

Elucidation of Deterioration Mechanism and Improvement of Durability for Lean NOx Catalyst

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ABSTRACT

The exhaust gas temperatures of diesel engines have been falling gradually due to engine efficiency improvement and body weight reduction. Thus, an NOx aftertreatment system that has high NOx conversion at lower temperature is required for these engines. To meet demand, the development of a new Lean NOx Catalyst with a new De-NOx mechanism has been carried out. However, it has recently been found that Lean NOx Catalyst has a durability issue during aging in an actual exhaust gas environment. The deterioration mechanism of Lean NOx Catalyst was clarified and durability enhancement of the material was conducted. As a result of an analysis using a combination of surface analysis and ab-initio calculation, it was found that the sulfur in exhaust gas was irreversibly adsorbed onto platinum in the form of sulfate, which reduced catalyst activity. A new Lean NOx Catalyst that has high durability even after aging with exhaust gas was developed by improving NO₂ adsorption activity and NO₂ reduction activity, which had been degraded by sulfur poisoning.

1. Introduction

Diesel engines are promising as low fuel consumption engines because of their high thermal efficiency. In order to comply with strict emission regulation in America, Japan, Europe, and other places, exhaust gas after-treatment technology that provides high performance and high efficiency is required. Since the exhaust gas of a diesel engine is oxygen-rich atmosphere (lean), purification of the nitrogen oxide (NOx) in the exhaust gas is an issue, and various NOx purification systems have been proposed (Fig. 1).

One system is the Urea Selective Catalytic Reduction^{(1),(2)} (Urea-SCR) NOx purification system. Urea-SCR is a system that uses aqueous urea to purify NOx by an NH₃-selective reduction reaction, and it has high NOx catalytic reduction performance. However, Urea-SCR involves such issues as high system costs because of urea tank, injector, and other added devices, high weight, and so on. When exhaust gas temperature is low, an increase in exhaust gas temperature is needed to convert urea water to NH₃.

By contrast with this, the NOx Storage Catalyst (NSC) system has been developed⁽³⁾⁻⁽⁷⁾ as a simple, low-cost system that does not involve added devices. In an NSC system, after the NOx in exhaust gas is stored in an alkaline earth metal or other such material in the catalyst, the stored NOx

is purified by such reducing agents as carbon monoxide (CO) and hydrocarbon (HC), which are produced by rich control. However, the alkaline earth metal that is mainly used as an NOx storage material needs a temperature of approximately 300°C to store NOx. In order to obtain high catalytic reduction performance at low temperatures, large amounts of precious metals are required.

In recent years, exhaust gas temperatures of diesel engines have been decreasing gradually due to the engine efficiency improvement and body weight reduction. Therefore, the Urea-SCR system and the NSC system face the issues of catalytic reduction performance at low temperatures. Thus, an NOx aftertreatment system that has high NOx conversion at lower temperatures and offers low cost is required.

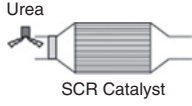
	System configuration	Equation
Urea-SCR	 SCR Catalyst	$4\text{NO} + 4\text{NH}_3 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$ $6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$ $4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$
NSC	 NSC Catalyst	Lean: $\text{NO} + 1/2\text{O}_2 + \text{MO} \rightarrow \text{MNO}_3$ Rich: $\text{MNO}_3 + 2\text{CO} \rightarrow \text{MO} + 2\text{CO}_2 + 1/2\text{N}_2$ $\text{MNO}_3 + 2\text{H}_2 \rightarrow \text{MO} + 2\text{H}_2\text{O} + 1/2\text{N}_2$ $9/2\text{MNO}_3 + \text{C}_3\text{H}_6 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} + 9/2\text{MO} + 9/4\text{N}_2$

Fig. 1 Conventional NOx reduction technology

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A Lean NOx Catalyst (LNC) system⁽⁸⁾ that has high catalytic reduction performance at low temperatures using a new purification concept has been proposed by Honda. The LNC system is like the NSC system in the respect that additional equipment is unnecessary and rich spike control is necessary to purify NOx. Whereas the NSC approach has issues with NOx purification at low temperatures, the LNC approach provides high catalytic reduction performance at low temperatures by means of a new NOx mechanism of catalytic reduction.

On the other hand, automotive catalyst is required to be highly durable under severe exhaust gas environment conditions, and durability is also an important issue for LNC. In the course of confirming LNC durability, it became clear that NOx catalytic reduction performance diminished when the LNC was aged under an exhaust gas environment. This report therefore considers the causes of LNC deterioration, sets forth methods for countering it, and describes the beneficial effects of those methods.

