B-16.5 Reduction techniques of methane and nitrous oxide from automobiles

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Abstract

To find a clue to reduction techniques for Nitrous Oxide (N_2O) emission from three-way catalyst equipped vehicles, four test samples of three-way catalysts with typical noble metal compositions were fabricated by way of experiment and their N_2O formation characteristics have been experimentally studied. Then, these catalyst samples were conditioned artificially by aging with real automotive exhaust gas and the N_2O formation characteristics after aging has been also observed.

As results, catalyst temperature zones and concentration levels of N_2O formation varies greatly by the catalyst composition. In general, a catalyst with lower metal content showed lower N_2O mass emission at both fresh and after aging conditions. The tendency of the increase in N_2O mass emission due to the deterioration is also different among the tested catalyst samples.

It was also clarified that the main cause of N_2O increase with aged catalyst was the shift of maximum N_2O formation temperature zone to the higher regions. Catalyst deterioration effects on N_2O emission of a vehicle were predicted using model gas experiment and catalyst temperature distribution of a passenger vehicle driven on a chassis dynamometer with various test procedures.

Key Words Green house effect gas, Nitrous oxide, Automobile exhaust gas

1. Introduction

In order to prevent the global warming, measures that reduce greenhouse gases such as CO_2 from transportation should be taken. Recently, not only CO_2 but also CH_4 and N_2O are required to be reduced. CH_4 and N_2O have strong greenhouse effect and are considered to be a important component in the future. Although automobiles are not major source of CH_4, it was estimated that vehicles emitted N_2O is about 300Gg/year in whole world, which included 20Gg/year in Japan and 145Gg/year in U. S. A. [1),2)] and these figures are not negligible in the percentage. So, in this study, we have concentrated upon N_2O for the research subject.

One of measures for reducing CO_2 from vehicles is improvement of thermal efficiency of engines. Generally it cause NOx increase and exhaust gas temperature decrease, which need development of a new type of catalyst[3),4)]. Due to stringent exhaust gas regulation, improving conversion performance of catalyst is necessary, and catalysts which activates even relatively low temperature are begun to be used. There are some papers [5] [6] which analyze that catalyst deterioration cause N_2O increase. If effects of catalysts compositions and deterioration of a

catalyst on N_2O emission are clarified, they are great help to develop countermeasures of N_2O emission control from vehicles.

In this study, a pair of four test samples of three-way catalysts with different metal compositions were made for experiments. Four catalysts were used under fresh condition and the other four catalysts were used under aged condition with equivalent mileage to 50,000km for durability tests. Then, comparing fresh catalysts of N_2O formation characteristics of catalyst temperatures with aging catalysts, the aging effect of three-way catalysts on N_2O emission was experimentally studied.

Beside catalyst component test, N_2O emission and catalyst temperature of an actual vehicle have been also experimentally analyzed with chassis dynamometer test.

2. Experimental equipment and method

2.1 Catalyst component test

Table 1   Specifications of tested catalysts

Catalyst type		Composition	Structure
(A)	Pt / Rh 5:1	Pt 1.25g/L, Rh 0.25g/L	Monolith, 1inch Diameter 60mm,Honeycomb,400cpsi
(B)	Pt / Rh 5:1	Pt 0.8g/L, Rh 0.16g/L	Monolith, 1inch Diameter 60mm,Honeycomb,400cpsi
(C)	Pd	Pd 3.0g / L	Monolith, 1inch Diameter 60mm,Honeycomb,400cpsi
(D)	Pd / Rh 5:1	Pd 1.0g /L, Rh 0.2g/L	Monolith, 1inch Diameter 60mm,Honeycomb,400cpsi

Table 2   Catalyst aging condition

Feed Gas	Gasoline Engine Exhaust Gas
Cycle of Air-Fuel Ratio	Stoich. A/F 14.6 ± 0.9 (0.4Hz) Oxidizing A/F 17 Reducing / Oxidizing = 870 sec / 30 sec
Gas Temperature	900 deg.
Equivalent Mileage	US 30,000 miles

Tested three-way catalyst and test bed

The catalyst test pieces have a monolith structure with cordierite honey-comb and alumina for the carrier. Table 1 shows the specification of tested catalysts.

Platinum/Rhodium (Pt/Rh) which are commonly used for three-way catalytic converters and Paradigm (Pd) which is begun to use recently were selected as the catalyst component metals.

Durability experiment

Catalysts which had the same composition as shown in Table 1 were deteriorated artificially equivalent to 50,000 km accumulated mileage and used for durability experiment, of which aging conditions are shown in Table 2. In this paper, the word "aging" stands for change of the catalyst performance by mileage accumulation of the vehicle.

