B-16.2 Reduction Techniques of Nitrous Oxide Emissions from Automobiles

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Abstract

Automobiles equipped with a three-way catalytic converter account for the majority of N_2O emissions from automobiles. It has also been reported that deterioration of the catalyst radically increases N_2O emissions 1),2),3),4). Thus, it is important to work on the catalyst to reduce N_2O emissions from automobiles. If we can succeed in preventing the increase in N_2O emissions resulting from deterioration of the catalyst in particular, we can expect to drastically reduce N_2O emissions from automobiles.

Therefore, we started the present study by conducting a catalyst unit experiment to find out why deterioration of the catalyst increases N_2O emissions. As a result, we found that deterioration of the catalyst did not increase the concentration of N_2O generated. Instead, we found a mechanism in which the N_2O conversion capacity of the catalyst weakened as the catalyst deteriorated, and thus an increasing volume of N_2O was emitted from cars without any chemical conversion. The results of the study suggested that the use of a catalyst with high N_2O conversion efficiency is effective in reducing N_2O emissions and that the development of a new durable catalyst whose N_2O conversion capacity does not degrade is effective in preventing increases in the N_2O emissions induced by catalyst deterioration.

We also studied the feasibility of another technique for reducing N_2O emissions, in which the oxygen concentration of the atmospheric gas for the catalyst is controlled. As a result, we demonstrated the feasibility of the technique for drastically reducing N_2O emissions without compromising the harmful-emissions purification performance by the air-fuel ratio control that limited the oxygen concentration of the feed gas to 200ppm or less.

1. Introduction

Greenhouse gases (GHG) such as methane (CH_4) and N_2O are emitted from automobiles in addition to CO_2. That is why some techniques that are designed to reduce CO_2 emissions may result in increased GHG emissions5). Thus, it is necessary to evaluate techniques for reducing GHG emissions in terms of its overall effect on global warming including emissions of GHG as well as CO_2. This report deals with our latest study about the mechanism for N_2O emissions from automobile catalysts that requires further clarification and about techniques for reducing N_2O emissions.

2. Study Objectives

The three-way catalyst in the emission control system of gasoline-powered vehicles is known to emit N_2O when reducing NOx emissions. Although decreasing the air-fuel ratio into the lean range may reduce the amount of N_2O generated from the catalyst; such setting will rapidly increase levels of harmful NOx emissions [6], [7]. Thus, a technique that selectively reduces N_2O emissions yet will not increase emissions of NOx and other harmful substances will be required if N_2O emissions reduction is to be achieved by regulating the air-fuel ratio. However, only a few reports have been published to clarify the mechanism for N_2O generation from three-way catalysts. And the impacts of changes in the catalyst and in the air-fuel ratio setting, on N_2O emissions are mostly unknown. Therefore, we conducted an in-depth study on this particular mechanism and attempted to clarify the elements that reduce N_2O emissions from automobiles equipped with three-way catalytic converters.

3. Examination of N_2O Emissions Reduction Techniques

3.1. N_2O Emissions Reduction Technique Based on Catalyst Composition

Prevention of catalyst deterioration is the essential element in the technique for reducing N_2O emissions from automobiles. If the increase in N_2O emissions resulting from catalyst deterioration is deterred, the amount of N_2O released into the atmosphere can be reduced. That is why we investigated the characteristics of N_2O generation from the three-way catalyst and N_2O conversion by the catalyst, and then examined a technique for preventing N_2O generation from the catalyst by changing the catalyst composition.

3.2. N_2O Emissions Reduction Technique Based on Oxygen Concentration Control

The N_2O emission concentration of a catalyst depends heavily on the engine's air-fuel ratio, i.e. O_2 concentration of the feed gas. The amount of N_2O generated from the catalyst may be reduced by setting a lean air-fuel ratio. However, the O_2 concentration cannot be increased dramatically because it' worsens the catalytic NOx purification rate. Thus, we examined the technique for selectively reducing N_2O emissions while minimizing the increase in NOX emissions by increasing the O_2 concentration exclusively in the catalytic temperature range where N_2O

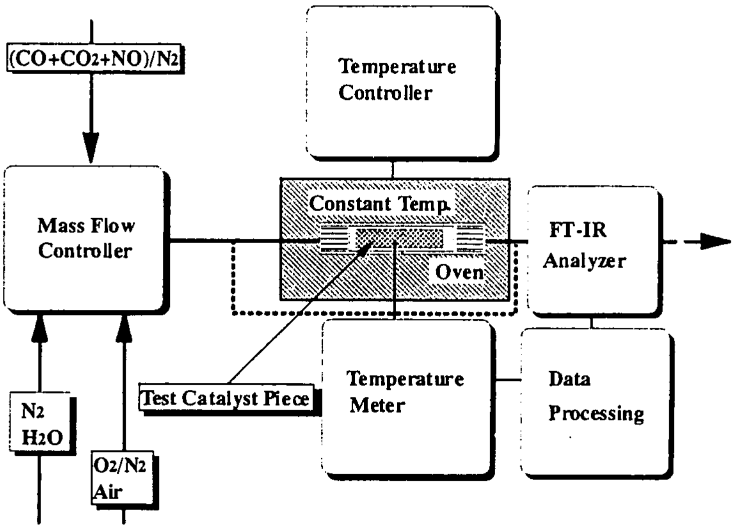

Figure 1. Schematic of Catalyst Test Bed

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. C**
Equivalent Mileage	**US 30,000 miles**