2. LNC Characteristics and Durability Issues

2.1. LNC Characteristics

LNC yields high NOx catalytic reduction performance at low temperatures by means of a new NOx mechanism of catalytic reduction. The mechanism of NOx purification by the LNC and details of its NOx purification performance have been previously reported⁽⁸⁾. The mechanism of NOx reduction with LNC is shown in Fig. 2. The LNC has a two-layered configuration, comprising a layer employing a NOx adsorption material, which possesses NOx adsorption and reduction functions, and a layer employing zeolite, which functions to reduce NOx by means of NH₃. This two-layered configuration realizes efficient NOx purification. With regard to the mechanism of NOx purification, first, NO is oxidized to NO₂ by Pt in the NOx adsorption material layer, and the NO₂ adsorbs on the NOx adsorption material. Following this, the NO₂ desorbs from the NOx adsorption material when the exhaust gas becomes rich, and is converted to N₂ or NH₃ on the Pt and the NH₃ adsorbs on the zeolite layer. In the lean phase after that, the NH₃ in the zeolite layer purifies NOx. As NOx adsorption material, the catalyst uses cerium (Ce) compound, which has high NOx

Table 1 Model gas composition for LNC and NSC

	Lean (55 sec)	Rich (5 sec)
O ₂ (%)	6	0
CO (%)	0.09	2
C ₃ H ₆ (ppmC)	500	
CO ₂ (%)	6	
NO (ppm)	110	
H ₂ O (%)	7	
N ₂ (%)	Balance	
GHSV (h ⁻¹)	50000	

adsorption performance from low temperatures, and also uses zeolite, which is capable of NH₃-selective reduction even at low temperatures. This NOx mechanism of catalytic reduction enables the LNC catalyst to yield high catalytic reduction performance from low temperatures. Figure 3 shows a comparison⁽⁸⁾ of the purification performance of conventional NSC and LNC. Table 1 further shows the test conditions that were used in the comparison. The results show that where the peak of NSC catalytic reduction performance occurs at 400°C, LNC has its peak at 250°C and possesses high catalytic reduction performance at low temperatures. Thus LNC is a catalyst system that yields high NOx catalytic reduction performance from low temperatures by means of a new NOx mechanism of catalytic reduction.

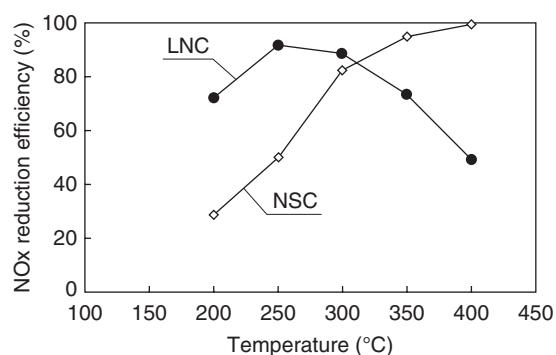


Fig. 3 Comparison of LNC and NSC in NOx reduction efficiency

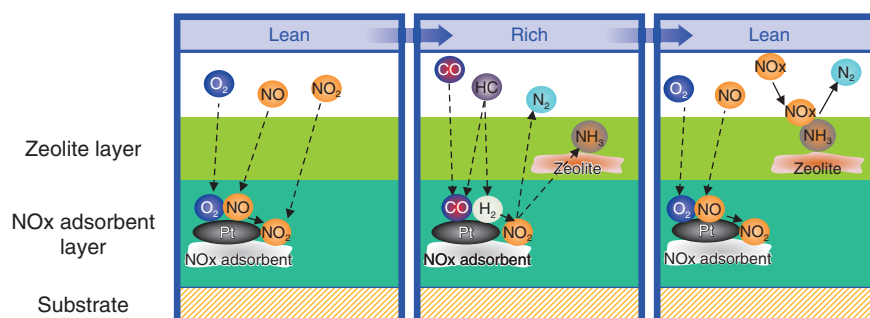


Fig. 2 Reaction mechanism of LNC

2.2. NOx Emission Behavior in Vehicles Testing

Figure 4 shows the configuration of an emission gas purification system that uses LNC. This system places a diesel oxidation catalyst (DOC) and catalyzed diesel particulate filter (cDPF) in a position close coupled with the engine, and places the LNC under the floor. In this system, CO and HC are purified by the DOC, soot is removed by the cDPF, and NOx is purified by the LNC. The durability of this emission gas purification system was verified by carrying out emission testing with actual vehicles using aging catalyst in FTP-75, which is a US emission test mode. Two types of aging were conducted. One was engine emission gas aging (engine aging), in which the system was placed downstream of the engine emission gas and controlled to bring the LNC to a certain temperature. The other was aging by an electric furnace to verify only the influence of heat on the catalyst (thermal aging). For both methods, the heat load was made equivalent to both aging temperature and time at 120000 miles of operation. The gas conditions for the thermal aging were oxygen 10% and water 6%.

Figure 5 shows a comparison of NOx emission behavior of thermal aging catalyst and engine aging catalyst in FTP-75 mode. The thermal aging catalyst shows virtually zero NOx emissions following the warm-up time of approximately 200 seconds after start-up. The engine aging catalyst, however, shows NOx emissions throughout the entire mode procedure. The amount of NOx emissions was particularly large at the rich spike times marked by arrows in Fig. 5. It can be inferred that this occurs because the NOx desorbed from the adsorption material during the rich spikes is emitted without undergoing full reduction, and it appears that NOx catalytic reduction performance is reduced under rich conditions. Furthermore, the engine

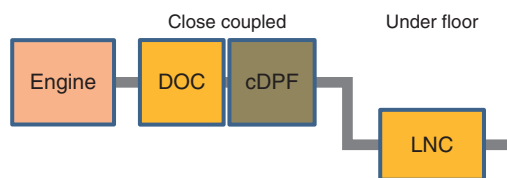


Fig. 4 Exhaust aftertreatment system using LNC
Engine: 2.2 L direct-injection diesel, close coupled catalysts: DOC 1.0 L, CSF 2.2 L, under floor catalyst: LNC 2.0 L

Table 2 Model gas composition

	Lean (55 sec)	Rich (5 sec)
O ₂ (%)	6	0
C ₃ H ₆ (ppmC)	0	4000
CO (%)	0	1
CO ₂ (%)	10	
NO (ppm)	200	
H ₂ O (%)	7	
N ₂ (%)	Balance	
GHSV (h ⁻¹)	75000	

aging catalyst shows NOx emissions even in the high gas flow rate region due to high acceleration at around 1600 seconds, so it appears that NOx catalytic reduction performance is also reduced under lean conditions.

