

Study of a Selective Catalytic Reduction Type Lean NOx Catalyst System

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ABSTRACT

The focus of this study on NOx reduction during lean-burn conditions was a Selective Catalytic Reduction (SCR)-type lean NOx catalyst. The SCR-type lean NOx catalyst exhibits stable NOx reduction performance under excess oxygen conditions.

We selected iridium (Ir) as the active species and an improved support material for enhanced selectivity of NOx reduction in competitive HC oxidation reaction under excessive oxygen conditions. This resulted in advanced NOx conversion.

Furthermore, catalyst durability, always a problem in SCR-type lean NOx catalysts, was improved by coating the catalyst with the material LaCoO₃, which can convert NO to NO₂.

Using this improved SCR-type Ir catalyst and performing engine control correlated with the conversion characteristics, a 63% NOx conversion rate was achieved under all lean-burn conditions in the 10-15 mode.

1. Introduction

Concern for global warming has increased in recent years, and, thus, improvements in automobile fuel economy are being demanded around the world to reduce CO₂ emissions.

Lean-burn combustion is an effective means of improving the fuel economy of gasoline engines. However, lean-burn exhaust gas contains a high oxygen concentration, making it difficult for conventional automobile three-way catalysts to reduce NOx. Thus, it is necessary to develop a catalytic system capable of converting NOx under excess oxygen conditions in order to improve the fuel economy of gasoline engines.

This study focused on selective-type catalysts that exhibit NOx conversion performance under excess oxygen conditions, and developed a catalytic system functional under all lean operating conditions in the Japanese 10-15 mode. The details are described below.

2. Focus and Approach

The dry adsorption method⁽¹⁾ has been proposed as a method of converting NOx under excess oxygen conditions using a catalyst. This method adsorbs and desorbs NOx using various precious metals, and performs catalytic reduction at the theoretical air-fuel ratio and reduction area. In addition, selective reduction methods using Zeolite catalysts⁽²⁾, compound oxide catalysts⁽³⁾ and precious metal catalysts⁽⁴⁾⁽⁵⁾ have also been proposed.

In order to achieve high fuel economy effects, this study promoted development focusing on methods using SCR

(Selective Catalytic Reduction)-type precious metal catalysts which are capable of stable NOx conversion even under excess oxygen conditions.

Development also aimed to improve heat resistance⁽¹⁾⁽⁶⁾⁽⁷⁾, which had been a problem for selective-type catalysts thus far.

3. Study Targets

This study focused on developing a catalytic system that is capable of stable NOx conversion even under excess oxygen conditions.

The development targets were NOx conversion ratios of 60% or more under all lean-burn conditions in the 10-15 mode when applied in an actual vehicle, and 60% or more for the discrete catalyst with a model gas which simulated exhaust gas.

4. Catalyst Development

4.1. Selecting the Active Species

Selective-type catalysts exhibit a competitive HC oxidizing reaction with O₂ and NOx under excess oxygen conditions. Thus, there tends to be insufficient HC and CO oxidization as NOx reduction selectivity is increased. Therefore, when developing the catalyst, the active species was selected from the following perspectives and assuming the application of a downstream oxidizing catalyst.

(1) The NOx conversion temperature range should be a temperature range that allows conversion by a downstream oxidizing catalyst.

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- (2) The NO_x conversion ratio should be high, and the conversion temperature range should be wide.

Fig. 1 shows the NO_x conversion characteristics by temperature for various catalyst active species.

Based on these results, iridium (Ir) was selected as the active species having a performance that most satisfies the conditions (1) and (2) above.

4.2. Setting the Model Gas

Ir catalysts have been reported to possess the characteristic of specifically reducing NO_x depending on the low boiling point unsaturated HC species. Therefore, the authors investigated NO_x conversion characteristics according to HC species. Fig. 2 shows the effects of HC species on NO_x conversion characteristics according to temperature. This shows that Ir catalysts convert NO_x for olefins and aromatics, which have unsaturated bonds, and that the conversion temperature range also changes according to the HC species. Therefore, this team set a model gas with a paraffin, olefin and aromatic component ratio matching

that of exhaust gas for evaluation. Table 1 shows the formulation of the set model gas.