Table 1. Composition of the Experimental Catalystss

Catalyst type	Composition	Structure Monolith, 1inch Diameter 60mm,Honeycomb,400cpsi
Pt / Rh High	**Pt 1.25g/L, Rh 0.25g/L** CeO_2 23.0%, ZrO_2 3%, La_2O_3 13%, Al_2O_3 61.0%	
Pt / Rh Low	**Pt 0.8g/L, Rh 0.16g/L** CeO_2 23.0%, ZrO_2 3%, La_2O_3 13%, Al_2O_3 61.0%	
Pd High	**Pd 3.0g / L** CeO_2 19.0%, ZrO_2 3%, La_2O_3 2%, BaO 17.0% Al_2O_3 59.0%	
Pd / Rh Low	**Pd 1.0g /L, Rh 0.2g/L** CeO_2 19.0%, ZrO_2 3%, La_2O_3 3%, BaO 17.0% Al_2O_3 61.0%	

emissions are substantial.

4. Experimental Method

4.1. Catalyst Test Bed and Catalyst Composition Used in the Experiment

In the experiment to determine the N_2O conversion efficiency for each catalyst, N_2 from the N_2O unit and air balance gas were fed through the catalyst at a space velocity of 15,000 hr-1. The N_2O conversion efficiency was obtained by comparing N_2O concentrations of the feed gas and the catalyst output gas. The test catalyst piece was heated in certain increments from 100°C to 700°C, and the FT-IR analyzer was used to continuously analyze N_2O concentrations of the feed gas and the catalyst output gas. The catalyst test bed used in the experiment is shown in Figure 1.

As sample catalysts, we prepared the platinum/rhodium (Pt/Rh) catalyst as a standard three-way catalyst, and another catalyst carrying palladium (Pd) that showed excellent low-temperature activation performance. These samples were used to determine N_2O generation and conversion characteristics at different temperatures. In the catalyst-aging test, these catalysts were aged to a mileage equivalent to 50,000 km and their N_2O generation and conversion behaviors were determined. These sample catalysts are monolithic catalysts with a cordierite honeycomb and γ-alumina carriers, which are common types of catalysts for automobiles. Specifications for sample catalysts are shown in Table 1, and the catalyst aging test conditions are shown in Table 2.