2.3. Elementary Reaction Characteristics in Model Gas Testing

Next, the LNC used in the emission test was made into a test piece and a catalytic reduction performance test was carried out using the model gas exposure test system manufactured by Horiba in order to clarify the deterioration characteristics of the catalyst. Catalyst performance was evaluated by alternately passing lean gas and rich gas through the LNC. The average purification rate for lean and rich gases was used as a criterion in these evaluations. Figure 6 shows the model gas testing results. Table 2 shows the test conditions. The fresh catalyst achieves a

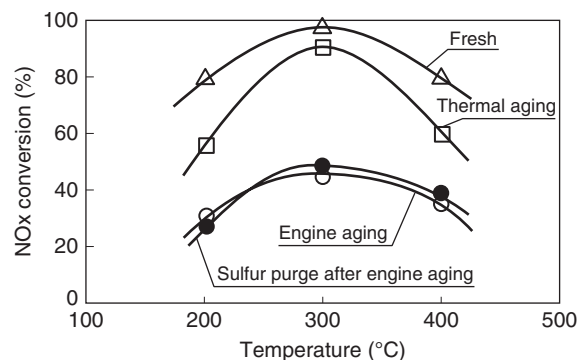


Fig. 6 Comparison of NOx conversion between thermal aging and engine aging in model gas test

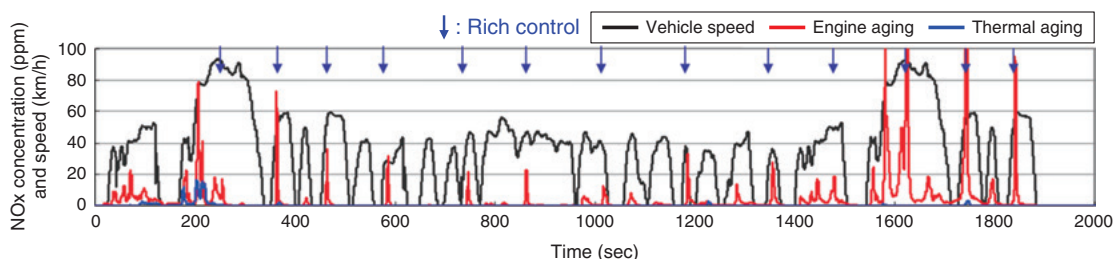


Fig. 5 Comparison of NOx emission profile between thermal aging and engine aging in FTP-75 mode

Table 3 Performance in elementary reactions

	Thermal aging (%)	Engine aging (%)	Material	Model gas composition
(1) NO oxidation	52	68	Pt	NO 500 ppm, O ₂ 0.5 %, N ₂ balance
(2) NO ₂ adsorption	75	45	Pt, Ce-compound	NO ₂ 500 ppm, O ₂ 0.5 %, N ₂ balance
(3) NH ₃ -SCR	71	69	Zeolite	NO 100 ppm, NO ₂ 100 ppm, NH ₃ 200 ppm, O ₂ 6%, H ₂ O 7%, N ₂ balance
(4) NO ₂ reduction	98	32	Pt	NO ₂ 500 ppm, CO 1000 ppm, N ₂ balance

high purification rate of around 80% at every temperature, but the purification rate shows a decline for both aging catalysts. The purification rate of the engine aging catalyst in particular is low, showing significant deterioration with a decline of from 30% to 50%. In addition, it is known that the type of catalyst that adsorbs or stores NO_x accumulates sulfur from the exhaust gas, and this causes a reduction in NO_x catalytic reduction performance. Therefore the engine aging catalyst was subjected to sulfur removal treatment by rich gas at 650°C for 10 minutes to investigate whether the diminished NO_x catalytic reduction performance would recover. The results show that catalytic reduction performance was largely unchanged, suggesting that this was not ordinary deterioration due to sulfur accumulation.

This suggested that NO_x purification performance of engine aging LNC was due to some irreversible factor other than heat.

LNC is a catalyst in which the NO_x purification reaction proceeds by a combination of elementary reactions. Therefore engine aging catalyst and thermal aging catalyst were subjected to model gas testing for the elementary reactions in Eq. (1) through (4). These tests were used to determine which elementary reactions performance was declining and which materials this performance decline originated. Table 3 shows the test conditions and test results. According to these results, the NO oxidation reaction in Eq. (1) and the NH₃-SCR reaction in Eq. (3) had generally the same performance with both forms of aging, but the NO₂ adsorption reaction in Eq. (2) and the NO₂ reduction reaction in Eq. (4) showed diminished performance with the engine aging catalyst. Since platinum (Pt) or the cerium (Ce) compound is related to these performance parameters, it was considered that the functions of these materials were declining.

Lean phase



Rich phase



3. Elucidation of LNC Deterioration Mechanism

In order to clarify the causes of LNC deterioration, analyses of the platinum and the cerium compound considered to be declining in performance were conducted. Morphological analysis was conducted by surface analysis and configuration simulation using ab-initio calculation was carried out to obtain theoretical corroboration.

