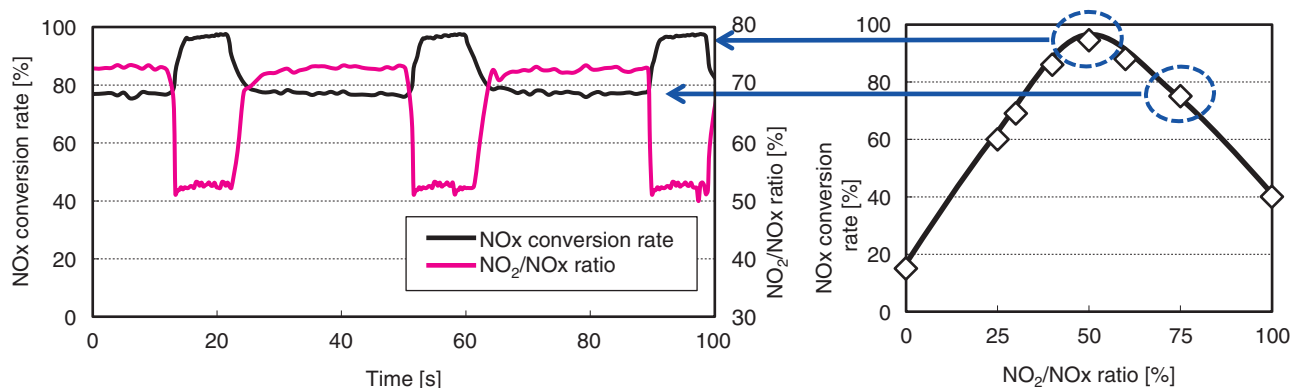


Fig. 7 Results of synthetic cycle gas test (Mode 2)

on the low NO₂ ratio side, so the adsorbed NO₂ was not consumed, and the excess NO₂ could not be adsorbed at a high NO₂ ratio. Therefore, the Mode 2 results could be said to support the NO₂ ratio buffer concept approach.

Next, the NO₂ behavior was verified when the time on the low NO₂ ratio side (NO₂ ratio = 30%) was changed to vary the excess NO feed quantity. Compared to Mode 1 in Table 2, Table 4 shows Mode 3 in which the low NO₂ ratio time was shortened to 5 s, and Table 5 shows Mode 4 in which the low NO₂ ratio time was lengthened to 30 s. Figure 8 shows the time-base trend in the NO₂ gas concentration in each test mode in order to investigate the detailed NO₂ gas behavior.

The NO₂ concentration behavior in Mode 1, which uses the same conditions as those described in the previous section, was as follows. The NO₂ concentration remained low for approximately 7 s after switching to the high NO₂ ratio, and then rose to reach a steady state at around 50 ppm (NO_x conversion rate 78%). The NO_x conversion rate in this steady state matched the NO_x conversion rate in the NO₂ ratio 75% steady state shown in Fig. 3, indicating that only the reduction reactions (Fast-SCR and Slow-SCR) were occurring. The low NO₂ concentration range behavior before reaching the steady state is thought to result from other than reduction reactions, and the NO₂ concentration rises over time, so this can be understood as the NO₂ adsorption behavior to the Fe-Zeolite catalyst.

In contrast, the time to reach the steady state was shorter in Mode 3, which had a shortened low NO₂ ratio time. Conversely, in Mode 4 which had a lengthened low NO₂ ratio time, the time until the NO₂ concentration began to rise was also longer, and it was observed that the steady

Table 4 Synthetic gas conditions for cycle test (Mode 3)

	High NO ₂ /NO _x ratio	Low NO ₂ /NO _x ratio
NO [ppm]	50	350
NO ₂ [ppm]	150	150
NO ₂ /NO _x ratio [%]	75	30
NH ₃ [ppm]	200	200
O ₂ [%]	6	6
H ₂ O [%]	7	7
N ₂	Balanced	Balanced
Time [s]	30	5
Space velocity [1/h]	37500	
Temperature [°C]	250	

Table 5 Synthetic gas conditions for cycle test (Mode 4)

	High NO ₂ /NO _x ratio	Low NO ₂ /NO _x ratio
NO [ppm]	50	350
NO ₂ [ppm]	150	150
NO ₂ /NO _x ratio [%]	75	30
NH ₃ [ppm]	200	200
O ₂ [%]	6	6
H ₂ O [%]	7	7
N ₂	Balanced	Balanced
Time [s]	30	30
Space velocity [1/h]	37500	
Temperature [°C]	250	

state was not reached by the 30 s mark.