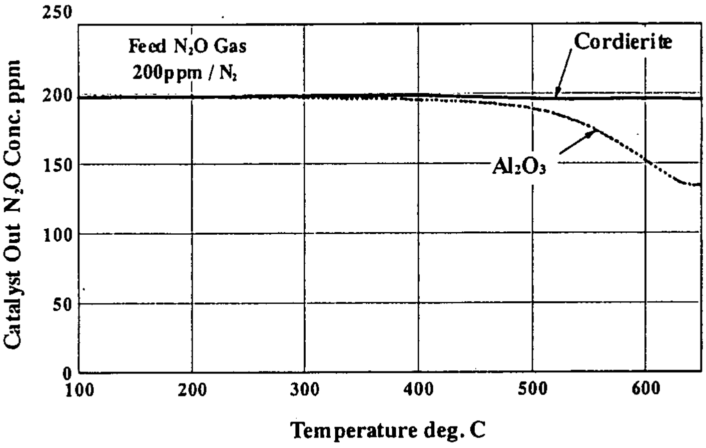

Figure 2. N_2O Decomposition Charactristics with Temperature

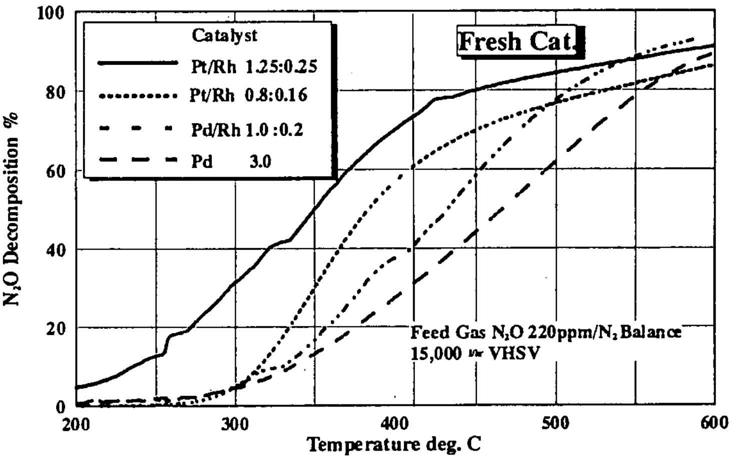

Figure 3. N_2O Decomposition Characteristics of Fresh Catalysts

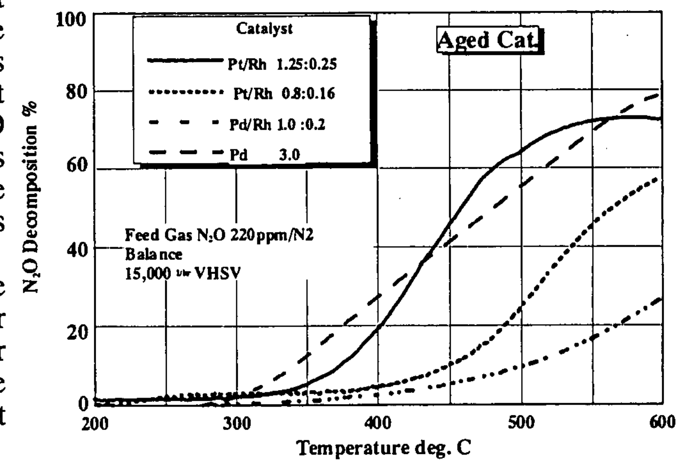

Figure 4. N_2O Decomposition Characteristics of Aged Catalysts

4.2. Model Gas Conditions

The model gas was prepared by mixing the N_2-diluted mixed gas containing NO (730 ppm), CO (730 ppm) and CO_2 (4.1%) in a high-pressure container with O_2 (30 ppm) and water vapor (3%). In the N_2O conversion experiment, the N_2-diluted mixed gas containing N_2 at a concentration of 200 ppm and air was used.

5. Results and Discussion

5.1. N_2O Conversion

The N_2O conversion rate of the cordierite monolithic piece carrying no catalyst was determined at different temperatures. As shown in Figure 2, the cordierite piece carrying no catalyst converted little N_2O even when the temperature was raised to 600°C. Thus, it may be concluded that N_2O will not be converted even at high temperatures without a catalyst. On the other hand, the N_2O conversion rate was high with catalysts carrying precious metals as shown in Figure 3. New catalysts ("fresh catalysts") started converting N_2O at low temperatures and achieved a high rate of conversion at high temperatures. The conversion efficiency of each fresh catalyst is indicated by a solid line. The Pt/Rh catalysts and other catalysts shown in Figure 3 were all capable of converting N_2O.

When compared with the fresh catalyst, the N_2O conversion starting temperature of the aged catalyst shown in Figure 4 was 150°C higher, and the N_2O conversion capability was far inferior. This experiment showed that the catalyst lost its N_2O conversion capability as it was aged.

5.1.1. Catalyst Aging and Amount of Precious Metals Carried by Catalyst Versus N_2O Conversion Rate

Based on the N_2O conversion rate-catalyst temperature curves shown in Figures 3 and 4, N_2O conversion characteristics of catalysts carrying different amounts of precious metals were determined. At a catalyst temperature of 400°C, the conversion rate of the aged catalyst carrying a large amount of precious metals (a "high-carrying" catalyst) was less than one-third of the fresh catalyst. Nevertheless, the high-carrying catalyst retained a 20-30% conversion capability even when it was aged. On the other hand, the catalyst carrying a small amount of precious metals ("low-carrying" catalyst), indicated by a broken line, showed a conversion capability of only several percent when it was aged. The catalyst temperature of about 400°C, the temperature range used in this comparison, is the most frequently used catalyst temperature range in commercial applications. It is shown that the low-carrying catalyst is expected to achieve little N_2O conversion and thus N_2O emissions reduction after it is aged despite its high conversion rate in initial phases of service.

On the basis of this experiment, we can easily predict that the N_2O generated from the low-carrying catalyst will be emitted without conversion and that N_2O emissions will increase if the low-carrying catalyst ages. It is true that even the aged catalyst will have higher N_2O conversion efficiency at higher catalyst temperatures, but the aged low-carrying catalyst will have only a moderate conversion efficiency of about 50% at higher catalyst temperatures. In contrast, the aged high-carrying catalyst will have less decrease in the conversion efficiency and retains about 80% of the initial conversion efficiency. The N_2O conversion capability will be less affected by aging, and therefore the higher the amount of precious metals in the catalyst, the more effective the catalyst is for reducing N_2O emissions.

5.1.2. Comparison of Catalyst Experiment Results with N_2O Emissions Behaviors of Automobiles Equipped with a Three-way Catalytic Converter

N_2O emissions behaviors at different catalyst temperatures as determined in the catalyst unit test are shown in Figure 5, and N_2O emissions behaviors of actual automobiles equipped with three-way catalytic converter are shown in Figure 6. The driving mode used in the exhaust gas test was the cold-start 11 mode, which would allow observation of the behavior of N_2O emissions from the catalyst for actual vehicles from room temperature to 450°C, at which the catalyst is normally used.