3.1. Clarification of Deterioration Configuration by Surface Analysis

The effects of thermal deterioration in platinum and the cerium compound were first investigated. It is known that crystal growth in Pt and the cerium compounds occurs. X-ray diffraction (XRD) was therefore employed in order to measure crystallite diameter, an index of agglomeration. The results show that crystallite diameter in both platinum and cerium compound had generally the same values under both thermally aging catalyst and engine aging catalyst conditions. This result suggested that there was no difference in degradation due to heat for the different types of aging. Next, the influence of poisoning deterioration due to the accumulation of sulfur (S) and phosphorus (P) of exhaust gas was investigated. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) was used to quantify the amounts of sulfur and phosphorus accumulated on the engine aging catalyst. As a result, the amounts were found to be very small, with sulfur at 0.02% and phosphorus at 0.02%. This is the equivalent, converted from fuel and oil consumption, of the amounts from driving several tens of kilometers. However, it was conceivable that very small amounts of poisoning components were adhering to certain specific areas, and so the state of the poisoning components in the platinum and the cerium compound was investigated. The engine aging catalyst was first examined using a Scanning Transmission Electron Microscope (STEM). This identified platinum particles and cerium compound particles, and the various particles were subjected to element analysis by Energy Dispersive X-ray Spectrometry (EDS) to investigate where the poisoning substances were located. Figure 7 shows the EDS results. A peak of sulfur at around 2.3 keV was detected in the EDS

spectrum for the platinum particles in Fig. 7(a), indicating that platinum and sulfur existed together. In Fig. 7(b), however, no sulfur was detected in the particles of cerium compound, indicating that cerium compound and sulfur did not exist together. This suggested that sulfur was poisoning the platinum particles, and it was inferred that sulfur was being selectively adsorbed onto the surface of the platinum particles.

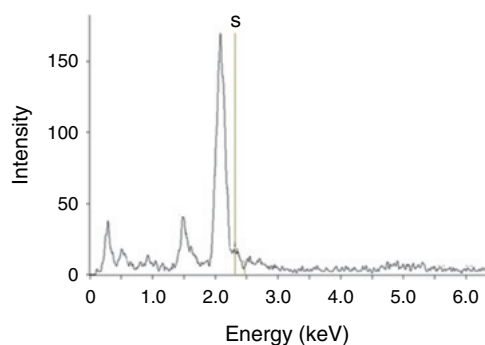
In the case of selective adsorption of sulfur onto the surface of platinum particles, a reduction in the active surface area of the platinum particles can be expected. Therefore the amount of CO adsorption was measured by Fourier Transform Infrared Ray spectroscopy (FT-IR), which is a method for measuring the active surface area of a metal, and the change in the active surface area due to deterioration was investigated. Figure 8 shows the results. The peak at around 2090 cm⁻¹ can be identified as the peak of Pt-CO adsorption. As a result, it was found that the amount of Pt-CO adsorption by the engine aging catalyst had become smaller than that by the thermally aging catalyst, and that the active surface area of the platinum particles had grown smaller. The results of XRD analysis described above showed that platinum crystallite diameter was the same under the two types of aging, so that the extent of platinum particle aggregation is thought to be about the same. Therefore this reduction in the active surface area is considered to be due to the adsorption of

sulfur on the surface of the platinum particles.

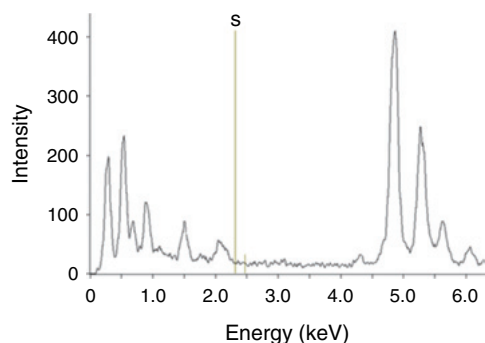
A structural analysis of surface chemical species was then carried out by X-ray Absorption Near Edge Structure (XANES) in order to investigate the structure of sulfur covering the surface of platinum particles. A structural analysis of the sulfur in engine aging catalyst was carried out by comparison with calcium sulfide (CaS) and calcium sulfate (CaSO₄), for which the structure was already known. Figure 9 shows the sulfur K-edge XANES spectra. It was apparent that the engine aging catalyst peaks at around 2.48 keV, resembling the CaSO₄ spectrum. This suggested that the sulfur on the surface of the platinum particles is adsorbed in the form of a sulfate (SO₄).

