

50 Reduction Characteristics of NO_x Storage Catalyst for Lean-burn Natural Gas Vehicles

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This study investigates the effects of basic reaction characteristics of NO_x storage reduction catalyst on the emission conditions of lean burn natural gas vehicles. For the increases of surface area and thermal durability performance of the catalyst, we designed various catalysts by the double layer washcoat. The experiments were conducted with 5 kinds of NO_x storage catalysts, which were manufactured with a honeycomb cordierite substrate. The experiments investigated the performance of the catalysts according to the content ratio of precious metal and additive barium(Ba). Excess amount of deposit barium in NO_x storage reduction catalyst decreases the NO_x storage capacity of lean exhaust as well as the cycle NO_x conversion efficiency. For superior NO_x conversion of NO_x storage reduction catalyst, the amount of Ba should be controlled to about 43g/L, approximately. And for the best NO_x conversion efficiency, the appropriate ratio of Pt, Pd and Rh should be 7:7:1.

Keywords: NO_x storage catalyst, Natural gas, CH₄, Double layer washcoat, Adsorption, Desorption

1. INTRODUCTION

Because insufficient petroleum supply can create an anxious atmosphere at the thought of another possible oil shock, improvement of fuel consumption efficiency as well as reduction of harmful gas of vehicles using petroleum as the main fuel has become an important subject for automobile manufacturers. The most effective method for increasing the automobile fuel consumption efficiency is lean combustion of air and fuel in combustion chamber of engine. However, the lean combustion restricts to usage of TWC which can effectively reduce gaseous pollutants under stoichiometric air fuel conditions, because the excess oxygen in the exhaust gas reduce NO_x conversion efficiency⁽¹⁻³⁾.

NO_x storage reduction catalyst, which was developed for advance the fuel consumption efficiency and NO_x reduction under lean air fuel conditions, could not be applied with sufficient effectiveness to lean burn engine systems, because of the sulfur poisoning and durability deterioration of catalyst. Recently, the oil refining technique has reduced the sulfur concentration in gasoline fuel, and catalytic additives increased the performance of the catalyst to reduce sulfur poisoning and increase hydrothermal durability of fuel. Therefore, NO_x storage reduction catalyst may mass-produced commercially in future⁽⁴⁻⁵⁾. A vehicle that uses natural gas, which is an alternative fuel of petroleum for automobiles, produces power performance similar to that of a gasoline fueled vehicle. On the other hand, the vehicle emits more clean exhaust gas than the gasoline vehicle. However, lower

heating value per unit volume and lower storage capacity of natural gas have limited the use of natural gas as fuel for automobile⁽⁶⁾. In addition, more stringent emission standards have required that the natural gas vehicle use a catalyst to reduce its emission. Generally, natural gas vehicle demonstrates more clean emission than that of gasoline vehicle due to fuel quality as itself when the combustion occurs under lean air fuel conditions. If the combustion is operated with stoichiometric condition for using TWC and better emission, the advantages of natural gas vehicle are reduced. Because of these reasons, NO_x storage reduction catalyst must be used for natural gas vehicles. NO_x storage catalyst can prevent sulfur poisoning when it applied to natural gas vehicles. Because almost all of the fuel consists of methane, natural gas vehicles emit just a small amount of non-methane hydrocarbon(NMHC). Because CH₄, which is a type of reductant, is more difficult to resolve than C₃H₆ or C₃H₈ at lower temperatures, the catalyst for a natural gas vehicle must be designed differently from that of a gasoline vehicle⁽⁷⁻⁸⁾.

In this work, we designed and manufactured various NO_x storage catalysts for the natural gas vehicle. And the catalysts were tested with experiment of synthetic model gas reaction. In NO_x storage catalyst, a almost all the alkaline earth metal is a NO_x adsorbing material with a representative material being barium(Ba). Reaction studies were performed with the barium-based catalysts. NO_x storage capacity and NO_x conversion efficiency were investigated according to Ba content and precious metal deposit ratio with the catalysts.