Fig. 3 shows a comparison of NO_x conversion characteristics according to temperature for the model gas and the exhaust gas. Note that the temperature in this figure is the catalyst inlet gas temperature in the model gas tests, and the catalyst bed temperature in the actual vehicle tests. These results confirmed that the model gas could accurately simulate both the NO_x conversion temperature range and the NO_x conversion ratio for exhaust gas.

4.3. Improving NO_x Conversion Performance

SCR-type lean NO_x catalysts have a reaction mode that converts NO_x using HC as the reducing agent under excess oxygen conditions. This HC oxidizing reaction is a competitive reaction by the oxidizing agents O₂ and NO_x.

For that reason, an improved NO_x conversion ratio and expanded NO_x conversion temperature range can be expected by inhibiting HC oxidation by O₂ and increasing the selectivity of the NO_x reduction reaction. Therefore, the

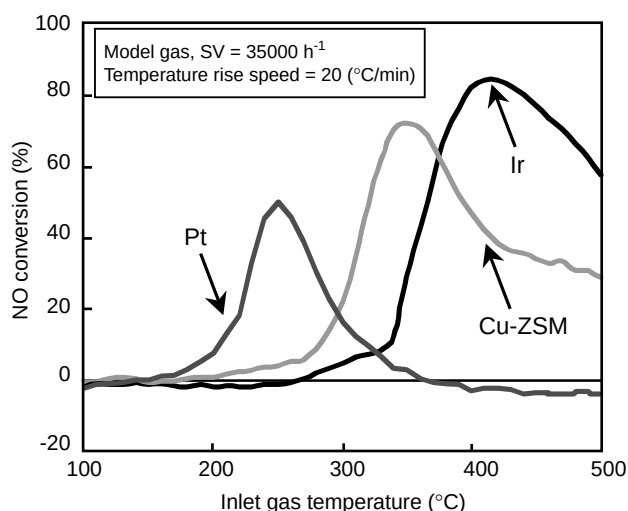


Fig.1 NO conversion characteristics of Ir, Pt and Cu catalysts

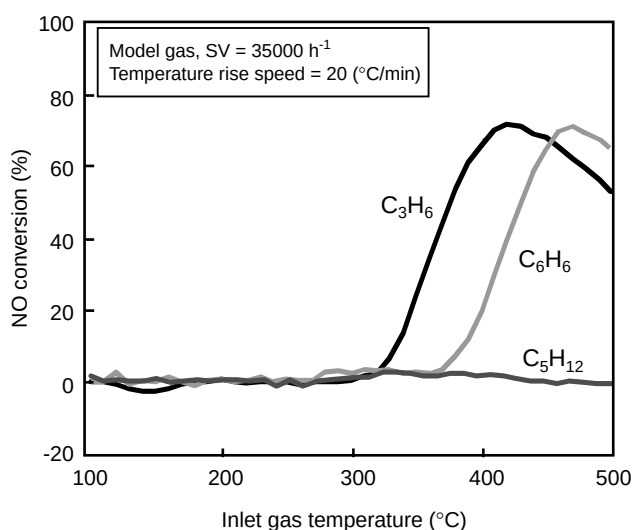


Fig.2 NO conversion characteristics of kinds of HC

Table 1 Formulation of model gas

Gas	Concentration
O ₂	7.4%
CO ₂	9.5%
T-HC	2800 ppmC
CO	800 ppm
NO	130 ppm
H ₂	300 ppm
N ₂	Bal.
H ₂ O	10%