3.2. Verification of Deterioration Configuration by Ab-Initio Calculation

Ab-initio calculation relating to the bonding of platinum and sulfur was carried out in order to obtain theoretical



(a) Pt particle



(b) Ce-compound particle

Fig. 7 EDS patterns of catalysts under engine aging

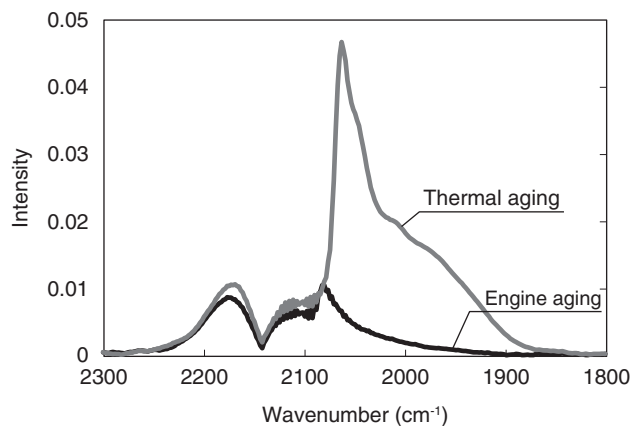


Fig. 8 FT-IR spectra of CO adsorption
Temperature: 300°C, gas condition: CO
1000 ppm, He balance

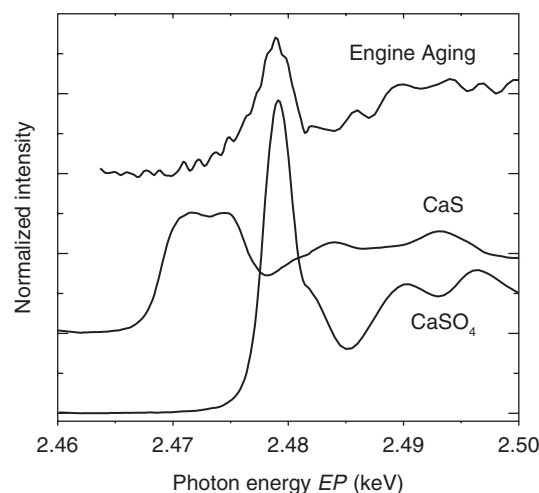
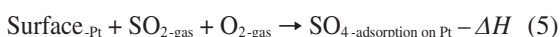


Fig. 9 XANES spectra of various samples

Table 4 Condition for ab-initio calculation

Item	Contents
Program	D-Mol3 ⁽⁹⁾
Functional	VWN (LDA) ^{(10), (11)}
Basic function	DND basis set
Inner core calculation	ECP (Effective core potential)
Model	Pt (111) surface with periodic boundary condition

verification of the structure of sulfur adsorption described in the previous section. A model was fabricated of a cluster of 12 platinum atoms with 111 facets exposed on the surface of which one sulfur oxide (SO_x) molecule (S, SO, SO₂, SO₃, SO₄, SO₅) is adsorbed. This was examined with the adsorption enthalpy in a reaction equation such as that in Eq. (5) (taking the case of SO₂ as an example) as the index of stability.



When the adsorption enthalpy (ΔH) derived by this calculation is smaller, then the state of SO_x adsorption on the platinum is thought to be more stable. Figure 10 shows the results of this calculation, and Table 4 shows the conditions for the calculation. As the number of oxygen (O) atoms increases with respect to the sulfur, the adsorption enthalpy is reduced, reaching its lowest point with SO₄ and then increasing again with SO₅. From this it was inferred that SO₄ is the most stable form of sulfur poisoning of platinum. The adsorption enthalpy with SO₄ on CeO₂ is also shown for purposes of comparison, but the adsorption enthalpy with platinum is even smaller than with CeO₂, suggesting that SO₄ is more strongly adsorbed onto platinum than onto CeO₂. This suggests that the reason there was no recovery of catalytic reduction performance in Fig. 6 even when sulfur removal treatment was carried out was that the SO₄ poisoning of the platinum

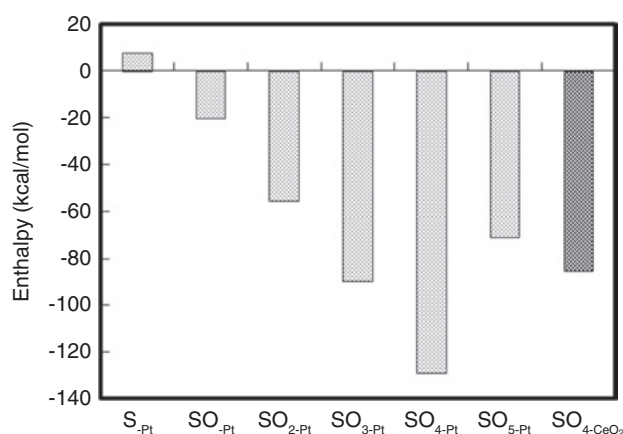


Fig. 10 Comparison of adsorption energy among various sulfur oxides on Pt and CeO₂

was so stable that the sulfur was not desorbed. Platinum poisoning by SO₄ can be considered to cause irreversible deterioration in the temperature range of actual diesel operation. Figure 11 shows a conceptual image of the structure of SO₄ bonded to platinum as derived from ab-initio calculation. The poisoning of platinum by SO₄ takes the structure of three oxygen atoms bonding each to one of three platinum atoms. One SO₄ molecule therefore poisons three atoms on the platinum surface, so that even a small amount of SO₄ can be expected to have a significant influence.

The results of surface analysis and ab-initio calculation considered in combination suggest that the causal factor in deterioration of LNC performance due to engine aging is that the platinum particle surface, which is an activation site, is poisoned by the strong adsorption structure of SO₄. This appears to be the case even though the amount of sulfur poisoning is very small.

