

# REDUCTION CHARACTERISTICS OF NO<sub>x</sub> STORAGE CATALYST FOR LEAN-BURN NATURAL GAS VEHICLES

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**ABSTRACT**—Various types of NO<sub>x</sub> storage catalysts for NGV's were designed, manufactured, and tested in this work on a model gas test bench. As in most of other studies on NO<sub>x</sub> storage catalyst, alkaline earth metal barium (Ba) was used as the NO<sub>x</sub> adsorbing substance. The barium-based experimental catalysts were designed to contain different amounts of Ba and precious metals at various ratios. Reaction tests were performed to investigate the NO<sub>x</sub> storage capacity and the NO<sub>x</sub> conversion efficiency of the experimental catalysts. From the results, it was found that when Ba loading of a catalyst was increased, the quantity of NO<sub>x</sub> stored in the catalyst increased in the high temperature range over 350. With more Ba deposition, the NO<sub>x</sub> conversion efficiency as well as its peak value increased in the high temperature range, but decreased in the low temperature range. The best of de-NO<sub>x</sub> catalyst tested in this study was catalyst B, which was loaded with 42.8 g/L of Ba in addition to Pt, Pd and Rh in the ratio of 7:7:1. In the low temperature range under 450°C, the NO<sub>x</sub> conversion efficiencies of the catalysts were lower when CH<sub>4</sub>, instead of either C<sub>3</sub>H<sub>6</sub> or C<sub>3</sub>H<sub>8</sub>, was used as the reductant.

**KEY WORDS** : NO<sub>x</sub> storage catalyst, Natural gas, CH<sub>4</sub>, Double layer washcoat, Adsorption, Desorption

## 1. INTRODUCTION

Improvement of fuel economy and reduction of harmful gas emissions are the top-ranked technological goals in the automobile manufacturing industry due to the public anxiety over another oil shock and environmental crisis. The increasing emissions of green-house gases have stimulated new strategies for fossil fuel combustion in transportation. The objective of these strategies is to decrease the amount of carbon dioxide (CO<sub>2</sub>) emissions by increasing combustion efficiency through the use of lean-burn or low carbon number fuel as natural gas. One of effective methods for enhancing fuel consumption of spark-ignited automobiles is the combustion of lean air-fuel mixtures. Lean combustion, however, is not compatible with TWC (three way catalyst, simultaneous oxidation of CO (carbon monoxide), HC (hydrocarbons) and reduction of NO<sub>x</sub> (nitrogen oxides)), which is indispensable in meeting the ever-tightening emission regulations. TWC can effectively reduce gaseous pollutants only under stoichiometric air-fuel conditions. Excess oxygen in the lean-burn exhaust gas reduces NO<sub>x</sub> conversion (Miyoshi *et al.*, 1995; Takahashi *et al.*, 1996; Kaspar *et al.*, 2003).

Current after-treatment technologies for NO<sub>x</sub> removal

are unsuitable for lean NGVs. Automotive TWCs are ineffective outside of stoichiometric conditions, while ammonia SCR (selective reduction catalyst) is less attractive for the vehicle system due to cost and infrastructure concerns. Urea SCR has potential especially for mobile applications, but has the same limitations as ammonia SCR. An ideal after-treatment system would make use of the HCs present in the exhaust (or fuel) to reduce the NO<sub>x</sub> (Holmgren *et al.*, 2007).

A possible solution to the problem of NO<sub>x</sub> reduction during lean combustion is the NO<sub>x</sub> storage and reduction (NSR) (Takahashi *et al.*, 1996). The materials in the NSR catalysts are the same as those in the TWC with the addition of a NO<sub>x</sub> trapping materials. The NSR concept is based on a periodic lean/rich engine operation. During the lean periods, NO<sub>2</sub> is stored on the adsorption materials. This NO<sub>2</sub> is released during short rich pulses (call rich spark), and subsequently, reduced by HCs, CO, and hydrogen over precious metals (PM) sites to form CO<sub>2</sub>, N<sub>2</sub>, and water. The NSR catalyst was developed for NO<sub>x</sub> reduction under lean air-fuel conditions, but it could not be applied to lean burn engines because of the insufficient durability of the catalyst due to its poisoning by sulfur in the fuel (Rohr *et al.*, 2005). Recent advances in oil refining technology have reduced the sulfur concentration in gasoline, and catalytic additives have also been found to resist sulfur poisoning (Matsumoto,

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2004) and therefore, to increase the hydrothermal durability of the catalyst. As a result, the NO<sub>x</sub> storage reduction catalyst may be successfully commercialized in the near future (Brogan *et al.*, 1995; Matsumoto *et al.*, 2000; Theis *et al.*, 2004).