2. EXPERIMENTAL

2.1 Catalyst preparation

For this work, 5 kinds of NO_x storage catalysts were manufactured with a honeycomb cordierite substrate. The substrate was 1L, and had a cell density of 600cpsi(93cell/cm²). The contents of the catalyst consisted of precious metals Pt, Pd, Rh, and the Ba additive. The structure of the washcoat, which was supported with γ -Al₂O₃, had a double layered, impregnated with Pt and Rh on the upper layer and Pd on the bottom layer. The sample catalysts for reaction test were extracted from original catalyst(ϕ =19mm, L=26mm).

Table 1 shows specification of the catalysts.

	PMs	PM Loading ratio	Total PMs Weight(g/L)	BaO Loading weight(g/L)
A	Rh/Pd/Pt	1/1/13	4.5	24.9
B	Rh/Pd/Pt	1/7/7	5.5	42.8
C	Rh/Pd/Pt	1/7/7	5.5	46.0
D	Rh/Pd/Pt	1/10/3	5.5	42.8
E	Rh/Pd/Pt	1/5/8	5.5	42.8

2.2 Experimental apparatus

Fig. 1 shows the experimental apparatus.

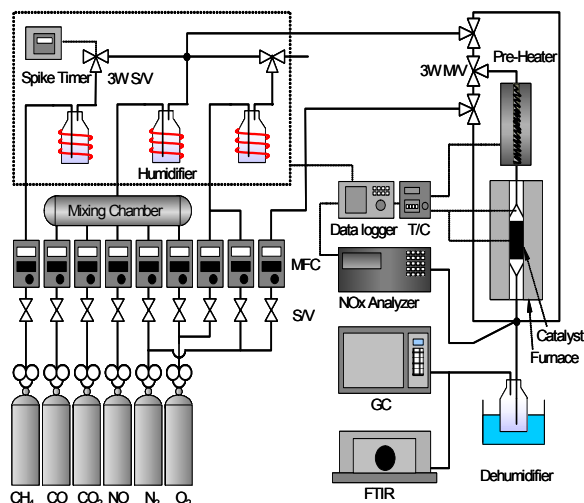


Fig. 1 Schematic diagram of experimental apparatus.

The NO_x analyzer(MEXA-120NO_x) of sensor type was used to measure the NO_x concentration in sequence. FR-IR was used for verify the NO_x concentration from the NO_x analyzer and check the components of the emission,. Excess air ratio was controlled by a spike timer (Autonics, FX4-2P), which was calibrated in one hundredths of a second. Mass flow controllers were used to mix the standard gas. For initialization of the catalyst

and calibration of the analyzer, 3-way solenoid valves and shut-off manual valves were used. The temperatures of the preheater and furnace were controlled by a temperature controller. A data-logger (Yokogawa DL750) was used to measure the temperature from the reactor, and to sample the NO_x concentration from the NO_x analyzer.

2.3 Test procedure

First, the catalyst sample core was inserted into the reactor and flushed with nitrogen gas at a rate of 2.5L/min at 600°C, for 2 hours. The mixing gas was released into the reactor until the NO_x concentration reached a point of rich excess air ratio. If the NO_x concentration remained low, the excess air ratio of the fluid was changed to that of the lean condition. This condition was maintained until the NO_x concentration reached the saturation point of lean excess air ratio. If the NO_x concentration remained at the same value, the cycle of the rich spike and lean fluid of 60s was repeated until the NO_x concentration formed a regular curved shape. Space Velocity(SV), model gas temperature, excess air ratio and duration of the rich spike were the parameters used for the experiment. SV was fixed to 20,000h⁻¹. The temperature of the model gas, through the catalyst, was varied from 300°C to 600°C. The excess air ratio was varied according to the concentrations of the CH₄ and O₂ gases. The excess air ratio of the lean and rich conditions were $\lambda=1.6$ and $\lambda=0.7$, respectively. The duration of the rich spike was varied from 1s to 9s. Excess air ratio was calculated by the following equation.