Catalyst test bed

For the observation of N_2O formation in the catalyst, a catalyst test bed shown in Fig.1 was used. A model gas which simulated actual automotive exhaust gas was composed by diluting a mixing gas in a high pressure vessel and introduced
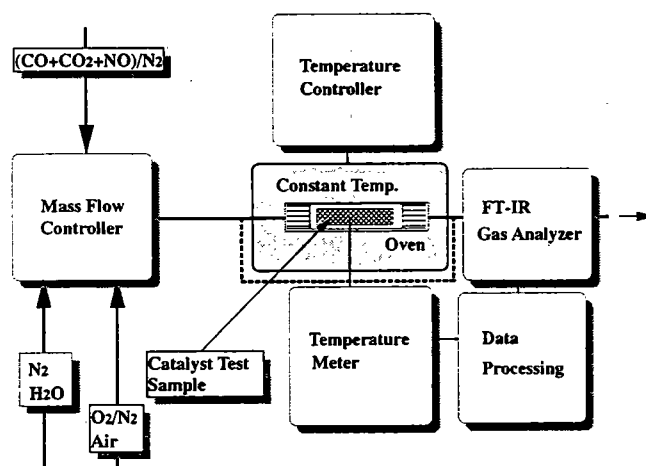

Fig. 1   Schematic of catalyst test bed

into a quartz tube filled with catalyst test piece with a space velocity of 50,000 hr^{-1}. CO, NO, CO_2, and N_2O concentration versus catalyst temperature was observed continuously with FTIR. The catalyst temperature was measured with a thermocouple, which was inserted into the center of a catalyst. The measurement was done with test gas flowed after catalyst reached stable temperature.

Model gas and gas analyzers

The model gas used for experiments was originally nitrogen balanced mixed gas with CO:2820ppm, NO:2840ppm, and CO_2:15.9% in concentration and adjusted to the similar concentrations as actual automotive exhaust by diluting it with nitrogen gas, that is, CO:730ppm, NO:735ppm, and CO_2:4.1%. However, the maximum N_2O formation appears in a inlet gas condition with a little oxygen content rather than without oxygen content [6]. Then, O_2 and water vapor were added to the model gas. Changes of such as N_2O formation by O_2 addition is shown in Fig.2.

$$nNO + lCnHm \rightarrow nNH_3 + lCO_2 \qquad (1)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (2)$$
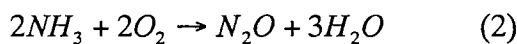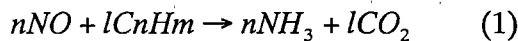
Actual exhaust gas includes H_2 and HC, which work as deoxidizers of NO besides CO. However, H_2 and HC formed ammonia(NH_3) on a catalyst as indicated in equation (1). The NH_3 is oxidized further and N_2O is produced as shown in equation (2).

Fig.3 shows conversion from NO to NH_3 with model gas. Fig.4 shows NH_3, N_2O, and NO emission from a passenger vehicle with three-way catalyst under

Fig. 2 Oxygen concentration versus emissions from a catalyst
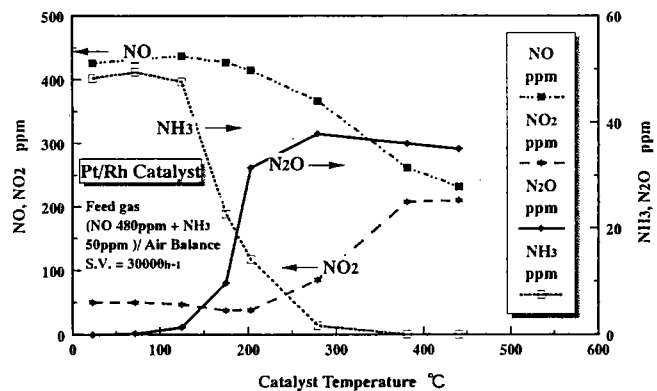
Fig. 3 N_2O formation for NH_3 contain model gas
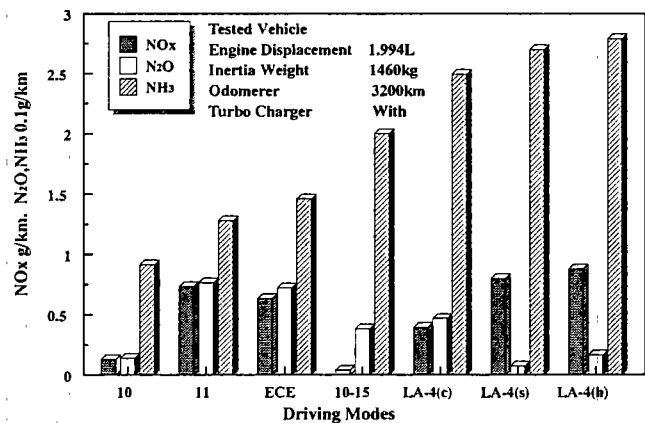
Fig. 4 NOx, N_2O, and NH_3 mass emissions from a three-way catalyst vehicle

various test procedures measured with FTIR. NH_3 produced by catalyst has high absorption characteristic. The NH_3 formation and NH_3 originated from N_2O produce complicated effect on experiment. In this study only carbon monoxide was chosen for NO deoxidizer to simplify the experiments [7],[8].