The other effective method for reducing CO<sub>2</sub> is the use of low carbon number fuels such as natural gas. NGV's (natural gas fueled vehicles) have power output similar to that of the gasoline fueled vehicles, but their exhaust gas is cleaner. Lower heating value and poor transportability in the form of compressed gas are the major factors that limit their wide use on automobiles (Kim and Choi, 2001). NGVs operating in the lean combustion regime reach higher thermal efficiencies and produce less pollutant emissions than the more common stoichiometric engines. Although these lean-burn NGVs produce cleaner engine-out emission, the effluent streams still contain significant levels of CO, HC and NO<sub>x</sub>. These CO and HC emissions can be controlled by oxidation catalysts, but the NO<sub>x</sub> emission and CH<sub>4</sub> slip are difficult to control in lean conditions.

Catalyst for a NGV must be designed differently from that of a gasoline vehicle since the hydrocarbons in the NGV exhaust gas are mostly methane, the main constituent of natural gas. This is why NSR catalyst for the reductant of CH<sub>4</sub> should be applied to the NGV. Methane is more difficult to convert at lower temperatures than C<sub>3</sub>H<sub>6</sub> or C<sub>3</sub>H<sub>8</sub>, the major constituents of HC in gasoline engines (Lee *et al.*, 2004; Lee and Choi, 2005). The reactivity of adsorbed NO<sub>x</sub> species on different Co species in Co/ZSM-5 with CH<sub>4</sub> has been studied to investigate NO conversion efficiency of CH<sub>4</sub>-SCR in the presence of oxygen (Sadovskaya *et al.*, 2004). Pd is a more effective catalyst for oxidizing the CH<sub>4</sub> slip. Pd sulfated zirconia for the lean reduction of NO with CH<sub>4</sub> has a resistance to water vapor and sulfur oxides in the exhaust stream (Ohtsuka *et al.*, 2000; Ohtsuka and Tabata, 2001). As for sulfur, poisoning is not a problem of NGV's because the fuel does not contain sulfur. The formation of adsorbed NO<sub>2</sub> has been proposed as a key intermediate step in the NO-HC reaction (Centi and Perathoner, 1996). To take advantage of this behavior, the catalyst for the lean-burn NGV has to contain Pt and Pd (for oxidation of CH<sub>4</sub> slip). Barium oxide (BaO) and alkali metal adsorbers provide superior NO<sub>x</sub> conversion (Matsumoto *et al.*, 2000; Lee *et al.*, 2005). Double-layer washcoat can promote thermal stability and light-off performance and durability of the TWC (Choi *et al.*, 2005). The advanced washcoat technology for the gasoline vehicle may applied to NGVs.

Various types of NO<sub>x</sub> storage catalysts for NGV's were designed, manufactured, and tested in this work on a model gas test bench. As in most other studies on NO<sub>x</sub>, alkaline earth metal BaO, the storage catalyst, was used

Table 1. Specifications of the catalysts.

Cat	PM weight ratio		PM components (g/L)	BaO loading(g/L)	
	Bottom (Pd)	Upper (Rh/Pt)		Bottom	Upper
A	13	1/1	4.5	15	9.9
B	7	1/7	5.5	30	12.8
C	7	1/7	5.5	30	16.0
D	10	1/3	5.5	30	12.8
E	5	1/8	5.5	30	12.8

here as the NO<sub>x</sub> adsorbing substance. The barium-based experimental catalysts were designed to contain different amounts of BaO and precious metals (Pd, Rh/Pt) in various ratios. Reaction tests were performed to investigate the NO<sub>x</sub> storage capacities and NO<sub>x</sub> conversion efficiencies of the experimental catalysts.

## 2. EXPERIMENTAL WORKS

### 2.1. Catalyst Preparation

In this work, five kinds of NO<sub>x</sub> storage catalysts were made by coating the honeycomb type of cordierite substrates with a washcoat first and then with a formulated catalytic substance. The substrates had a volume of 7.4 mL ( $\phi=19$  mm, L=26 mm) and a cell density of 93 cell/cm<sup>2</sup> (600 cpsi). The formulated catalytic substance consisted of precious metals Pt and Rh (upper layer), Pd (bottom layer), and additive Ba. Gamma-alumina based washcoat had a double-layered structure, where Pt plus Rh and Pd were impregnated, respectively, on the top layer and the bottom layer. Catalyst A was loaded with higher Pd for effective oxidation of CH<sub>4</sub>, and catalysts B and C were loaded at the same ratio of Pd/Pt for the effective oxidation of both CH<sub>4</sub> and NO. Small specimens of the catalysts, cut out from the full sized catalysts, were subjected to reaction tests.