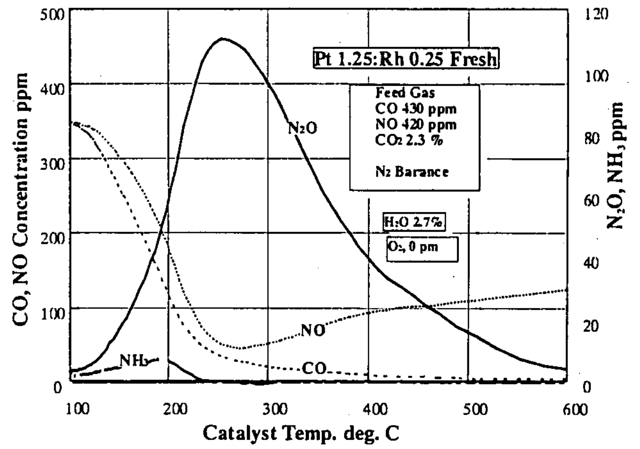

Figure 5. Typical Catalyst Out gas N_2O Emission Concentration (0% O_2)

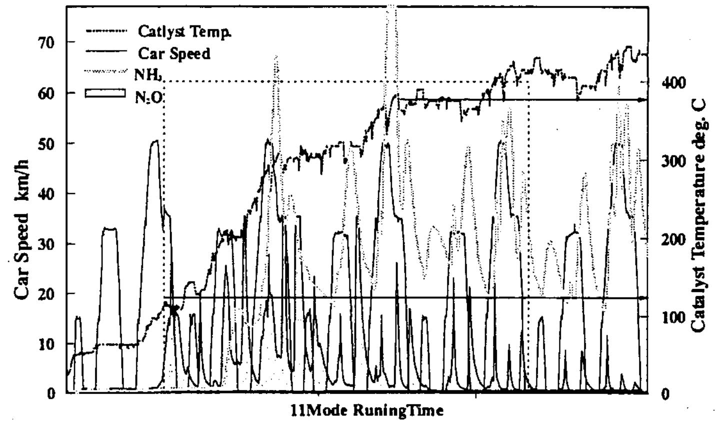

Figure 6. Behavior of TWC-Car N_2O Emission (11 Mode Test)

N_2O emissions from the actual vehicle start when it has started the driving mode and when the vehicle catalyst temperature has reached about 150°C. N_2O emissions reach the peak concentration at about 300°C and become negligible when the catalyst temperature reaches 500°C and above. This N_2O emissions trend versus the temperature of the catalyst on the actual vehicle is quite consistent with the N_2O emissions trend versus the temperature of the catalyst obtained in the catalyst unit experiment. Thus, the N_2O emission concentration characteristics versus the catalyst temperature as obtained in the catalyst unit test can be applied directly to the analysis of the N_2O emissions behavior of automobiles equipped with catalytic converters. Therefore, for automobiles equipped with the exhaust gas purification systems such as the three-way catalytic converter in which the air-fuel ratio is always controlled at a constant level, N_2O emissions in various driving modes can be roughly estimated from the catalyst temperature frequency distribution for the driving mode and N_2O generation and conversion characteristics diagrams obtained in the catalyst experiment.

5.1.3. Effect of Catalyst Deterioration on N_2O Emissions in Various Driving Modes

The N_2O emissions performance diagram was used to clarify the effect of the phenomenon by which the catalyst deterioration described in 5.1 drastically reduces N_2O conversion efficiency for N_2O emissions in an actual automobile.

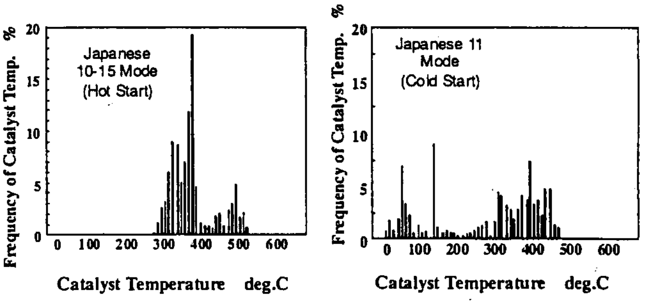

Figure 7. Catalyst Temperature Distribution in Various Driving Cycle

The results of the catalyst temperature frequency distribution analysis for the Japanese cold-start 11-mode and hot-start 10-15 mode are shown in Figure 7. The 11-mode contains the temperature range (100-300°C) where the N_2O generation is significant since the engine starts operating at room temperature. The sizeable N_2O generation temperature range will be lost if the catalyst deteriorates. However, catalyst deterioration lowers the N_2O conversion efficiency in the high temperature range, and increases N_2O emissions. Therefore, the effect of catalyst deterioration on total N_2O emissions during the driving mode is either zero or negligible.