A paper by Gifhorn and Meyer [9] which discusses detail N_2O formation mechanism from NO and HC should be referred.
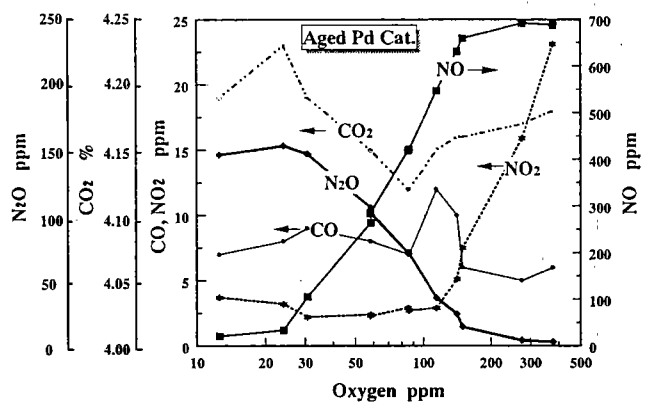
Mass flow rate of inlet gas of the catalyst was controlled at constant flow with gas flow meter. Behaviors of gas components at catalyst outlet was monitored continuously with heated FTIR. Components of outlet gas from the catalyst was also observed with FTIR.

2.2 Measurement of N_2O mass emissions from catalyst equipped vehicles

Compact passenger vehicles equipped with a three-way catalyst were chosen as test vehicles, which were driven on a chassis dynamometer with various driving cycles. Concentrations of each exhaust gas components in both tail pipe were measured with CVS system, NDIR for CO and CO_2, HFID for HC, and CLD for NOx as shown in Fig. 5. N_2O concentration in direct exhaust gas and CVS bag were measured gas chromatograph and FTIR.
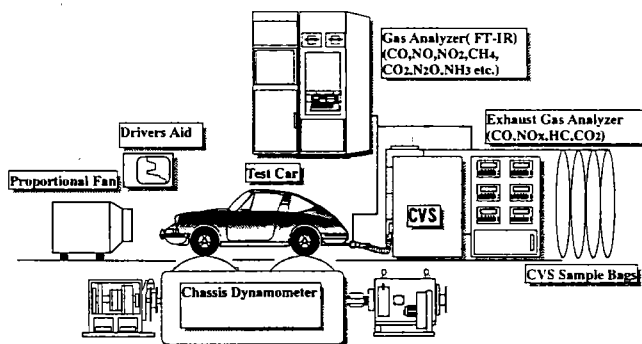

Fig. 5 Schematic of the experiment system

3. Results and discussions

3.1 Effect of catalyst composition on N_2O formation behaviors

<u>Pt/Rh high metal content catalyst</u>

Fig.6 through Fig.9 show catalyst temperature versus CO, NO, and N_2O concentrations emitted from catalyst before and after aging.

Catalyst A shown in Fig.6 is a typical Platinum/ Rhodium (Pt/Rh) catalyst with 5:1 in Pt/Rh composition ratio. This catalyst has the highest metal density with 1.25g/l in Pt and 0.25g/l in Rh among tested catalysts in this study.

Fig. 6 NO, CO, and N_2O behaviors versus catalyst temperatures (Catalyst A)

Fresh catalyst indicated as solid line shows that the purification of CO and NO starts when the catalyst temperature comes up to around 100 deg.C, where N_2O formation also starts.

The peak value of N_2O concentration is 160 ppm at around 320 deg.C, and goes down to 50 ppm as catalyst temperature exceeds 550 deg.C. This catalyst showed the highest N_2O formation characteristics among tested fresh catalysts and conversion rate from NO to N_2O was about 25% at the maximum. NO reduction rate indicates its maximum at the catalyst temperature range of about 320 deg.C. When it exceeds this temperature, NO reduction rate goes down again.