4. Countermeasures to LNC Deterioration

4.1. Conceptual Approach to Deterioration Countermeasures

This suggested that the degradation of the LNC due to engine aging resulted from the covering of the Pt by SO₄. The ab-initio calculation suggests that the state of SO₄ adsorption on the platinum surface is thermodynamically very stable. It seems to be difficult to prevent SO₄ poisoning of the catalyst, it was therefore considered that the introduction of modifications to reduce the effect of SO₄ poisoning on performance would be desirable. In Section 2, the reactions that resulted in a decrease in function due to SO₄ poisoning were shown to be the NO₂ adsorption reaction in Eq. (2) and the NO₂ reduction reaction in Eq. (4). Therefore catalyst improvement that would lessen the impact of SO₄ poisoning on these functions was investigated. Figure 12 shows the reaction mechanism in deteriorated LNC. First, in the NO_x adsorption reaction under lean conditions, the Eq. (1) reaction that forms NO₂ from NO progresses even on the platinum that has been poisoned. However, since the migration of NO₂ on the surface of Pt is interfered with by the adsorbed SO₄

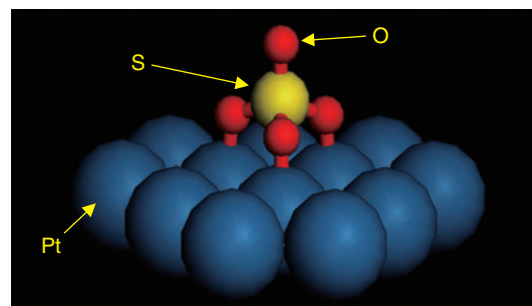


Fig. 11 Image of SO₄ structure on Pt surface

molecules, the rate of NO₂ adsorption on the Ce compound declines. The presence of SO₄ molecules on the platinum in the NO₂ reduction reaction also similarly impedes the adsorption of the desorbed NO₂ and the reducing gas such as CO on the platinum surface. As a result, it is inferred that NO₂ is emitted because the Eq. (4) reduction reaction of NO₂ and CO does not progress. A structure like that shown in Fig. 13 was therefore considered as a high-durability LNC.

First of all, a key consideration is how to cause NO₂ to move smoothly from the platinum surface to the cerium compound in the course of NO₂ adsorption. When the platinum particles are large, the NO₂ formed on active sites that are distant from the boundary surface between the platinum particle and the cerium compound has farther to travel to reach the cerium compound, so there is greater likelihood that the movement will be obstructed by SO₄. Consequently, it appears that the key to improvement will not be a method of simply increasing the platinum content in order to increase the platinum active surface area, but rather in making the platinum particles small in order to lessen the distance moved by the NO₂ that is formed. A cerium compound had previously been used as the support for the Pt, however, high-surface-area Al₂O₃ was now employed in order to promote the formation of small platinum particles. In addition, a higher quantity of Al₂O₃ than the cerium compound was employed. Figure 14 shows the results from STEM confirmation of this trial. These results show that the average diameter of the platinum particles is 22 nm when Al₂O₃ is not employed, and 8 nm when it is employed, verifying that it was possible to form small platinum particles.

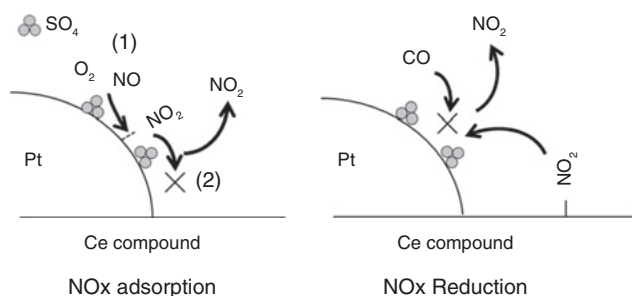


Fig. 12 Reaction mechanism of initial LNC

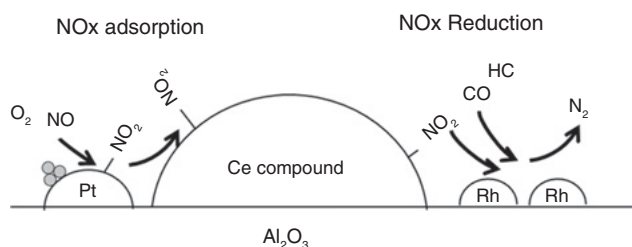
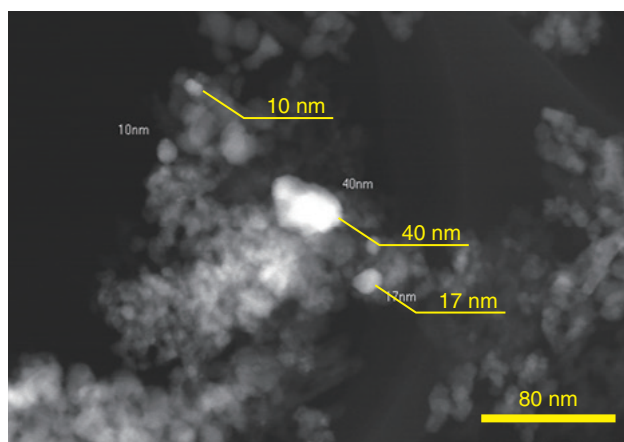