The 10-15 mode does not contain a catalyst temperature range where a high concentration of N_2O is emitted as in the low-temperature range of the 11-mode, and the catalyst service temperature is concentrated in the 300-400°C range. Thus, it will be sufficient to clarify changes in N_2O emissions resulting from catalyst deterioration in this temperature range.

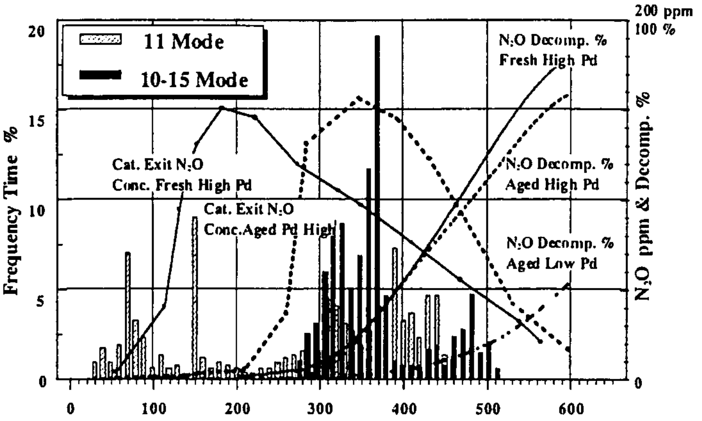

Figure 8. Influence of Deactivation on N_2O Emissions in Various Japanese Driving Cycle

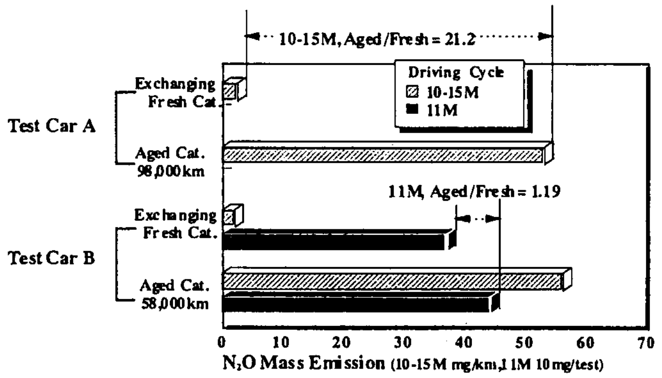

Figure 9. Comparison of N_2O Mass Emissions by Exchanging The Catalysts

As shown in Figure 8, catalyst deterioration increases the temperature range where N_2O emissions are at maximum by 150°C. Thus, the catalyst temperature range of 300-400°C overlaps the temperature range in which N_2O emissions are at maximum. This diagram also shows that catalyst deterioration dramatically increases N_2O emissions since the 10-15 mode is strongly impacted by catalyst deterioration.

Figure 9 represents an example of an experiment in which the catalyst of an old vehicle is replaced with a new catalyst, and N_2O emissions of old and new catalysts are compared for the 10-15 mode and the 11-mode [8]. N_2O emissions of the deteriorated catalyst in the 10-15 mode are nearly 20 times those of the fresh catalyst. The diagram also supports the prediction based on the above-mentioned N_2O emission performance diagram of the catalyst that catalyst deterioration will dramatically increase N_2O emissions in the 10-15-mode.

5.2. N_2O Emissions Reduction Based on Oxygen Concentration

The effect of the O_2 concentration conditions of the intake gas (feed gas) upon N_2O emissions in the temperature range where the catalyst in the actual vehicle operates,was thoroughly investigated in order to determine the catalyst temperature range and the O_2

concentration conditions that would achieve N_2O emissions reduction without increasing other harmful emissions. The fact that catalyst deterioration affected N_2O generation/conversion characteristics as described in 5.1.1 suggested that impact of the O_2 concentration of the feed gas on N_2O emissions from the catalyst might also be affected by catalyst deterioration. Thus, the effect of catalyst deterioration in this context was also investigated.

5.2.1. Effect of O_2 Concentration on N_2O Emissions

The effect of the O_2 concentration on emissions behaviors of N_2O and other harmful gases (including NO, CO, HC and NH3) in the catalyst temperature range of 150-550°C are shown in Figure 10-1, 10- 6.

N_2O emissions from the three-way catalyst increased as the O_2 concentration of the feed gas increased, and reached the maximum point at an O_2 concentration of about 0.05%, as shown in Figure 10 (4). From that point on, an increase in the O_2 concentration drastically reduced the N_2O emissions concentration at any catalyst temperature.

The results indicated that the O_2 concentration should be reduced or increased from 0.05% in order to control N_2O emissions. Moreover, with the exception of the O_2 concentration at 0.05%, the O_2 concentration affected N_2O emissions in the catalyst temperature range of 150-300°C. When the catalyst temperature was 350°C or greater, the O_2 concentration had no effect. These results suggest that N_2O emissions can be reduced by controlling the air-fuel ratio in such a way that the O_2 concentration is not near 0.05% at the catalyst temperature of 300°C or more.