The aged catalyst shown as dotted lines indicate that the light-off temperatures for CO and NO shift to higher side and reduction rates of them at low temperature go down. NO reduction rate goes down slightly under the temperature region of 300 deg.C or higher. The temperature of start of N_2O formation shifts to higher temperature regions. The temperature of the peak N_2O formation and its concentration level do not change comparing with those of the fresh catalyst. However, at the temperature exceeding peak N_2O formation, N_2O concentration
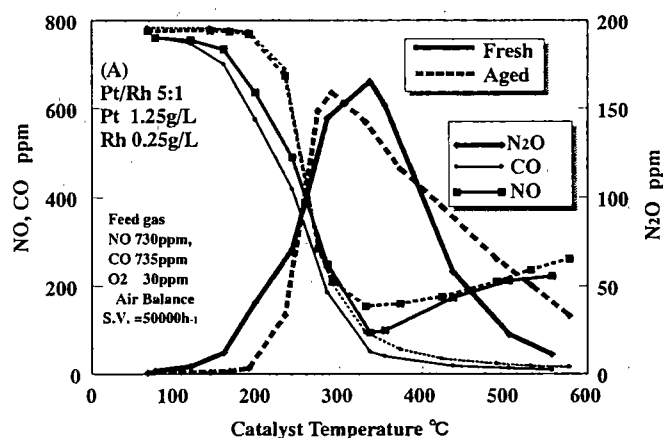
is almost twice as much as that of the fresh catalyst.

Pt/Rh low metal content catalyst

The catalyst B shown in Fig.7 has the same Pt/Rh ratio as the catalyst A but the noble metal content is lower.

In the case of the fresh catalyst, compared with the catalyst A light-off temperature shifted to higher side and CO and NO reduction rates are worse at low temperature regions. N_2O formation temperature also moved to higher side. Reduction rate of NO decrease but that of CO does not decrease under high temperature regions.

It is worthy of notice that the N_2O formation is lower when metal content of a catalyst is lower. N_2O is about one third of the catalyst A at 450 deg.C.

However, N_2O formation after aging goes up drastically and came up to the same level as the catalyst A. The reduction rate of CO did not decrease after aging but even goes up slightly. The reduction performance of NO worsens greatly at high temperature regions.

Pd high metal content catalyst

Fig.8 shows the test results of high metal content Pd three-way catalyst C. Pd

has outstanding low temperature activation performance and as shown in the figure, it is obvious that the light-off temperature is about 150 deg.C lower than the catalyst A.

However, N_2O is also formed from low temperature regions and the concentration level at 200 deg.C is much higher than that of catalyst A or B. Furthermore, the high N_2O formation zone after the peak is extended to 500 deg.C or higher.

On the contrary, after aging, the light-off temperature goes up to almost the same as Pt/Rh catalysts. Then the advantage of Pd catalyst for the low temperature activation performance is lost. The whole temperature of N_2O formation is shifted about 150 deg.C to higher side.
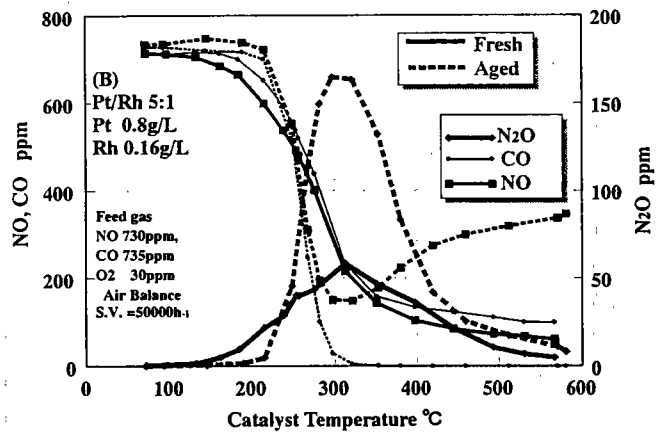

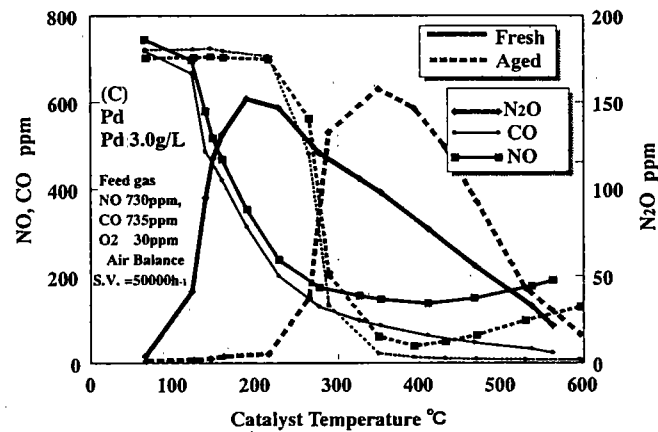Fig. 7 NO, CO, and N_2O behaviors versus catalyst temperatures (Catalyst B)