Based on these NO₂ behavior results, it is thought that the NO₂ adsorption quantity at the high NO₂ ratio increases as the low NO₂ ratio time becomes longer, that is to say as the excess NO feed quantity increases. This is thought to indicate that the excess NO undergoes local Fast-SCR

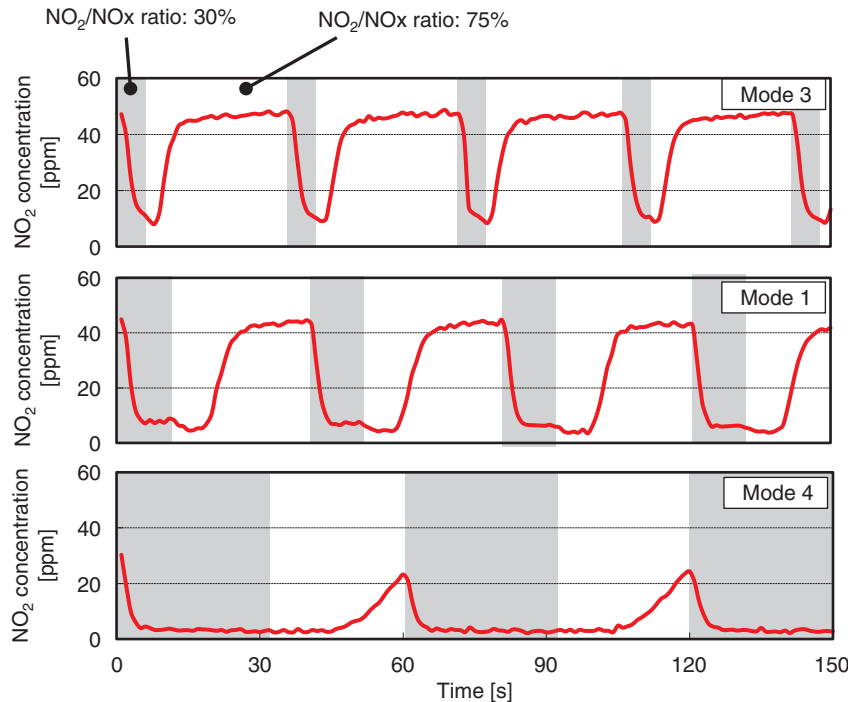


Fig. 8 Results of synthetic cycle gas test (Mode 1, Mode 3 and Mode 4)

reactions with the NO_2 adsorbed to the catalyst, with the result that the NO_2 is consumed, returning the NO_2 adsorption sites to a state that enables adsorption.

The above verification results and observations enabled to experimentally confirm the NO_2 ratio buffer concept proposed in the previous section. That is to say, the method of taking into account the NO_2 adsorption capacity of the Fe-Zeolite catalyst and intentionally supplying excess NO to the Fe-Zeolite catalyst before the NO_2 slips is an effective method for bringing out the maximum NOx reduction performance of the Urea-SCR system.

The following sections describe application of the NO_2 ratio buffer concept to a vehicle system, and the results of verifying these effects.

4. Urea-SCR System for LEV-III ULEV50

4.1. Urea-SCR System in a Vehicle

A mid-size passenger car (inertia weight: 4 000 lbs) equipped with a 2.2-liter inline four-cylinder intercooler turbocharged diesel engine was used as the test vehicle to measure emissions. Figure 9 shows the layout of the

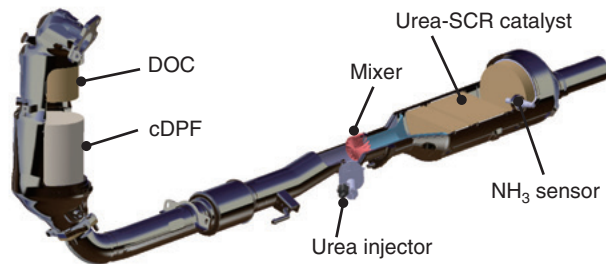


Fig. 9 Hardware configuration of Urea-SCR system

emission system in this study. A DOC and cDPF are located immediately after the engine, and an injector for Urea water dosing, a mixer for feeding the dosed Urea water to the catalyst in a homogeneous manner, and the Urea-SCR catalyst are located in that order under-floor. An NH_3 sensor is installed between the SCR catalysts, enabling optimum NH_3 supply and NH_3 slip control.