HC: C₃H₆, C₆H₆, i-C₅H₁₂

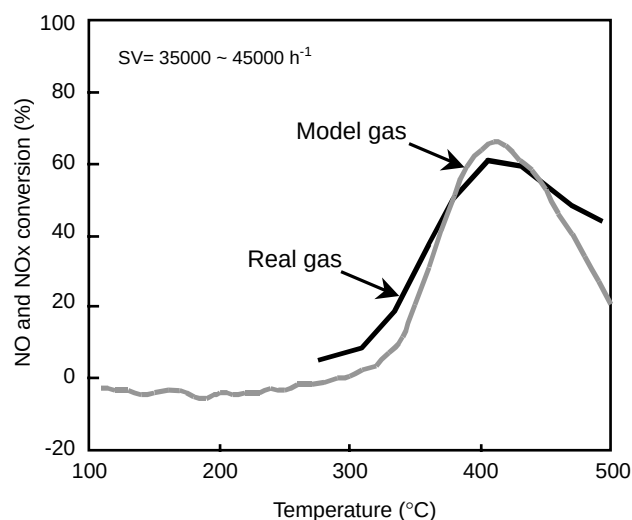


Fig.3 NO and NO_x conversion characteristics of experimental gases

Ir support materials were investigated as a means of inhibiting HC oxidation.

Fig. 4 shows the effects of different support materials on NO_x conversion characteristics using a flow method catalytic reactor in a fixed bed. These results show that when the support material has relatively little HC oxidation inhibition effect (Support C), the maximum NO_x conversion ratio is lower and the conversion temperature range is higher. In contrast, strengthening the inhibition effect of HC oxidation improved both the maximum NO_x conversion ratio and the conversion temperature range, thus improving the NO_x conversion performance.

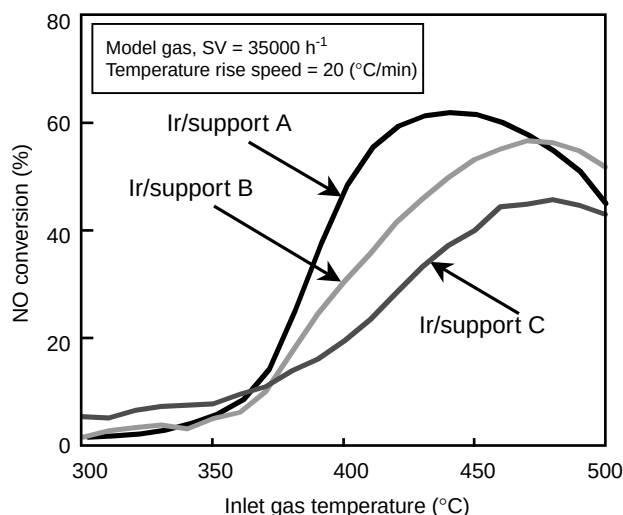


Fig.4 NO conversion characteristics of support materials

4.4. Improving Durability

4.4.1. Problems after Aging

Heat resistance is known to be an issue for selective-type catalysts⁽¹⁾⁽⁶⁾⁽⁷⁾. Therefore, durability was confirmed using a catalyst obtained by optimizing the support materials.

Fig. 5 shows the changes in NO_x and HC conversion characteristics using a flow method catalytic reactor in a fixed bed in a new condition and after aging equivalent to