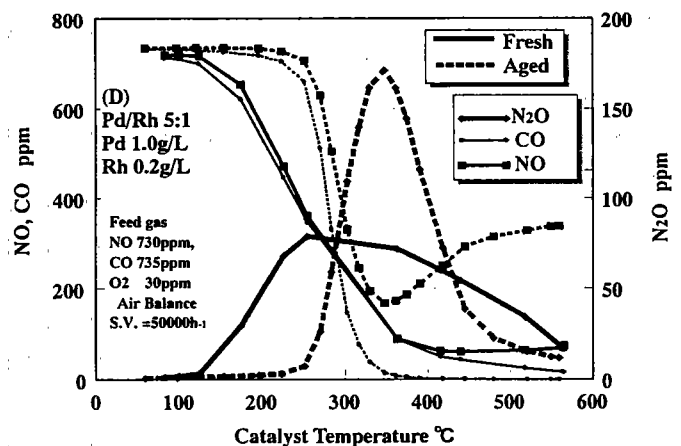Fig. 8 NO, CO, and N_2O behaviors versus catalyst temperatures (Catalyst C)

Fig. 9 NO, CO, and N_2O behaviors versus catalyst temperatures (Catalyst D)

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Pd/Rh catalyst

Fig.9 shows the test result of the catalyst D in which Rh is used in addition to Pd. The content of Pd is one third of the catalyst C.

In the case of the fresh catalyst, the light-off temperature is low and N_2O formation starts also from lower temperature like the catalyst C. However, the peak level of N_2O concentration is almost half of the high Pd content catalyst C.

On the contrary, the light-off temperature after aging moved from 100 deg.C to 250 deg.C and its low temperature activation performance was diminished. The peak level of N_2O formation increase to 160ppm, which is the same as other catalysts. However, its N_2O formation pattern is not so broad as the high Pd content catalyst C. In summary, this catalyst showed the neutral tendency on the light-off temperature and the N_2O formation pattern.

According to the results of experiments with model gas, it is concluded that a sort of noble metals which consist of a catalyst may determine the temperature of start of N_2O formation, and its quantity may determine its formation level.

3.2 Effect of NO to N_2O conversion on NO reduction performance of catalysts

Specifications of three-way catalysts are determined mainly by the requirement of NOx reduction performance. Then, the change of the specification for reduction of N_2O mass emission may affect NOx reduction performance.

Up to now, NO reduction by a catalyst have been considered that all NO is decomposed into nitrogen and oxygen as indicated equation (3). However, in the process of NO deoxidization in a catalyst, a part of NO may be converted to N_2O as indicated equation (4). Thereby NO decomposition reaction including N_2O formation was considered. Fig.10 shows the result of the prediction, in which NO reduction rate is defined as equation (5) for Pd catalyst.
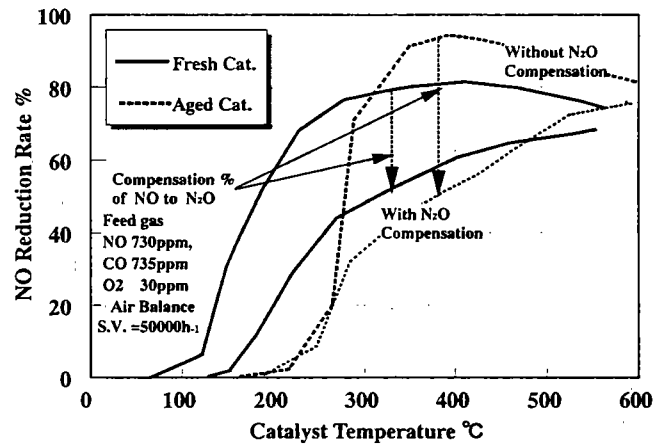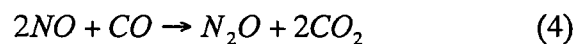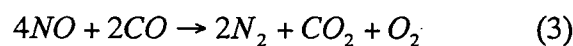

Fig. 10 NO reduction rate with and without N2O compensation

$$4NO + 2CO \rightarrow 2N_2 + CO_2 + O_2 \qquad (3)$$

$$2NO + CO \rightarrow N_2O + 2CO_2 \qquad (4)$$

$$(NO)_{reduction\_rate}$$

$$= \left\{ 1 - \frac{NO_{out} + 2(N_2O)_{out}}{NO_{in}} \right\} \times 100 \qquad (5)$$

NO reduction rate compensated with N_2O conversion decreased drastically. In the case of the fresh catalyst indicated as solid line, the NO reduction rate changes from 80% to 55% at 320 deg.C. After aging, it changes from 95% to 50%. NO reduction rate with the compensation decrease after aging.

It is notable that fresh Pd catalyst, which has good activation performance at low temperature, reduce NO between the catalyst temperature of 100 and 250 deg.C. However, this NO reduction effect includes NO to N2O conversion. Also in the case of the aged catalyst, the effect of this conversion on NO reduction rate between 280 and 550 deg.C is not small either.