### 2.2. Experimental Apparatus

Mass flow controllers were used in the experimental system shown in Figure 1 to meter the flow rates of the component gases before the gases were mixed to make the feed gas to the catalyst in the furnace. A spike timer (Autonics, FX4-2P), previously calibrated to one hundredth of a second, controlled the three-way valve to modulate excess air ratio of the feed gas. Temperature controllers regulated the temperatures of the pre-heater and the furnace. The initialization of the catalyst and the calibration of the analyzer were performed by using 3-way solenoid valves and manual shut-off valves. A sensor type of analyzer (MEXA-120NO<sub>x</sub>) was employed to continuously measure the NO<sub>x</sub> concentration in the exhaust gas in the rear of the catalysts. An FT-IR was instrumented to

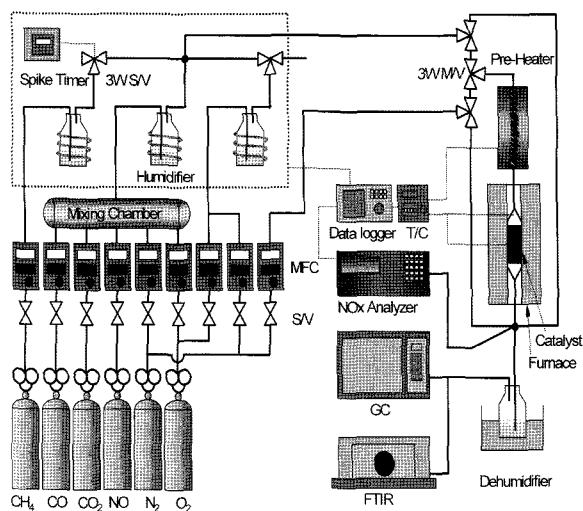


Figure 1. Schematic diagram of experimental apparatus.

confirm the measurement of the NO<sub>x</sub> analyzer as well as to check the various species that formed in the test chamber. A data-logger (Yokogawa, DL750) recorded the measured temperature of the reactor, and the NO<sub>x</sub> concentration.

### 2.3. Test Procedures

First step of the test is to locate a catalyst specimen inside the reactor and to flush the catalyst for 2 hours with nitrogen gas at 600°C at a rate of 2.5 l/min. The lean model gas from the mixing tank, containing 1000 ppm of NO<sub>x</sub>, then starts to flow into the reactor. The NO<sub>x</sub> concentration measured downstream of the reactor typically reads zero at first, and then starts rising as the catalyst adsorbs NO<sub>x</sub>, all at first but then at some fraction thereafter. When NO<sub>x</sub> concentration reaches the saturation value, the spike timer actuates the three-way valve at a predetermined interval (60 seconds) to turn the rich feed gas by adding CH<sub>4</sub>. Momentary rich feed gas causes the catalyst to desorb NO<sub>x</sub> to make the NO<sub>x</sub> concentration instantly increase before it starts decrease towards a bottom level as the catalyst starts again adsorbing NO<sub>x</sub> in the lean feed gas. When the next pulse of CH<sub>4</sub> arrives, NO<sub>x</sub> concentration repeats the uprising but with a lower peak than the previous one. The bottom level of the NO<sub>x</sub> concentration reaches a minimum level after several cycles. The quantity of the adsorbed NO<sub>x</sub> and conversion of NO<sub>x</sub> by the catalysts are evaluated from the recorded NO<sub>x</sub> concentration obtained in the tests, in which the temperature and excess air ratio of the model gas and duration of the rich spike (R/S) are varied while the SV (space velocity) is fixed at 20,000 h<sup>-1</sup>. Because the NO adsorption ability is slightly decreased as the SV increases, but the trends of the NO adsorption abilities are similar to the SV range of 20,000 to 50,000

l/h. In the present study, the temperature of the model gas varied from 300°C to 600°C, and the excess air ratio, varied by adjusting the concentrations of the CH<sub>4</sub> and O<sub>2</sub> gases, shifted between  $\lambda=1.6$  and  $\lambda=0.7$ . The duration of the rich spike varied from 1s to 9s. The excess air ratio is calculated according to the following equation.

$$\lambda = 1 + \frac{[\text{O}_2] + 0.5[\text{NO}] - 0.5[\text{CO}] - (x + y/4)[\text{C}_x\text{H}_y]}{20}$$

## 3. RESULTS AND DISCUSSION

### 3.1. Effects of Varying Ba Loading

NO<sub>x</sub> storage amount, the quantity of NO<sub>x</sub> stored in a catalyst, means the same as the NO<sub>x</sub> storage capacity in a lean air-fuel environment, and is considered very important because it has a direct influence on the NO<sub>x</sub> conversion efficiency of a catalyst. The NO<sub>x</sub> storage amount is proportionally increased by the NO<sub>x</sub> adsorption site on the catalyst. If the NO<sub>x</sub> concentration remains low for a longer time, it can be defined that the NO<sub>x</sub> storage amount and NO<sub>x</sub> storage capacity of the catalyst are big. Because Ba is a material that adsorbs NO<sub>x</sub>, one may presume that a high deposit ratio of Ba to a noble metal will increase the NO<sub>x</sub> adsorption site and hence, the NO<sub>x</sub> storage amount. However, the ratio of the two is limited because the additive (Ba) and precious metal need to interact with each other.