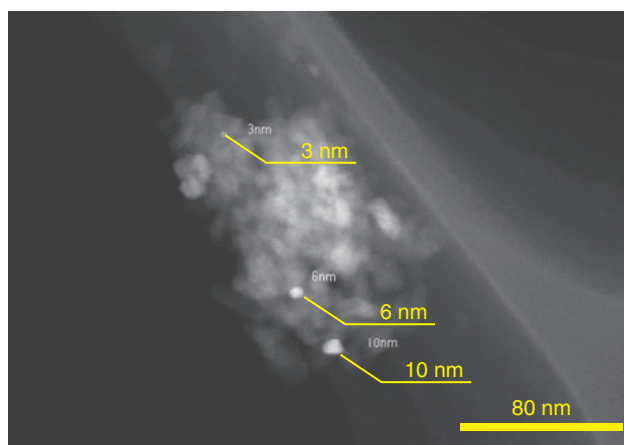
Fig. 13 Reaction mechanism of improved LNC

Next, in the course of reduction, it is important that the NO₂ desorbed from the cerium compound be caused to react immediately on a precious metal. Rhodium was therefore employed to promote a reduction reaction. Because rhodium is a precious metal which is not prone to agglomeration, it produces small particles. The use of small-particle rhodium increases the boundary surface between the rhodium and the cerium compound. This effect may enable the NO₂ desorbed from the cerium compound to move smoothly onto the rhodium and be reduced. Figure 15 shows a STEM image of Rh/Al₂O₃ after engine aging. It is apparent from these results that the rhodium maintains a small-particle state at about 2 nm, so that high NO_x reduction performance can be expected.

This effect was confirmed by conducting a model gas temperature-raising test with NO₂ and CO and investigating the activating temperature. Figure 16 shows the results. After thermal aging of the platinum-only LNC, it yielded high catalytic reduction performance from around 250°C. After engine aging, however, it yielded catalytic reduction



(a) Without Al₂O₃



(b) With Al₂O₃

Fig. 14 STEM images of initial LNC and improved LNC under engine aging

performance from around 400°C, showing a significant decrease in activity. On the other hand, the rhodium-added LNC showed virtually no difference after thermal aging and after engine aging, and it yielded high activity from low temperatures. In this way, the addition of rhodium was able to prevent the decrease in reduction performance after engine aging.

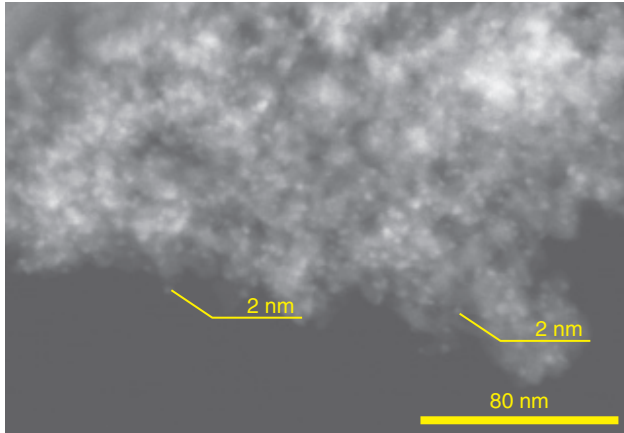


Fig. 15 STEM images of Rh/Al₂O₃ under engine aging

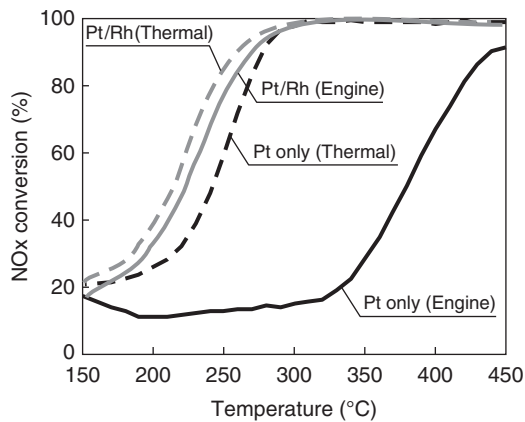


Fig. 16 Effect of Rh for improving durability under engine aging
NO₂ reduction: NO₂ 500 ppm, CO 1000 ppm, N₂ balance, GHSV 50000 h⁻¹

4.2. NO_x Purification Performance of a High-Durability LNC

The performance of the original LNC and the high-heat-resistance LNC was compared in order to determine the extent to which the modification boosted catalyst performance. The comparison was also extended to include the performance of the initial LNC after thermal aging. Figure 17 shows the results. The testing was conducted under the conditions shown in Table 2. The high-durability LNC after engine aging yields generally the same level of performance as the initial LNC after thermal aging. This confirms that the influence of SO₄ poisoning has been successfully reduced.

Vehicle tests were conducted in order to study the exhaust gas NO_x purification performance of the LNC. The original LNC and the modified LNC were aged in an engine to the equivalent of 120000 miles. The purification performance of the catalysts was compared in vehicle tests using FTP-75 mode. Figure 18 shows the results. With initial LNC catalyst, NO_x emissions are observed under both rich and lean conditions as stated above. With the high-durability LNC, however, emissions during rich spikes can largely be reduced, and performance during lean operation with high exhaust gas flow has also been improved.

These test results also verify the effectiveness of the modification of the catalyst in increasing durability in relation to engine aging.