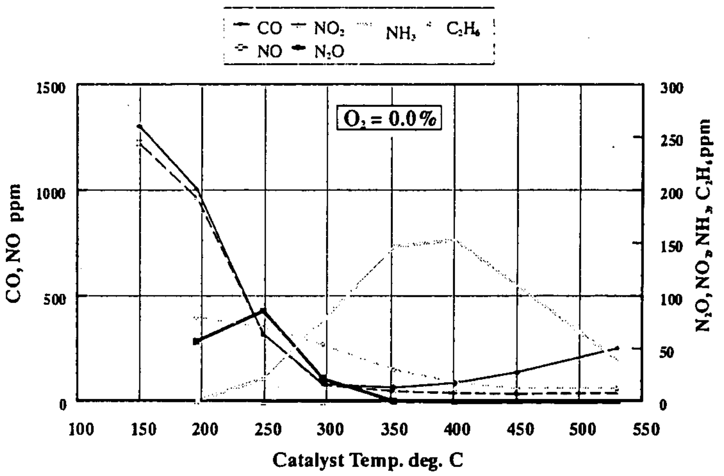

Figure 10- 1 : Effect of Oxygen on Catalyst Out Gas 0.0% O_2

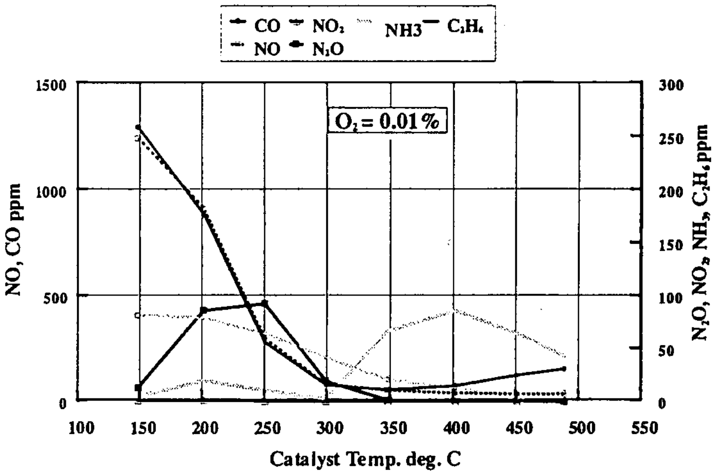

Figure 10- 2. Effect of Oxygen on Catalyst Out Gas 0.01%O_2

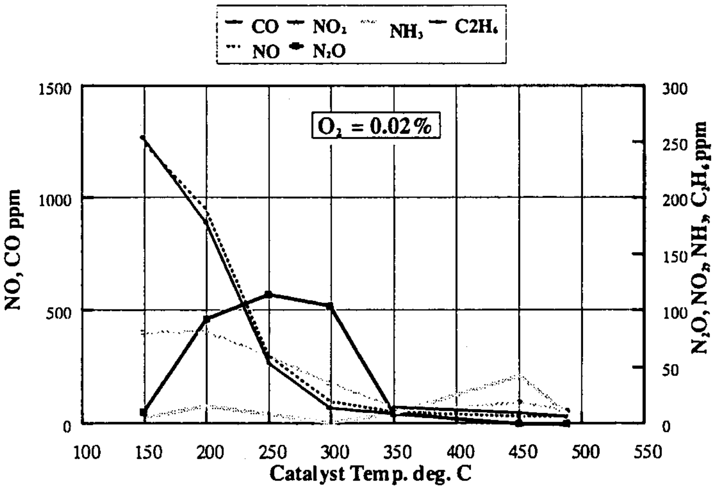

Figure 10- 3. Effect of Oxygen on Catalyst Out Gas 0.02%O_2

5.2.2. Effect of O_2 Concentration on Rise in N_2O Emissions due to Catalyst Deterioration

Then, the effect of the O_2 concentration on the phenomenon of increasing N_2O emissions by catalyst deterioration was investigated.

The effect of the O_2 concentration of the feed gas for the fresh Pt/Rh catalyst is shown in Figure 11. With the exception of the O_2 concentration at 0.05%, little N_2O N_2O is emitted from the fresh catalyst at a temperature of 300°C or more as mentioned above. However, N_2O emissions are observed for the aged catalyst even when the O_2 concentration is high. The catalyst for the actual vehicle is normally used in the catalyst temperature range of 300-450°C where N_2O emissions increase by catalyst deterioration. Therefore, those vehicles for which the air-fuel ratio has been set in the lean range and those vehicles with the appropriate air-fuel ratio setting in the driving range where the O_2 concentration increases by acceleration and deceleration will be strongly affected by catalyst deterioration; and N_2O emissions from these vehicles will increase.