$$\lambda = 1 + \frac{[O_2] + 0.5[NO] - 0.5[CO] - (x + y/4)[C_xH_y]}{20}$$

3. RESULTS AND DISCUSSION

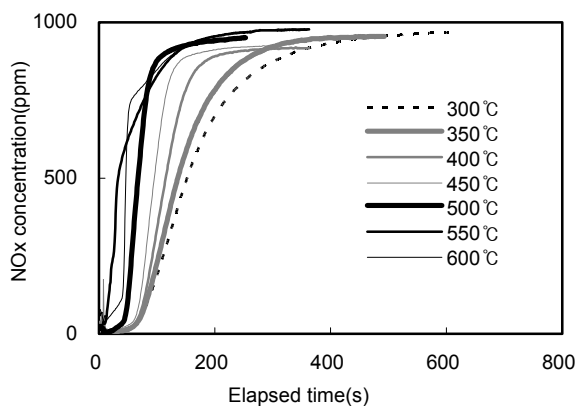
3.1. Effects of deposited Ba amount

The NO_x storage amount, which is considered to have the same meaning as the NO_x storage capacity under lean air/fuel condition, is very important because it has a direct influence on the NO_x conversion efficiency. The NO_x storage amount is proportional to the emitted NO_x concentration per unit time. If the NO_x concentration remains at a low value to a long time, it can be concluded that the NO storage amount and NO_x storage capacity are higher than these of other catalysts. Because Ba is a material of NO_x storage, we can presume that high deposit ratio of Ba to catalyst increase the NO_x adsorption site and NO_x storage amount. However, the ratio is limited because the precious metal and additive need to interact with each other.

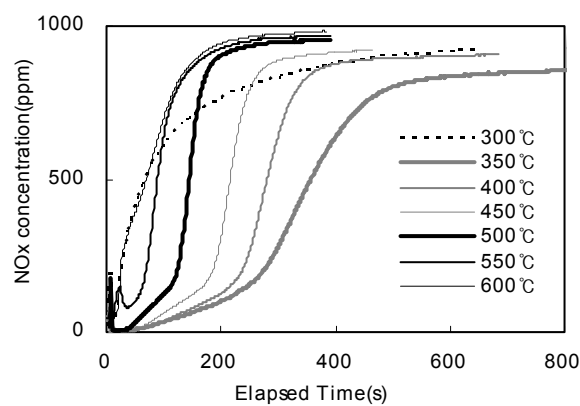
Fig. 2 shows the NO_x variation for different Ba deposit catalysts according to temperature of gas under the lean air fuel conditions. NO_x storage amount tends to decrease as the temperature of exhaust gases increases. Because physical adsorption of gaseous molecules is

possible when the catalyst temperature is a little higher than the boiling point and physical desorption occurs immediately when the temperature exceeds the boiling point⁽⁹⁾, we can suppose that the NO_x storage amount decreases as the temperature increases. Generally, NO_x storage amount increases when the Ba amount increases. But, if the deposited Ba amount to the catalyst increases, the NO_x storage amount tends to decrease at low temperature(in case of 300 °C). We can suppose that this phenomenon due to the conversion ratio of NO to NO₂ is lower at the temperature. The adsorption sites and NO_x storage amount increase as the Ba amount increase. However, the conversion ratio of NO to NO₂ is fairly low due to the reduction of the Pt sites.