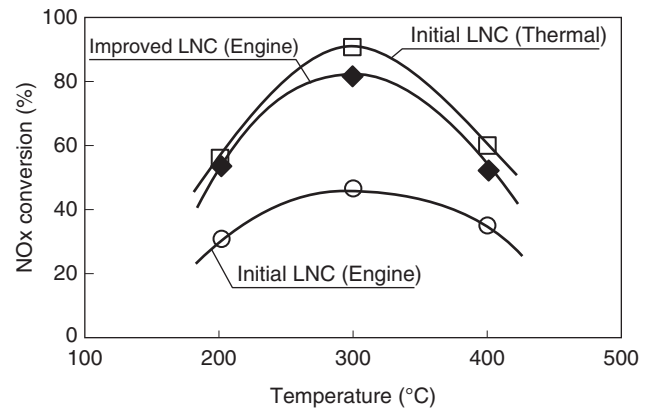


Fig. 17 Comparison of initial LNC and improved LNC in model gas test

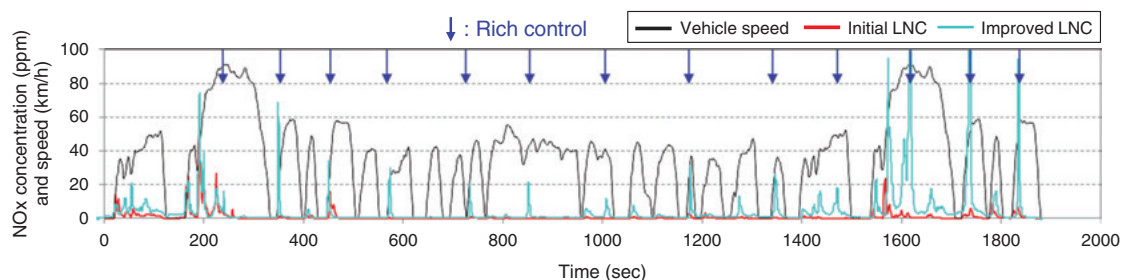


Fig. 18 Comparison of NO_x emission profile in FTP-75 mode between initial LNC and improved LNC under engine aging

5. Conclusion

An original Honda LNC system for diesel vehicles employing a new NOx purification mechanism was developed. It was observed that NOx purification performance declined when the catalyst was aged in an exhaust gas environment. The mechanism of catalyst degradation was elucidated and the catalyst materials were modified. As a result, a high-durability LNC was developed. This process yielded the following findings:

- (1) The factors resulting in a decline in the NOx purification performance of LNC when aged in an exhaust gas environment were analyzed. The results of this analysis suggested that the main factors in the degradation of the LNC were irreversible adsorption of the sulfur in the exhaust gas on the surface of the Pt as SO₄, and a decline in NO₂ adsorption performance and NO₂ reduction performance due to this SO₄.
- (2) Improvement of materials was carried out on the basis of the deterioration mechanism. As a result, the microparticulation of platinum promoted the movement of NO₂ to the cerium compound and the addition of rhodium enhanced the reduction function. By combining these results, a high-durability LNC catalyst that limits the decrease in NOx catalytic reduction performance was developed.
- (3) The NOx purification system using high-durability LNC catalyst was able to reduce NOx emissions during rich and lean operation, and the enhancement of purification performance was confirmed in vehicle testing.

References

- (1) Guo, G., Dobson, D., Warner, J., Ruona, W., et al.: Advanced Urea SCR System Study with a Light Duty Diesel Vehicle, SAE Technical Paper 2012-01-0371 (2012)
- (2) Moon, S., Choi, B., Lee, H., Hyun, G., et al.: Development of DPF/SCR System for Heavy Duty Diesel Engine, SAE Technical Paper, 2012-01-0369 (2012)
- (3) Adouane, D., Dutilleul, H., Guibert, P., Teixeira, M., et al.: Impact of Thermal and Engine Ageing on a Fully Formulated Lean NOx Trap, SAE Technical Paper, 2012-01-1746 (2012)
- (4) Kim, K., Cho, S.: The Emission Development for Lean NOx Trap System to Meet Tier2Bin5, SAE Technical Paper, 2010-01-0566 (2010)
- (5) Chen, X., Schwank, J.: Investigation on NOx Storage Characteristics and Aging Influence of Lean NOx Trap Model Catalyst BaO-Pt/Al₂O₃, SAE Technical Paper, 2010-01-0364 (2010)
- (6) Kouakou, A., Fresnet, F., Granger, P., and Dainhaut, F.: New Insight in Ammonia Formation During the Purge of a Lean NOx Trap in Vehicles Running Conditions, SAE Technical Paper, 2009-01-2710 (2009)
- (7) AL-Harbi, M., Epling, W., Yezerets, A., Currier, N., et al.: The Effects of Thermal Degradation on the Performance of a NOx Storage/Reduction Catalyst, SAE Technical Paper, 2009-01-0631 (2009)
- (8) Morita, T., Suzuki, N., Satoh, N., Wada, K., Ohno, H.: Study on Low NOx Emission Control Using Newly Developed Lean NOx Catalyst for Diesel Engines, SAE Technical Paper 2007-01-0239 (2007)
- (9) Delley, B.: An All-Electron Numerical Method for Solving the Local Density Functional for Polyatomic Molecules, J. Chem. Phys., 92, 508 (1990)
- (10) Delley, B.: From molecules to solids with the DMol3 approach, J. Chem. Phys., 113, 7756 (2000)
- (11) Vosko, S. H., Wilk, L., Nusair, M.: Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis, Can. J. Phys., 58, 1200 (1980)

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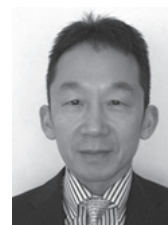
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