The feature of this system is that it assigns a role to each catalyst. The DOC immediately after the engine oxidizes the CO and HC, and the heat from these reactions is used for the initial heat-up of this system. The cDPF collects and reduces particulate matter (PM), and generates the NO_2 required for the Urea-SCR reaction by the platinum (Pt) based catalyst. The Urea-SCR catalyst has the role to reduce NOx by NH_3 . This system is an aftertreatment system that is able to reduce emissions effectively when all of these roles function properly.

4.2. Technical Issue for Clearing the LEV-III ULEV50 Standard

To clear the LEV-III ULEV50 standard, it is necessary to reduce 90% or more of the emitted NOx in FTP-75 mode. To clear this high requirement, emissions reduction was investigated by dividing the NOx reduction areas in FTP-75 mode (Fig. 10) and setting the catalyst functions required in each area (Table 6).

The approach to each area in Fig. 10 is as follows. In area (A), the catalyst system is rapidly heated up to the activation temperature, and in area (B), NOx is reduced using the NH_3 adsorbed to the Urea-SCR catalyst. Urea water is not dosed in area (B) because the catalyst system has not yet reached the Urea water hydrolysis temperature range. In the following areas (C) and (D), the exhaust

Table 6 Catalytic functions in each NOx reduction area

Catalyst	Area (A)	Area (B)	Area (C)	Area (D)
DOC	CO and HC oxidation	CO and HC oxidation to keep catalysts active		
cDPF	-	NO oxidation (NO_2 generation)		
SCR	-	NOx reduction by adsorbed NH_3	NOx reduction by adsorbed NH_3 and urea dosing	

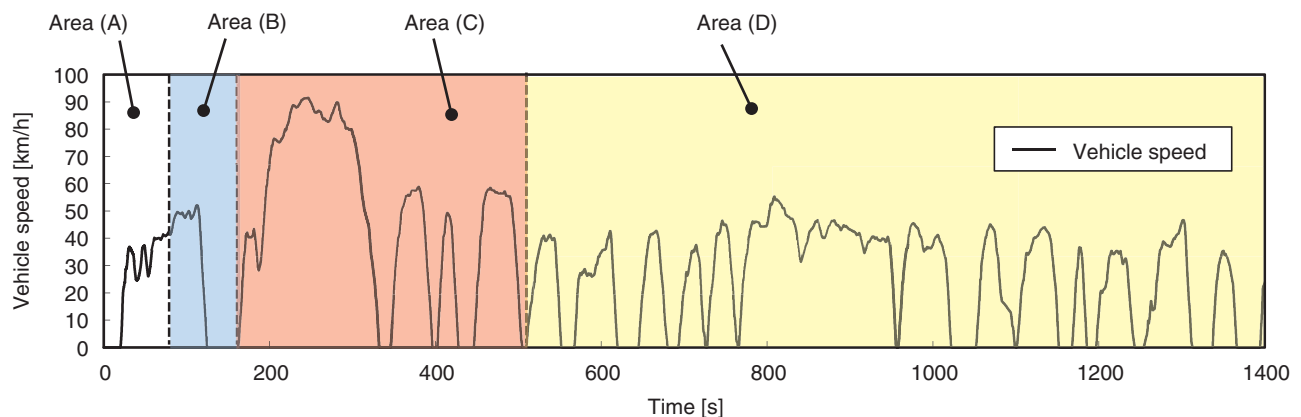


Fig. 10 Image of NOx reduction areas in Cold Transient (CT) and Cold Stabilized (CS) phases of FTP-75 mode

temperature is sufficiently high, so Urea water is dosed to generate NH₃, and NO_x is reduced at the high conversion rate of 95% or more.