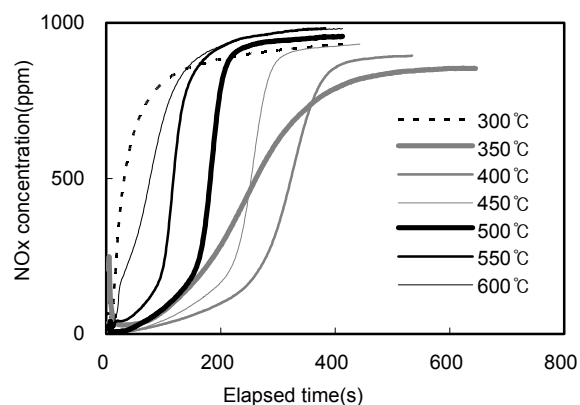
The duration of NO_x saturation could be the first comparison criterion of performance of each other catalysts. However, if the emitted NO_x concentration increases slowly near the saturation point, NO_x saturation point become difficult to detect, and can vary with the researcher. Therefore, for the comparing the NO_x storage amount of each other catalyst, the comparison of reach time for the NO_x saturation is required. Table 2 shows the duration to 500ppm NO_x emission, which is a better criteria for determining and comparing the NO_x storage amount. This table shows that the NO_x conversion efficiency of catalyst A would be lower than those of catalysts B and C. Moreover, catalyst C is expected to give the best NO_x conversion efficiency. These results correspond to NO_x conversion efficiencies at temperature conditions. However, opposite results were given at the temperature range of 300-400 °C.



(a) catalyst A



(b) catalyst B



(c) catalyst C

Fig. 2 NO_x variation on the lean air fuel condition($\lambda=1.6$).Table 2. Duration(sec) to 500ppm NO_x emission.

Temp.(°C)	300	350	400	450	500	550	600
Catalyst							
A	148	131	111	91	62	28	42
B	63	352	276	211	139	84	65
C	27	257	318	248	177	112	72

Fig. 3 displays an example of NO_x variations during a cycle of lean/rich spike for the catalyst B. The rich spike and lean duration were fixed to 5, 60 seconds, respectively. And the temperature was varied from 300 °C to 600 °C with spacing 50 °C.

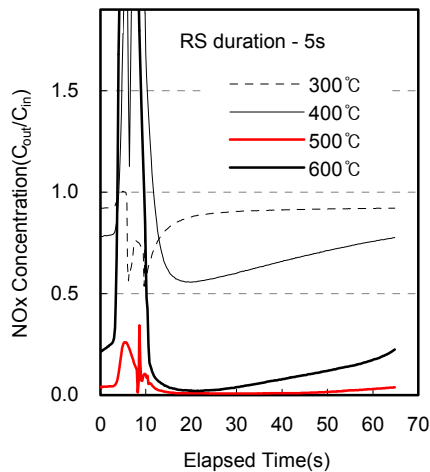


Fig. 3 Example of cycle NOx variation.

The NOx conversion efficiency was converted to a percentage value after a cycle NOx concentration was integrated and divided by the initial entrance value. NOx conversion efficiency was calculated by the equation below.

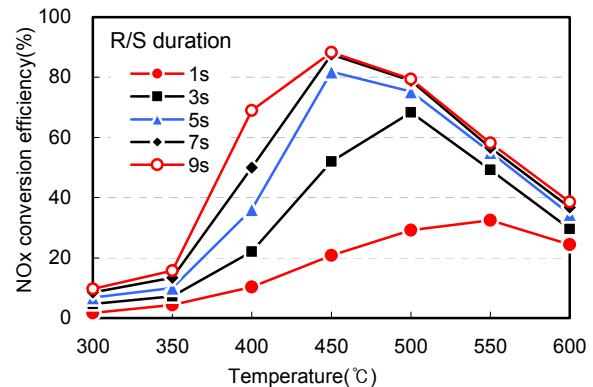
$$\text{NOx conversion efficiency(\%)} = \left(1 - \frac{\int_{t_1}^{t_2} \text{NOx}_{\text{out}} dt}{\int_{t_1}^{t_2} \text{NOx}_{\text{in}} dt} \right) \times 100$$

NOx conversion efficiency during a cycle varied according to the transient emitted NOx concentration by rich spike, emitted NOx concentration by oxidation and reduction reaction under stoichiometric air fuel atmosphere after rich spike, and emitted NOx concentration by NOx adsorption under lean air atmosphere. In addition, these sectional NOx concentration variations were affected by temperature. The NOx conversion efficiencies by sectional NOx variations are summarized according to temperature.