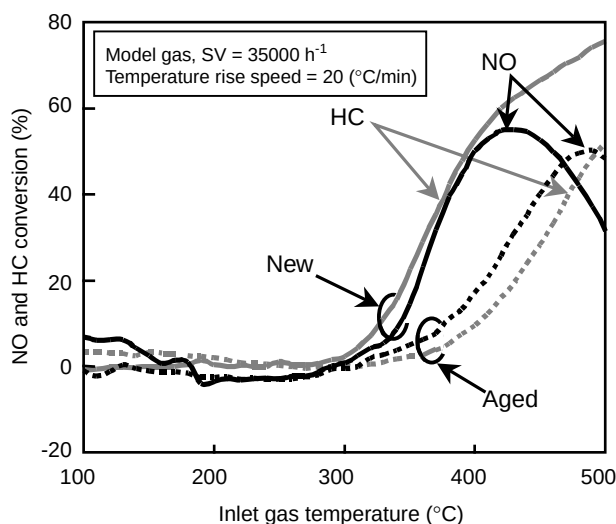


Fig.5 NO and HC conversion characteristics of aging

80,000 km. This shows that in addition to the oxidation capability for the HC that acts as the NO_x reducing agent, NO_x conversion also takes place at higher temperatures. Thus, under the aging conditions used in this study, the drop in NO_x conversion ratio and the higher NO_x conversion temperature range after aging are problems, and improvement is required in these areas.

4.4.2. Methods for Improving Durability

The NO_x reaction mechanism of the Ir catalyst was inferred, and the methods for improving this inferred reaction mechanism were investigated to solve the problems clarified in 4.4.1.

The NO_x reaction mechanism of the Ir catalyst under excess oxygen conditions is hypothesized to be as shown in Fig. 6. Here, the NO that accounts for the majority of the exhausted NO_x reacts with O₂ at the Ir surface to become the highly reactive NO₂, which is reduced by HC with unsaturated bonds⁽⁸⁾. Therefore, it is thought that if the NO has already been converted to NO₂ when it reaches the Ir surface, the reaction to convert NO to NO₂ at the Ir surface can be omitted, thus improving the NO_x conversion ratio and preventing a rise in the conversion temperature range. Coating the surface of the Ir catalyst with a material that converts NO to NO₂ was presumed to be an effective means for realizing this.

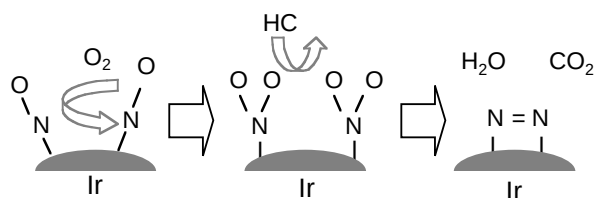
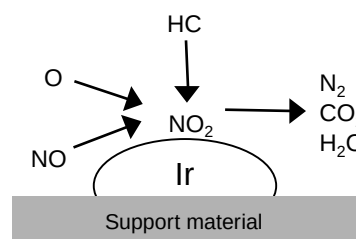


Fig.6 X Hypothesis of exhaust gas conversion mechanism

4.4.3. Investigation of NO₂ Conversion Materials

NO₂ conversion materials were investigated based on the hypotheses described in 4.4.2. The functions required of the NO₂ conversion material are as follows.

- (1) The material should have a high NO to NO₂ conversion efficiency.
- (2) The NO₂ conversion temperature range should match the NO_x conversion temperature range of the Ir catalyst.

Therefore, the authors focused on ABO₃ type compound oxides and base metal oxides as NO₂ conversion materials. When ABO₃ type compound oxides have an oxygen vacancy in their structure, this oxygen vacancy becomes a NO adsorption site as shown in Fig. 7, and at the same time the B site in the structure acts as an oxidation site. Therefore, a

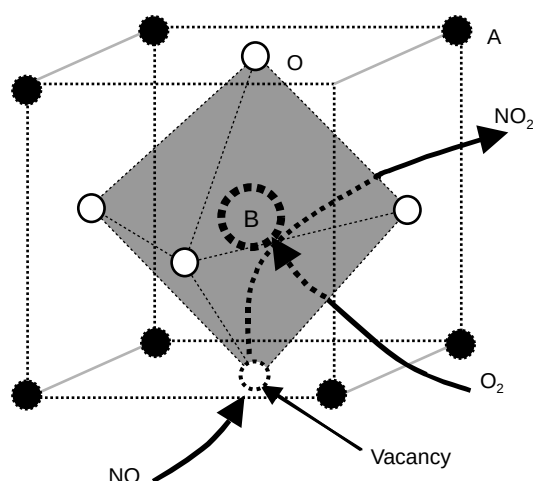


Fig.7 X Hypothesis of NO conversion to NO₂ mechanism

high NO₂ conversion efficiency can be expected due to the functions of both of these sites.