Accordingly when de-NOx catalyst is designed, N_2O formation should be taken into consideration from point of view of global warming.

Fig. 11 Behaviors of catalyst temperature and N2O concentration in diluted sample gas under LA#4

3.3 Estimation of N_2O mass emissions from actual vehicles

N2O emission tendency by mileage accumulation

N_2O formation characteristics of three-way catalyst described above has been obtained with component tests of catalyst using model gas. Results of these experiments are not applied directly to actual exhaust gas from vehicles. To analyze N_2O emission characteristics of actual vehicles equipped with a three-way catalyst, temperature of the catalyst under driving modes as well as composition and mileage accumulation of the catalyst should be considered.

Fig.13 shows an example of the catalyst temperature and N_2O concentration, which is continuously measured with CVS diluted sample gas from a passenger vehicle equipped with Pt/Rh catalyst for pre-catalyst and Pd catalyst for main catalyst under LA#4 mode. N_2O concentration of CVS is proportional to N_2O mass emission. Therefore, N_2O mass emission versus catalyst temperature can be observed under a test procedure.

As high N_2O emission is observed at low catalyst temperature regions of 200 through 300 deg.C during warming up Catalyst temperature of this region seems to give major effect on total N_2O emission. As the catalyst gains higher temperature, large N_2O emission decrease is observed. Effect of catalyst temperature on N_2O emission has the same trend indicated in the model gas experiment. The amount of N_2O emission is defined by catalyst temperature transition of a test procedure.

Fig.12 shows comparisons of temperature frequency distributions under cold starting driving mode used for exhaust emission test in various countries with the same passenger vehicle. Japanese 11 mode and ECE mode were operated under similar temperature distribution patterns. On the contrary, the pattern is different under LA#4 driving mode. However, LA#4 emission test procedure includes not only cold starting but also heavy load and high speed operations ,that is, LA#4 consists of three phases. Thereby LA#4 is convenient for analyzing a catalyst
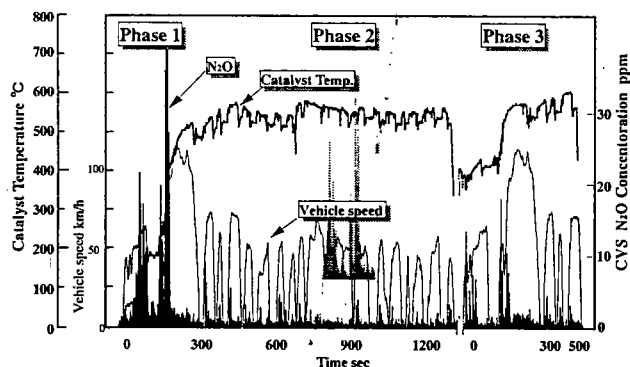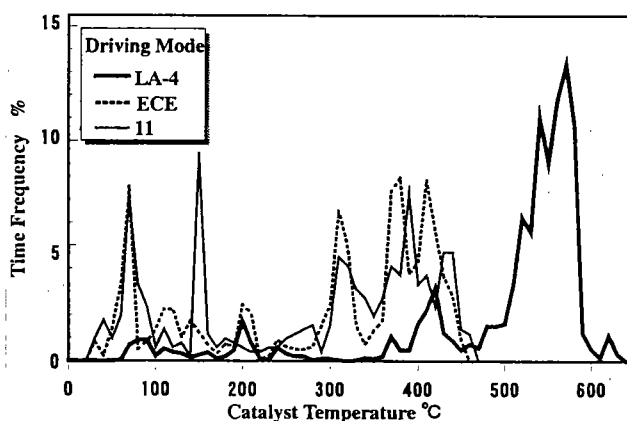

Fig. 12 Comparison of frequency distribution patterns of catalyst temperature among different modes

performance under wide temperature range. In this paper, effect of catalyst aging on N_2O mass emission with catalyst temperature range was analyzed separately at each phase of LA#4 test cycle.

In order to discuss N_2O emission from a passenger vehicle, N_2O formation characteristics of the low metal content Pt catalyst B (hereafter (B)Pt/Rh(low)) and high metal content Pd catalyst C (hereafter (C)Pd(high)), which are affected significantly by the aging, and the frequency distribution patterns of the temperature versus the catalyst temperature under the each phase of LA#4 driving are shown in Fig.13 through Fig.15.

Phase 1

Phase 1 as shown in Fig.13 starts from cold starting and the temperature range is separated mainly with low temperature regions of 100 to 250 deg.C and high temperature regions of 550 to 600 deg.C. In the fresh catalysts, N_2O emission of catalyst (C)Pd(high) at 100 to 250 deg.C is much higher than that of catalyst (B)Pt/Rh(low). Thereby fresh (C)Pd(high) catalyst has high N_2O emission characteristics at cold starting modes.