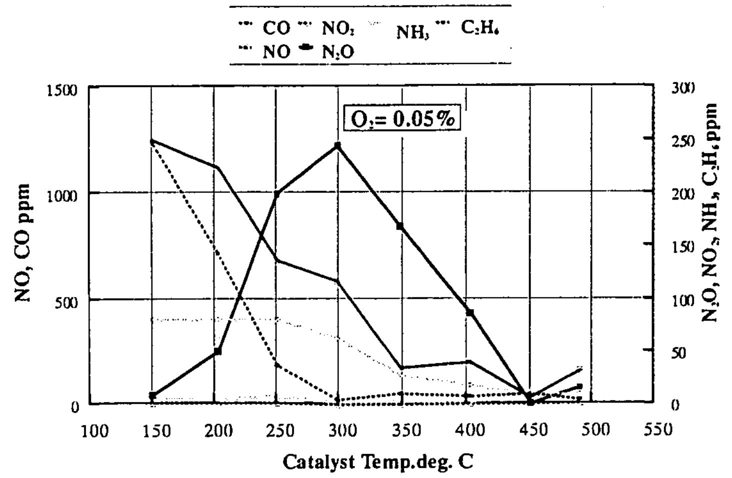

Figure 10- 4. Effect of Oxygen on Catalyst Out Gas 0.05% O_2

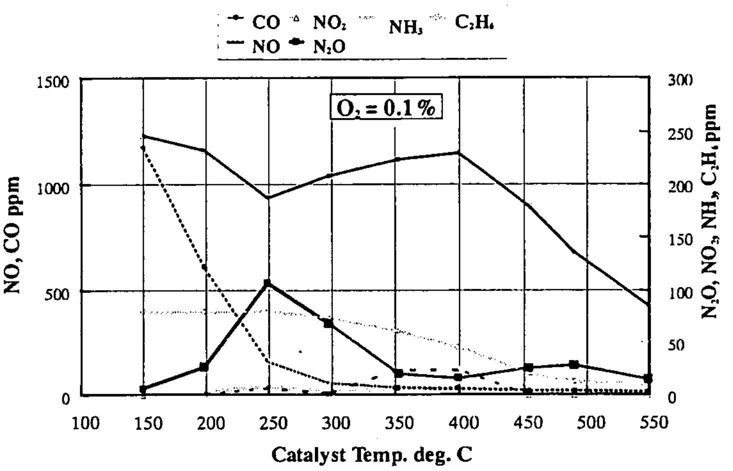

Figure 10- 5. Effect of Oxygen on Catalyst Out Gas 0.1% O_2

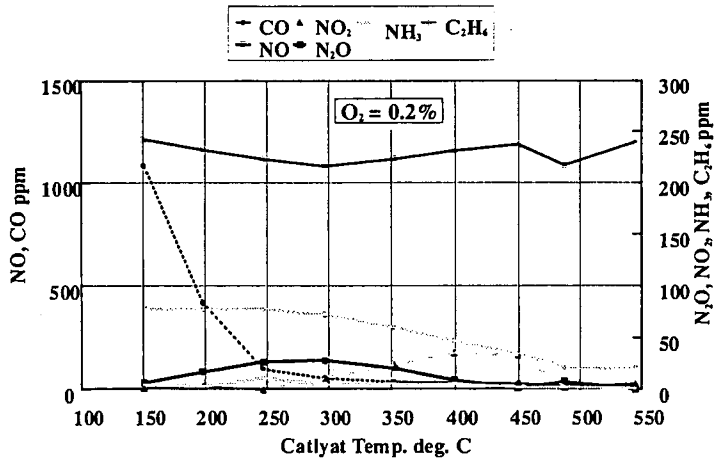

Figure 10- 6. Effect of Oxygen on Catalyst Out Gas 0.2% O_2

6. Summary

6.1. N_2O Emissions Reduction Based on Catalyst Composition

In order to explore the means of reducing emissions from automobiles of the greenhouse gas N_2O, we examined the effect of catalyst composition on N_2O emissions behavior in experiments using a model gas and a sample catalyst. In these experiments, we found:

(1) The three-way catalyst generated N_2O in the low temperature range, but converted N_2O in the high temperature range.

(2) The mechanism by which N_2O emissions increase as a result of catalyst deterioration played a crucial role not only in an increase in the concentration of the N_2O generated, but also in an increase in the concentration of N_2O due to reduction in the N_2O conversion efficiency in the high temperature range.

(3) Catalyst deterioration reduced the concentration of N_2O generated in the low temperature range, but increased the N_2O emissions concentration in the high temperature range. The effect of catalyst deterioration on N_2O emissions varied widely with the driving mode.