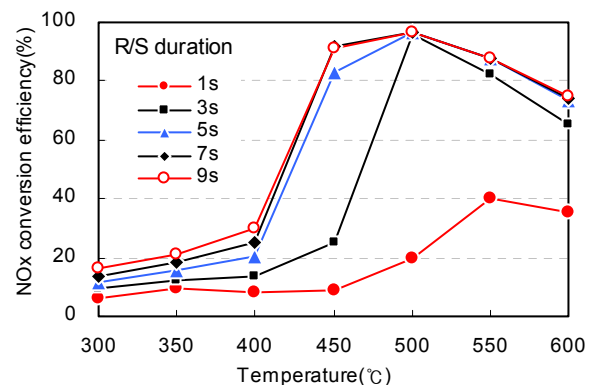
In case of 300°C, desorbed NOx amount by rich spike was not large. In addition, reduction NOx amount by reaction under stoichiometric air fuel atmosphere was not large. As a result, the NOx conversion efficiency was very low. At 400°C, the amount of desorbed NOx increased by rich spike. However, the reduction NOx amount by reaction under stoichiometric air fuel atmosphere was not large due to that the energy for reaction is not enhanced enough. As a result, the NOx conversion efficiency was low at this temperature. At 500°C, desorbed NOx amount by rich spike was large. In addition, the reduction NOx amount by reaction under stoichiometric air fuel atmosphere was very large. And, adsorbed NOx amount under lean air atmosphere was high. Because of cycle repetition, the curve of the NOx concentration was given form to low. As a result, the NOx conversion efficiency was very high. At 600°C, although the reduction NOx

amount by reaction under stoichiometric air fuel atmosphere was increased, the adsorbed NOx amount under lean air atmosphere was decreased due to the increasing NOx desorption energy.

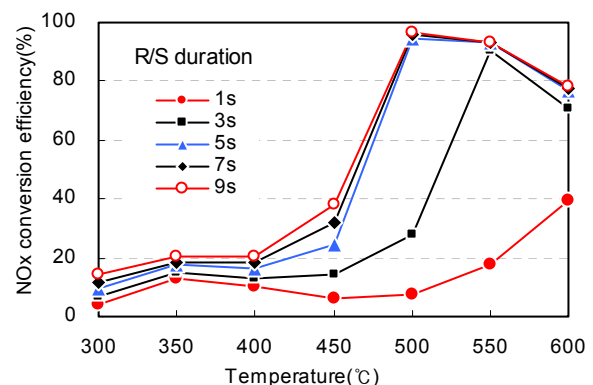
Even though rich spike duration is different, the results were similar to that above results according to temperature variations.



(a) catalyst A



(b) catalyst B



(c) catalyst C

Fig. 4 NOx conversion efficiency of the catalysts.

Figure 4 shows the NO_x conversion efficiencies of catalyst A, B and C according to temperature and rich spike duration. The maximum NO_x conversion efficiency and NO_x conversion efficiency of catalyst A at high temperature were lower than those of catalysts B and C. On the contrary, the NO_x conversion efficiency near 400°C was high. The more deposited Ba amount increases, the more maximum NO_x conversion efficiency increases, except for for the case of low temperature range. Because the adsorption sites and NO_x storage amount were increased, the NO_x conversion efficiency was increased for almost all temperature range. On the contrary, because there was relatively more reduction of Pt sites by the increase of the deposited Ba amount at low temperature conditions, the conversion ratio of NO to NO₂ and NO_x conversion were decreased.