N_2O formation of catalyst (C)Pd(high) at most frequently used temperature zone of 550 to 600 deg.C is also several times as much as that of catalyst (B)Pt/Rh(low). In both fresh and aged conditions and Pd catalyst may have high N_2O mass emission.

N_2O formation of catalyst (B)Pt/Rh(low) increases at the vicinity of 300 deg.C because of aging. However, the frequency of use at this temperature

Fig. 13 N_2O formation characteristics and frequency distribution patterns of catalyst temperature under phase 1 driving of LA#4

zone is low and the aging effect of catalyst (B)Pt/Rh(low) on N_2O emission is considered to be also small. In summary, under Phase 1 driving, the aging effect of catalyst on N_2O emission may be small, or in some cases the aging effect may even decrease N_2O emission.

Phase 2

The catalyst temperature zone under Phase 2 driving is concentrated to be at narrow zone of 550 to 600 deg.C as shown in Fig.14. The N_2O emissions of both catalysts may be affected little by the shift of N_2O formation peak temperature due to aging. Although the aging effect on N_2O emission increase may be small, N_2O emissions can increase in terms of ratio aged catalyst to fresh catalyst because the catalyst temperatures are mostly used in this zone .
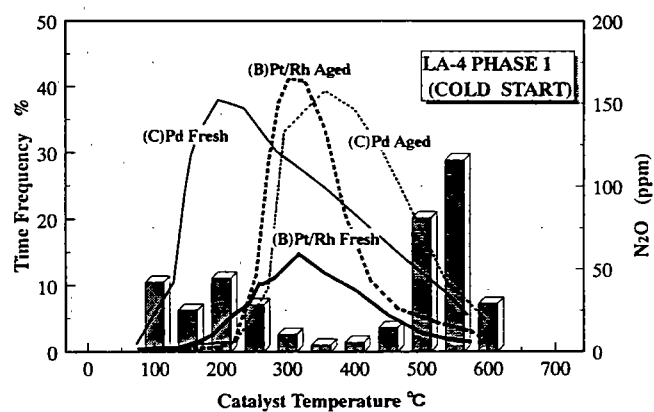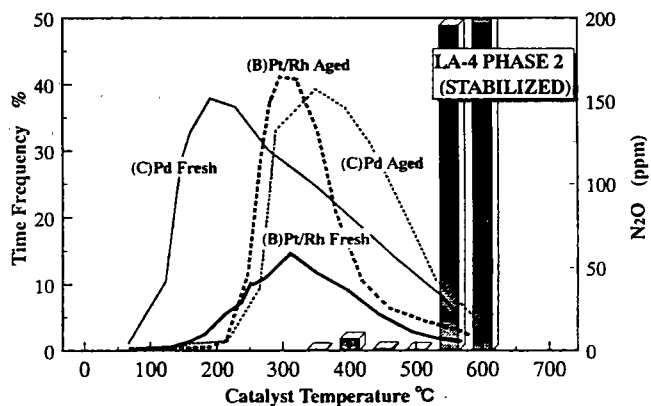

Fig. 14 N_2O formation characteristics and frequency distribution patterns of catalyst temperature under phase 2 driving of LA#4

Phase 3

Phase 3 is warmed up driving mode with 10 minutes of idling followed by the same driving pattern as Phase 1. The catalyst temperature has already come up to around 400 deg.C at the starting as shown in Fig.15. Thereby, the aging effect at low temperature zone does not affect N_2O emission in this phase. The increase in N_2O formation of (B)Pt/Rh(low) by aging at the zone from 450 to 600 deg.C is small and the emission at 600 deg.C is also a little.

On the contrary, (C)Pd(high) has high N_2O formation characteristics at 450 deg.C, of which zone appears in high frequency at this phase, and N_2O almost doubles by aging. In the case of Pd catalyst, the aging effect on N_2O mass emission can be also considerable in this phase.

Fig. 15 N_2O formation characteristics and frequency distribution patterns of catalyst temperature under phase 3 driving of LA#4

N_2O mass emission characteristics of actual vehicles with mileage accumulation

Fig.16 shows comparison of N_2O mass emissions of a compact passenger vehicle equipped with low Pt/Rh content three-way catalyst under various driving modes measured before and after five years in daily use with 50,000km mileage accumulation. N_2O mass emissions are generally increased with aging and this tendency agrees qualitatively with the estimation of the analysis of each phase in LA#4 test mode as mentioned above.

Then with the results of these catalyst tests and a statistical data of the number of vehicles with registered year, it may be possible to estimate the effect of catalyst aging by vehicle mileage accumulations on N_2O emission from automobiles and to improve the accuracy of total N_2O estimation emitted from automobiles to ambient air.