To realize this approach, low temperature CO and HC oxidation activity in area (A) is required of the DOC, and low temperature NO₂ generation capability in area (B) and NO₂ generation capability under high gas space velocity (SV) conditions in area (C), in which the engine operates at high load, are required of the cDPF. In this test it was important to achieve high NO_x reduction performance from the initial stages of the driving mode, so DOC and cDPF with high oxidation performance were set in consideration of the required performances for area (A) and for areas (B) and (C). Figure 11 shows the vehicle emission results at that time.

The expected NO_x reduction results were obtained in areas (B) and (C) of FTP-75 mode, but the NO_x reduction performance dropped in area (D) in the middle of the mode. Figure 11 shows that the NO₂ ratio trended at 50% or more in area (D), and almost all of the NO_x that passed through the Urea-SCR catalyst was exhausted as NO₂. This is because the catalyst is sufficiently warmed up in area (D) and the engine load and SV are also low, so excess NO₂ generated by the strong oxidation DOC and cDPF flows to the Urea-SCR catalyst. That is to say, setting DOC and cDPF with high oxidation performance to emphasize NO_x reduction in the initial stages of the driving mode creates the issue that the NO_x reduction performance drops in the low load area after warm-up. This means that the technical issue to clear LEV-III ULEV50 is NO₂ ratio control in the low-load area after catalyst warm-up.

Therefore, the NO₂ ratio buffer concept using an Fe-Zeolite catalyst confirmed in the previous section was applied to vehicle control, and the emissions were evaluated.

5. Application of NO₂ Ratio Buffer Concept to Vehicle Control

To apply the NO₂ ratio buffer concept to a vehicle, an engine system control method that controls the NO₂ ratio is needed. Therefore, the NO₂ ratio was adjusted by controlling the exhaust gas recirculation valve (EGR valve), the fuel injection quantity and other parameters to change the exhaust gas from the engine. Figure 12 shows the results of applying NO₂ ratio control under cruise driving conditions where excess NO₂ is emitted from the tailpipe. It was confirmed that by performing control to intentionally lower the NO₂ ratio (green bands in Fig. 12), NO₂ emissions from the tailpipe were reduced, and high NO_x reduction performance was obtained.

Next, Fig. 13 shows the results of applying NO₂ ratio control while driving in FTP-75 mode to verify the NO₂ ratio buffer concept during mode driving. It was confirmed that by applying NO₂ ratio control, NO₂ emissions during mode driving that involves acceleration and deceleration are suppressed in the same manner as during cruise driving conditions, and high NO_x reduction performance could be achieved even in area (D). These results indicate that the NO₂ ratio buffer concept is also effective at typical driving conditions, and that this concept is an effective means for addressing the technical issues described above.

Application of a Urea-SCR system incorporating the Fe-Zeolite catalyst NO₂ ratio buffer concept examined in this study achieved NO_x emissions of 0.025 g/mile and non-methane organic gas (NMOG) emissions of 0.015 g/mile in FTP-75 mode, which enabled to clear the LEV-III ULEV50 level emissions values (Fig. 14).