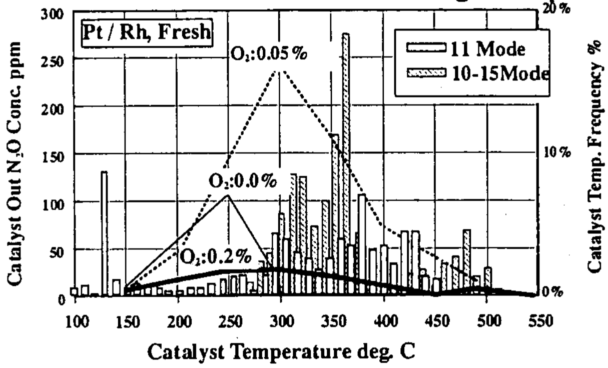

Figure 11. Oxigen Conc. VS Catalyst Out N_2O ppm on Test Modes Catalyst Temperature Frequence (Fresh Catalyst)

6.2. N_2O Emissions Reduction by Controlling Oxygen Concentration

We examined the effect of the O_2 concentration of the feed gas on N_2O emissions behavior in the experiments using the model gas and the sample catalyst. In these experiments, we found:

(1) Emissions of N_2O as well as of NO, CO, an HC could be reduced by controlling the air-fuel ratio in such a way that the O_2 concentration of the feed gas for the three-way catalyst would remain less than about 0.05% at catalyst temperatures of 300°C or more and by controlling the O_2 concentration of the feed gas to 0.02% or less at all times.

(2) Even the fresh catalyst reduced N_2O emissions at higher O_2 concentrations. However, catalyst deterioration produces N_2O emissions at higher O_2 concentrations. This accounted for increased N_2O emissions by catalyst deterioration in actual driving.

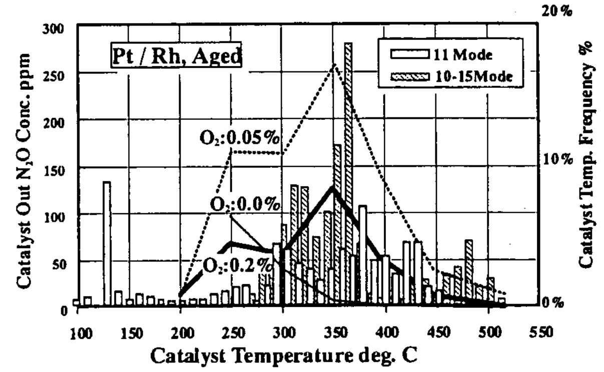

Figure 12. Oxigen Conc. VS Catalyst Out N_2O ppm on Test Modes Catalyst Temperature Frequence (Aged Catalyst)

7. Conclusion

In this study, we examined various means of reducing N_2O emissions from automobiles including changes in the composition of catalyst, prevention of catalyst deterioration, and control of the O_2 concentration of the feed gas. As a result, we succeeded in clarifying the phenomenon in which the three-way catalyst, which had only been known to generate N_2O, converted N_2O in the high temperature range. We also succeeded in clarifying the mechanism by which catalyst deterioration dramatically increases N_2O emissions, based on an understanding of the effect of catalyst deterioration on N_2O conversion characteristics. Moreover, the clarification of this mechanism led to several findings that would prove useful for reducing N_2O emissions from automobiles in the future. Findings include the effectiveness of the Pt-Rh catalyst in comparison with the Pd catalyst among those catalysts carrying precious metals, and the finding that high-carrying catalysts are less likely to deteriorate to provide an effective catalyst composition for N_2O emissions reduction.

Moreover, we examined the N_2O emissions reduction technique of controling the O_2 concentration of the feed gas. As a result of the experiment, we demonstrated that there existed an oxygen concentration condition that specifically produced N_2O emissions, and clarified the technical feasibility of an N_2O emissions reduction technique in which the engine air-fuel ratio is controlled in the oxygen concentration range where N_2O emissions are low. Now, we have good prospects for radically reducing N_2O emissions from automobiles by combining various techniques, e.g. changing the structure of catalysts currently in use based on our findings on the effects of various catalysts on N_2O conversion behaviors, and using the catalyst at higher temperatures in order to promote N_2O conversion.

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7. Presentation of Study Findings

(1) Oral Presentation

1.Noriyuki Koike, Hisakazu Suzuki and Matsuo Odaka: "Techniques for Reducing N_2O Emissions from Automobiles", JSAE 1998 Autumn Meeting 9839605, (1998).

2.Noriyuki Koike, Hisakazu Suzuki and Matsuo Odaka: "Techniques for Reducing Nitrous Oxide (N_2O) Emissions from Automobiles 2nd report: Elucidation of Deteriorated Catalyst-Induced N_2O Emissions Increase Phenomenon", Traffic Safety and Nuisance Research Institute 28th Presentation Meeting.

(2) Papers

1.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 1998 Autumn meeting No. 956, pp.153-156, 1995. (in Japanese)

2.Odaka, M., Koike, N., Suzuki, H., 1998. Deterioration Effect of Three-way Catalyst on Nitrous Oxide Emission. SAE Technical Paper Series 980676.

3.N. Koike, et al: Reduction of N_2O from Automobiles Equipped with Three-way Catalyst -Analysis of N_2O Increase Due to Catalyst Deactivation. SAE Technical Paper 1999-01-1081 (1999)