According to hydrothermal aging, NO_x conversion efficiency of the catalyst with high deposited Ba amount was reduced significantly than that of the fresh catalyst. We can suppose that due to the melting point of Ba is lower than those of other materials, catalytic metal easily sinters in the hydrothermal aging conditions. From these results, we know that NO_x storage catalyst required sufficient Pt sites to convert the NO to NO₂ at a low temperature range. Moreover, the deposited Ba amount should be minimized when appropriate NO_x adsorption sites have been secured.

We can evaluate that 29g/L of deposited Ba amount of catalyst A may be insufficient and 46g/L of catalyst C may be excessive to synthesize the optimal NO_x storage catalyst.

3.2 Effects of precious metal composition

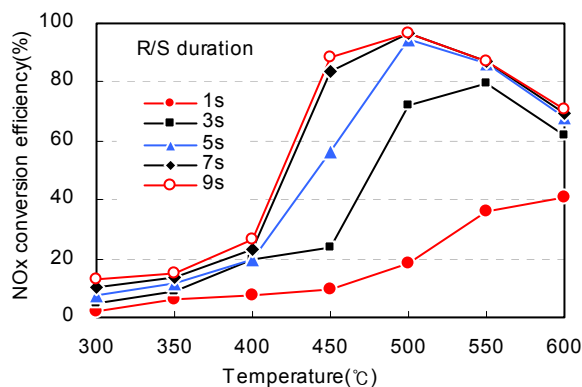
Because Pt has a role in the conversion ratio of NO to NO₂, a NO_x storage catalyst is needed essentially. In addition, Pd is an effective material for removal of carbon monoxide and hydrocarbon. Fig. 5 shows the NO_x conversion efficiency during a cycle of catalysts D and E that contain different content ratios of the precious metals Pt and Pd. The catalyst B, which has a equivalent condition in deposited B amount was compared with the catalyst D and E.

Pd was the highest deposited to the catalyst D, and it was the lowest deposited to catalyst E. On the other hand, Pt was the highest deposited to the catalyst E, and it was the lowest deposited to the catalyst D. Equal amounts of Pt and Pd deposits were loaded to catalyst B. The same amount of Rh deposit was loaded to all catalysts. NO_x conversion efficiency of the catalysts displayed equivalent in value except for case of rich spike duration of 3s and 5s. Among the catalysts, catalyst D showed lower NO_x conversion efficiency than those of others. Especially, catalyst B that was loaded with medium amount of Pt deposit gave the maximum NO_x conversion efficiency at almost all temperature range. Even though the catalyst E was loaded with the highest amount of Pt deposit, catalyst

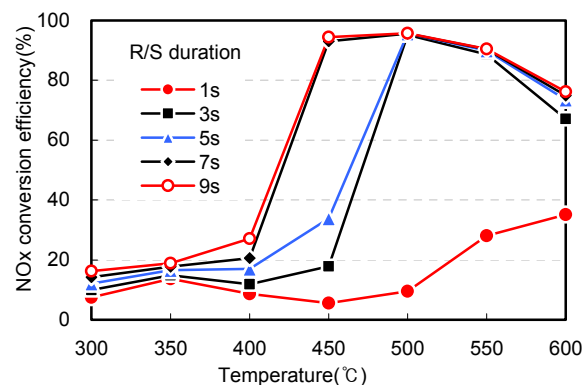
B showed better NO_x conversion. The amount of Pt deposit directly influence to the NO_x conversion efficiency of the NO_x storage catalyst, but deposited Pt amount has a limit due to the dispersion and aging catalytic material.

When the catalyst is aged at a high temperature, the NO_x conversion efficiency by a high Pt loaded catalyst is significantly reduced. Based on the results of these investigations, catalyst B had the proper amount of Pt deposit. Moreover, the appropriate ratio of Pt, Pd and Rh was 7:7:1 to achieve the best NO_x conversion efficiency.