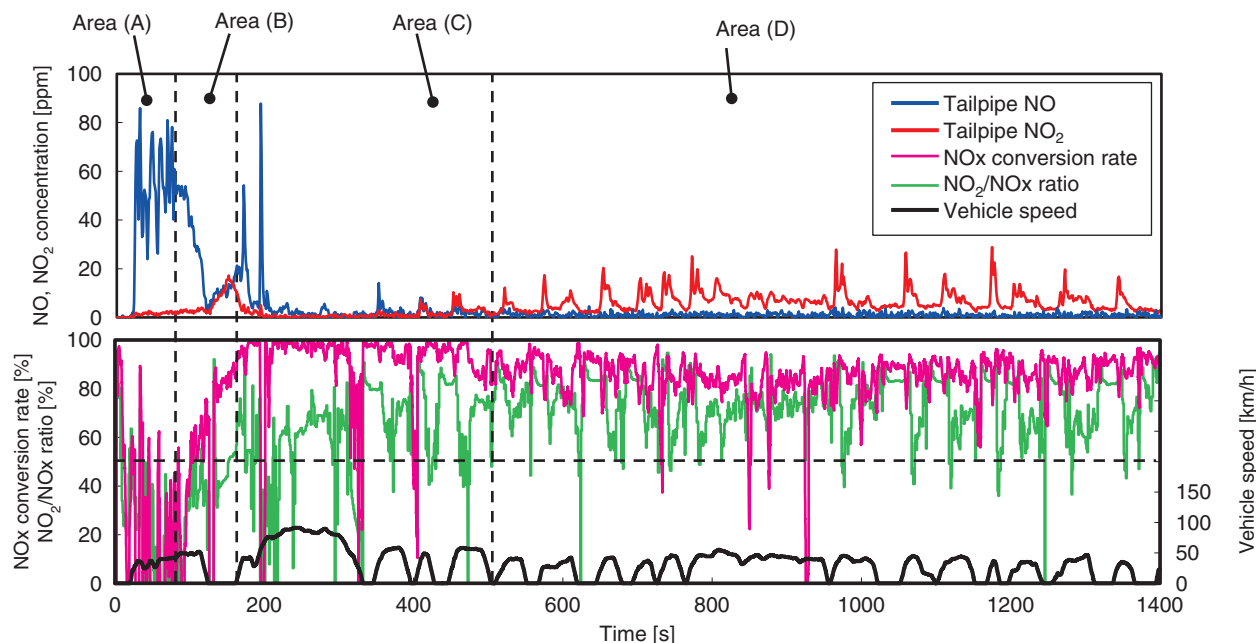
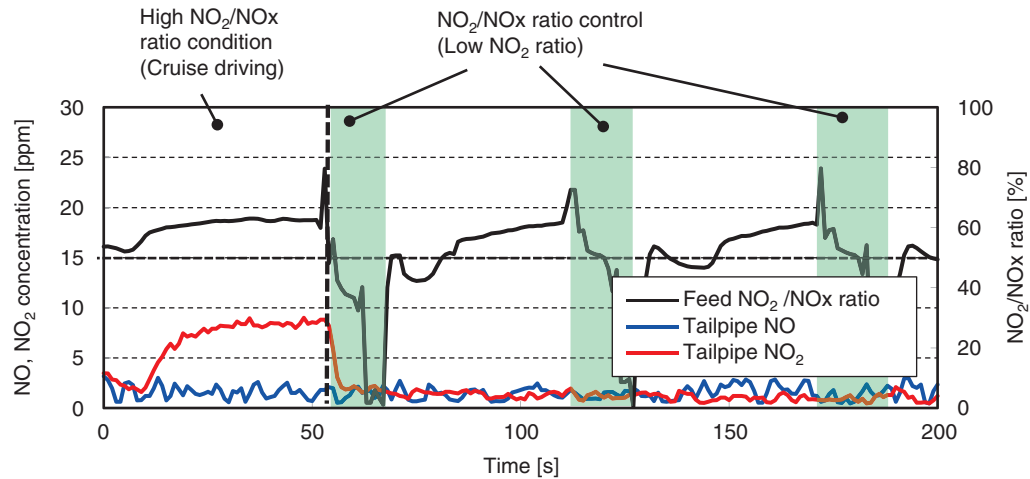
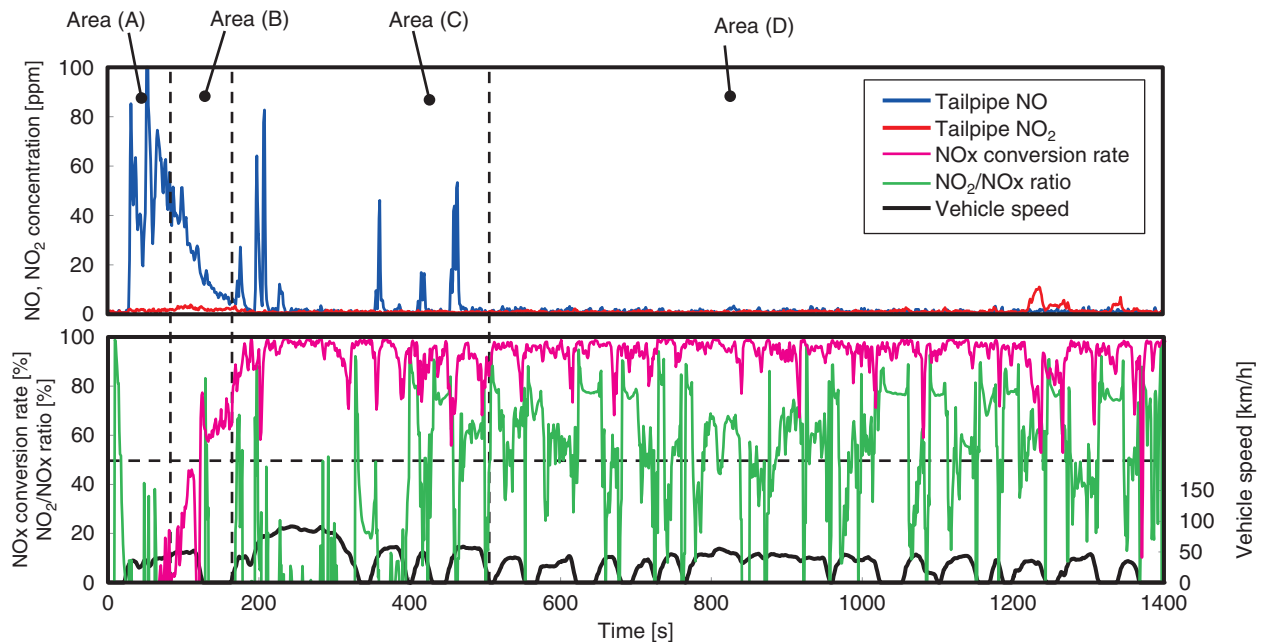
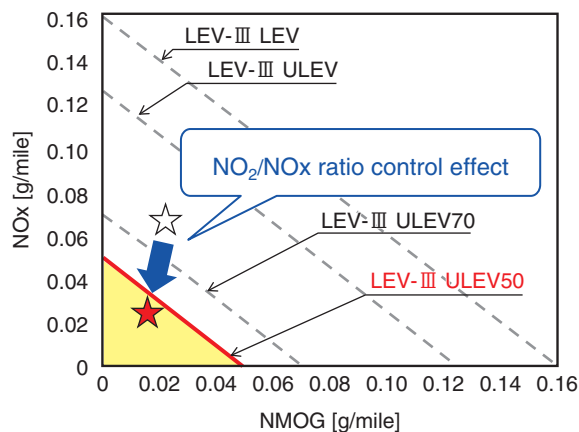