On the other hand, base metal oxides and particularly lanthanoid oxides typified by CeO₂ have NO_x adsorption capabilities and also exhibit oxidizing functions at temperatures of 300°C or higher, so a high NO₂ conversion efficiency can be expected.

Fig. 8 shows the NO₂ conversion characteristics of NO₂ conversion materials in a screening test using a flow method catalytic reactor in a fixed bed. These results show that in terms of NO₂ conversion characteristics, the LaCoO₃ compound oxide has a maximum conversion ratio of 70% in a temperature range which is near the NO_x conversion temperature range of the Ir catalyst, making it superior to the other materials. In addition, the LaCoO₃ compound oxide also has stronger oxidizing capability than the other materials, and can be expected to inhibit rises in the NO_x conversion temperature range. Based on these viewpoints, the LaCoO₃ compound oxide was selected as the NO₂ conversion material for coating the Ir catalyst surface.

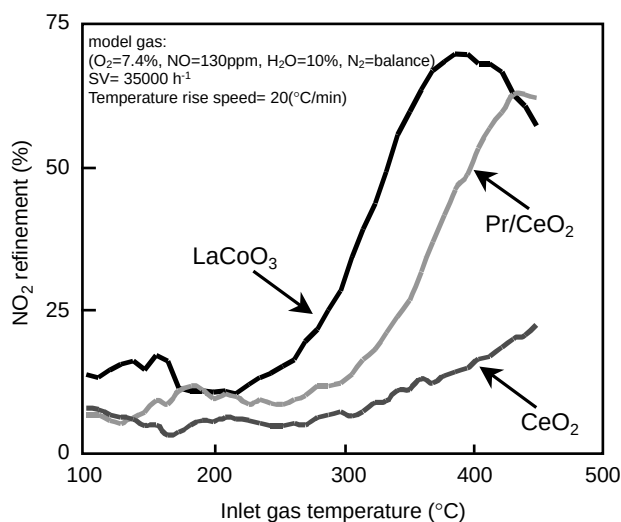


Fig.8 NO₂ conversion characteristics of materials

4.4.4. Performance Confirmation Results

Ir catalysts were coated with the LaCoO₃ obtained as described in 4.4.3. and the performance of catalysts aged to a mileage equivalent to 80,000 km was confirmed.

Fig. 9 shows the effects of the coated NO₂ conversion material on HC conversion characteristics, and Fig. 10 shows the effects on NO_x conversion characteristics in the new and aged conditions. The new material performance was improved by the high NO₂ conversion capability of the LaCoO₃. In addition, whereas oxidation occurred at higher temperatures without the coat, oxidizing performance was maintained by the NO₂ conversion capability which was preserved even after aging and also by the oxidizing power of the LaCoO₃ itself. As a result, the conversion temperature shift toward higher temperatures was inhibited, and the aged performance exhibited almost the same NO_x conversion characteristics as the new performance.

Thus, the NO₂ conversion material coat was able to solve the problems of a reduced NO_x conversion ratio and higher NO_x conversion temperature range in the aged condition.