Fig. 16 N2O mass emissions under various driving modes before and after aging

4. Conclusion

To search exhaust emission control method for N_2O, which is one of the green house effect gases from automobiles, N_2O formation mechanism has been studied with fresh and aged catalysts of different compositions using model gas.

The results are the following.

1.The change in N_2O mass emission characteristics with catalyst aging is caused by decrease in the low temperature activation and increase in N_2O formation at high temperature regions. The effect of aging differs with the driving cycles because of the major catalyst temperature zone.
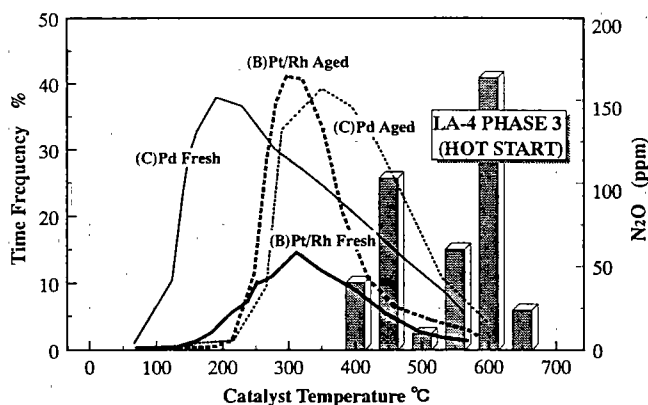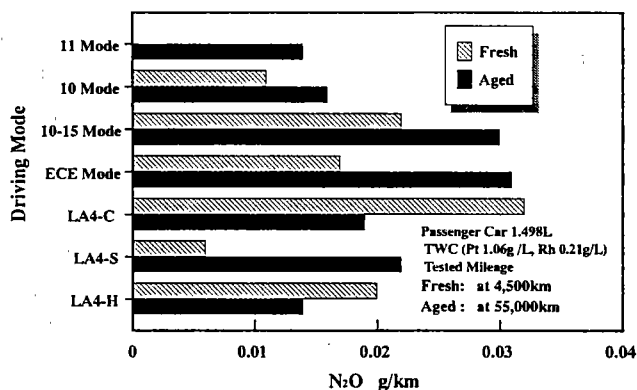
2.N_2O formed by three-way catalysts has a large effect on rate of NOx conversion. Pd catalyst has outstanding performance of NOx conversion under low temperature, of which performance probably bases on N_2O formation. It is a problem from a point of view of the global warming.

3.As N_2O emission goes up with the noble metal quantity increase in a catalyst, a low metal content catalyst may be favorable for N_2O control.

4.Making an approximate estimate of N_2O mass emission from three-way catalyst due to its deterioration may be possible taking the sort and quantity of metals and catalyst temperature frequency distributions of driving modes into consideration.

REFERENCES

1.Koike, N. and Odaka, M., "Methane and Nitrous Oxide (N_2O) Emission Characteristics from Automobiles", SAE Paper 960061, 1996.

2.Energy Information Administration, "Emissions of Greenhouse Gases in The United States", 1955.

3.Prigent, M. and De Soete, G., "Nitrous Oxide N_2O in Engines Exhaust Gases A First Appraisal of Catalyst Impact", SAE Paper 890492, 1989.

4.De Soete, G., "Experimental Studies and Models Related to Automotive 3-way Catalytic Reactors", Torsdag Denmark, 27th Oct.1994.

5.Sasaki, S. and Kameoka, A., "Nitrous Oxide Emissions from Automobiles", Proceedings of 5th International Workshop on Nitrous Oxide Emissions, 10-2, pp.1-8, 1992.

6.Jobson, E. et al., "Nitrous Oxide Formation Over Three Way Catalyst", SAE Paper 940926, 1994.

7.Koike, N. and Odaka M., "Exhaust Emission Behaviors of Nitrous Oxide from Automobiles - 2nd report : Effect of Oxygen Conditions on N_2O Emission from 3-way Catalyst Vehicles", Proceedings of JSAE 1994 Autumn Meeting No. 946, pp.49-52, 1994. (in Japanese)

8.Koike, N., Suzuki, H. and Odaka M., "Exhaust Emission Behaviors of Nitrous Oxide from Automobiles - 3rd report : Measurement of Nitrous Oxide and Ammonia Emissions from Three-way Catalyst", Proceedings of JSAE 1995 Autumn meeting No. 956, pp.153-156, 1995. (in Japanese)

9.Gfhon, A. and Meyery, R., "Influence of Different Exhaust Gas Component on the N_2O Formation at Three-way Catalysts", FISITA '96 Prague XXVI Congress Book of Abstracts, 1996.