Fig. 11 Vehicle emission results by using strong oxidation catalysts (DOC and cDPF) in FTP-75 mode (CT and CS)

Fig. 12 Effect of new NO₂/NO_x ratio control in vehicle cruise conditionFig. 13 Vehicle emission results by introducing new NO₂/NO_x ratio control in FTP-75 mode (CT and CS)Fig. 14 NO_x and NMOG emission results in FTP-75 mode

6. Conclusion

The NO_x reduction behavior of an Fe-Zeolite catalyst was understood, and an NO₂ ratio buffer concept was proposed.

This NO₂ ratio buffer concept makes use of the mechanism that excess NO₂ is adsorbed to the Fe-Zeolite catalyst at a high NO₂ ratio, and local Fast-SCR reactions occur on the catalyst between the excess NO and the adsorbed NO₂ at a low NO₂ ratio, enabling to manifest high NO_x reduction performance even when the NO₂ ratio deviates from around 50%. This concept enabled to manifest high NO_x reduction performance even in the vehicle condition without limiting the NO₂ ratio variation width, by intentionally varying the NO₂ ratio.

This concept was applied to a vehicle, and it was proven that the NO₂ ratio can be controlled by EGR and fuel injection. As a result, high NOx reduction performance could be obtained even at dynamic vehicle conditions.

These measures addressed the technical issue of the drop in NOx reduction performance in the low-load area after catalyst heat-up that appears when catalysts with the high oxidation performance required in the initial stages of the driving mode are set, enabling to clear the LEV-III ULEV50 standard.

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