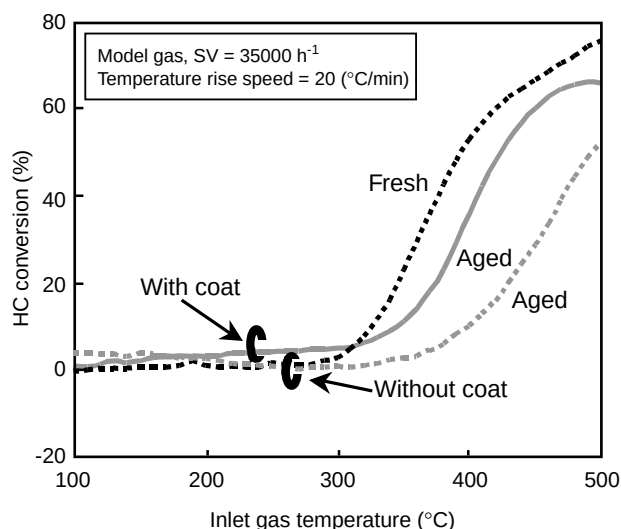


Fig.9 HC conversion improvements of the coating material

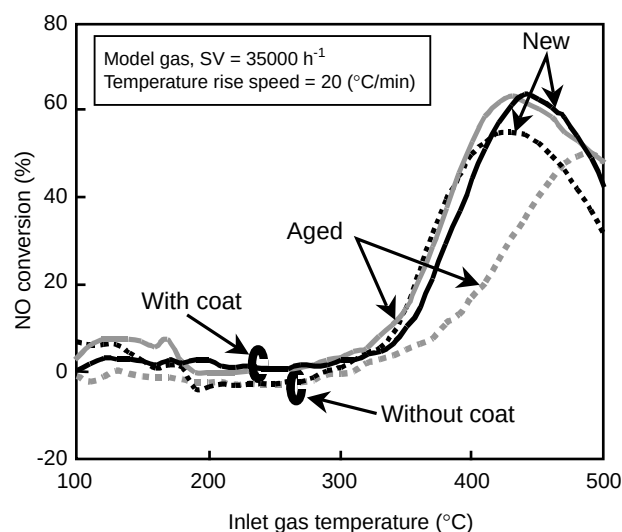


Fig.10 NO conversion improvements of the coating material

5. Evaluation of Actual Vehicle Emissions

5.1. Understanding Control Parameters

When constructing an actual vehicle system, it is important to obtain the maximum performance from the Ir catalyst. For this reason, the parameters governing NO_x conversion were investigated.

Fig. 11 shows the effects of O₂ concentration and HC/NO_x ratio on the NO_x conversion ratio using a flow method catalytic reactor in a fixed bed at 400°C. Note that the HC/NO_x ratio is the mass ratio. These results confirmed that lowering the O₂ concentration and increasing the HC/NO_x ratio are effective for improving the NO_x conversion performance of the Ir catalyst.

Based on these characteristics, HC/NO_x ratio and O₂ concentration control are required as engine control, so EGR control and air-fuel ratio feedback control using a UEGO sensor were adopted.

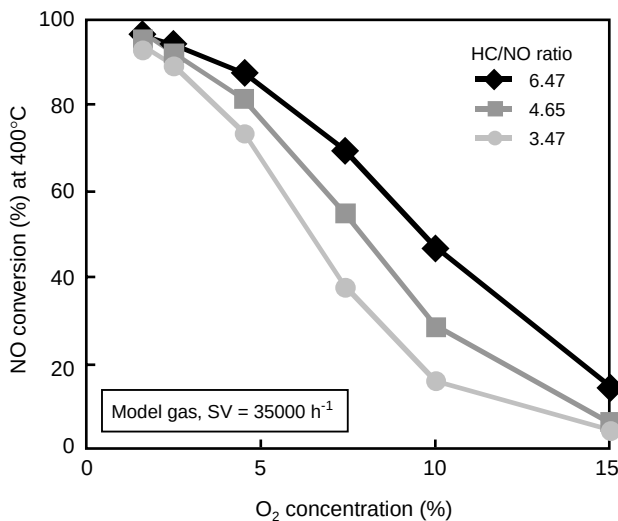


Fig.11 NO conversion characteristics of HC/NO ratios and O₂ concentrations

5.2. Conditions

The test vehicle was equipped with an in-line four cylinder 1.5 l prototype engine.