The effects of precious metal content ratio on CO and CH₄ conversions can be investigated by Fig. 5, which shows the CO and CH₄ variations according to temperature increase at lean air fuel conditions. The LOT of catalyst D for CO and CH₄ was expected to be lower than those of catalysts B and E due to high loading of Pd. However, the result showed the opposite. Because Pd is deposited to the bottom layer of the catalyst with a lot of Ba, the CO and CH₄ reactions by Pd was not effective. It is evaluated that the 65% deposited Ba amount to the bottom layer is exceed as to the appropriate Ba amount. Additionally, it seems that CH₄ conversion is more effected by Pt of the upper layer than Pd of the bottom layer. High Ba deposit of the bottom and upper layers could reduce the Pd reaction sites of CO and CH₄.



(a) catalyst D



(b) catalyst E

Fig. 5 NO_x conversion efficiency of the catalysts.

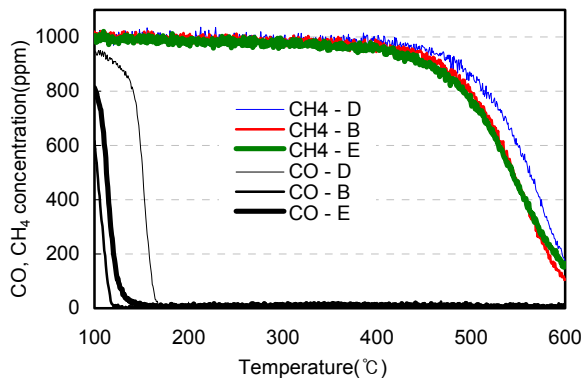


Fig. 6 CO, CH₄ variation on lean air fuel conditions.

3.3 Effects of HCs

A reason of low NO_x conversion efficiency at low temperature range is using of CH₄ as a reductant that reacts with NO_x under theoretical air fuel atmosphere.

Fig. 7 displays the NO_x conversion efficiency during a cycle of catalyst E when various hydrocarbons were used as reductant.

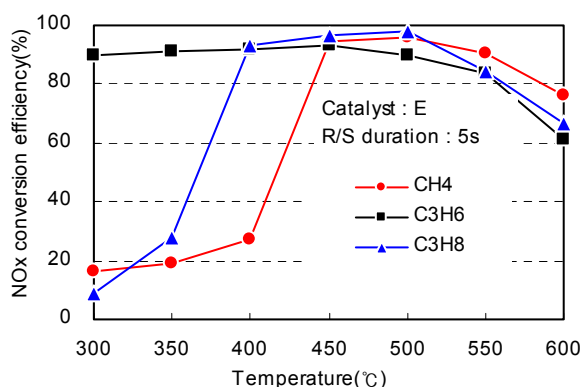


Fig. 7 NO_x conversion efficiency for various reductants.

When CH₄ was used as a reductant, the NO_x conversion was lower than those when C₃H₆ and C₃H₈ were used as a reductant. Because the CH₄ has a stable molecular structure, it does not easily oxidize with NO_x as well as decompose at low temperature. From the above results, NO_x conversion efficiency of NO_x storage catalyst for natural gas vehicle must be lower than those of other types of vehicles. Consequently, a better NO_x conversion efficiency of catalyst for natural gas vehicle is required another reductant.

4. CONCLUSIONS

From our study on the NO_x storage reduction catalyst of a lean burn natural gas vehicle, we have obtained the following results.

1. The NO_x storage amount increased at a high temperature range, but it decreased at a low temperature range when the amount of Ba deposit of catalyst increased.
2. The maximum NO_x conversion efficiency and NO_x conversion efficiency at a high temperature range increased, but decreased at a low temperature range when the amount of Ba deposit in the catalyst increased.
3. The amount of Ba in the NO_x storage reduction catalyst to achieve superior NO_x conversion was about 43g/L. Moreover, the appropriate ratio of Pt, Pd and Rh was 7:7:1.
4. When CH₄ was used as a reductant, the NO_x conversion efficiency of the NO_x storage reduction catalyst was lower than those when C₃H₆ and C₃H₈ were used at a low temperature range.

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