Based on the Ir catalyst characteristics, an EGR control system and an air-fuel ratio feedback control system using a UEGO sensor were adopted. In addition, emissions tests were performed in the 10-15 mode using a catalyst aged to an equivalent mileage of 80,000 km.

5.3. Results of 10-15 Mode Measurement

Figs. 12 and 13 show the instantaneous NO_x exhaust level, NO_x conversion ratio, and HC/NO_x ratio as defined by the mass ratio in the 10-15 mode using modal measurement.

These figures confirmed that NO_x conversion was obtained under all lean-burn conditions by controlling the HC/NO_x ratio which governs the NO_x conversion performance of Ir catalysts. Note that a conversion ratio of 63% was obtained in the 10-15 mode.

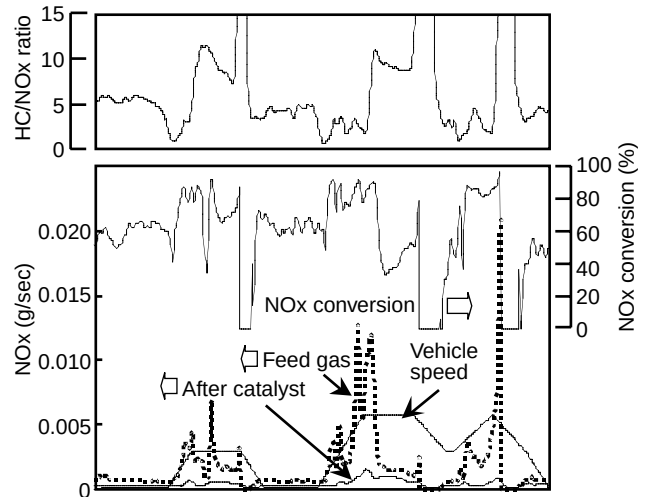


Fig.12 MODE test results (10 MODE)

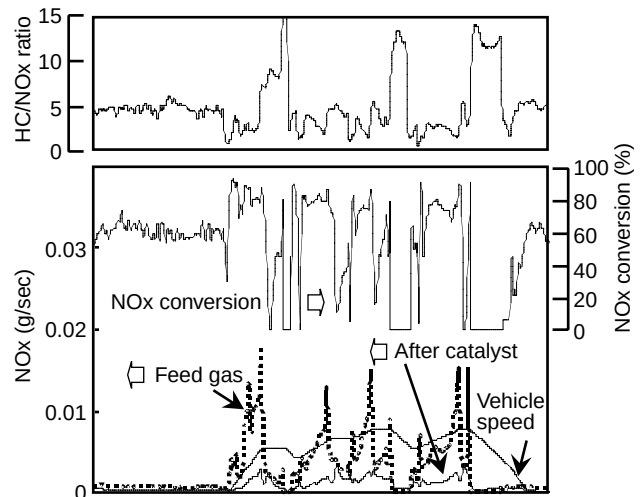


Fig.13 MODE test results (15 MODE)

6. Conclusion

Catalytic systems were studied focusing on SCR-type lean NO_x catalysts which exhibit stable conversion performance under excess oxygen conditions for NO_x conversion in lean-burn exhaust gas, and the following results were obtained.

- (1) Ir was selected as the active species, and it was confirmed that improving the support materials improved the NO_x selectivity in the HC and NO_x competitive reaction under excess oxygen conditions.
- (2) The problems of performance drops and higher conversion temperature ranges after aging were solved by coating the Ir catalyst surface with a LaCoO₃ compound oxide which has superior NO to NO₂ conversion capability in the NO_x conversion temperature range of the Ir catalyst.
- (3) Engine control was performed in accordance with the catalyst conversion characteristics, and a NO_x conversion ratio of 63% was obtained under all lean-burn conditions in the 10-15 mode.

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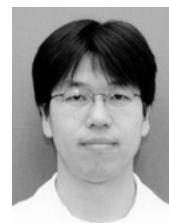
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