Figure 2 shows the time variation of NO<sub>x</sub> concentration in the exhaust stream for catalysts of different Ba loadings, when a lean mixture flows into the reaction chamber at various temperatures. As time goes on, NO<sub>x</sub> concentration curves are seen to asymptotically rise towards the 1000 ppm level for all types of the catalysts and gas temperatures tested. A close observation of the figures (a), (b) or (c) readily reveals that the concentrations tend to rise faster when the gas temperatures are higher, indicating less quantity of NO<sub>x</sub> stored in the catalyst. Uniform microporous solids, where the pressure at which adsorption takes place, depends on surface-adsorbate interactions, and shows isotherms with various steps each corresponding to the adsorption on a group of energetically uniform sites. At higher catalyst temperatures, if the kinetic energy of gaseous molecules is higher than that of the energetically uniform sites, physical desorption occurs (Jun and Shu, 2002; Fridell *et al.*, 1999; Ryan, 2006).

Comparing figures (a), (b), and (c) in Figure 2, it is evident that NO<sub>x</sub> storage amount increases in general as more Ba is deposited. NO<sub>x</sub> storage amount also increases as more Pt is loaded. One may attribute this phenomenon to the conversion ratio of NO to NO<sub>2</sub> by Pt catalyst.

There will be high conversion of NO to NO<sub>2</sub> due to the numerous Pt sites on those catalysts of high Pt loading, and additional Ba for adsorption of NO<sub>2</sub> increases the

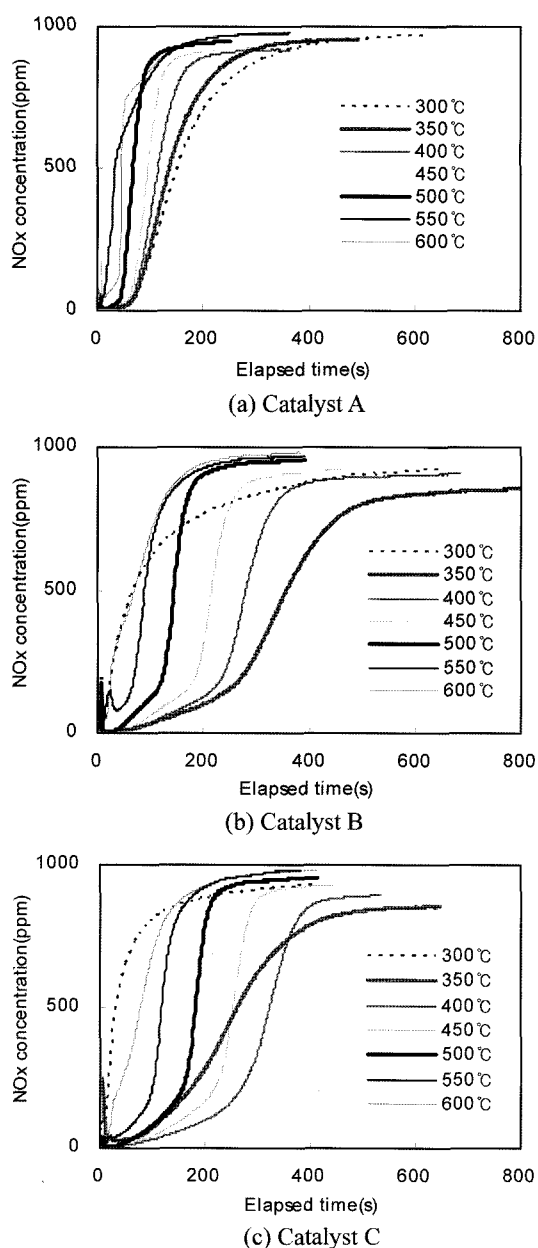


Figure 2. NOx variation on the lean air fuel condition ( $\lambda=1.6$ ).

number of adsorption sites and NOx storage amount. However, in the case of 300°C, the effect of Ba loading on NOx storage shows an opposite tendency. This phenomenon represents the indefinite state.

The time duration for NOx concentration to saturate may be the first parameter for the performance comparison of the catalysts. Time to saturation is, however, difficult to determine since most concentration curves asymptotically approach their ultimate values. Time to reach a value somewhat lower than saturation is therefore

Table 2. Time (sec) to reach 500 ppm NOx.

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

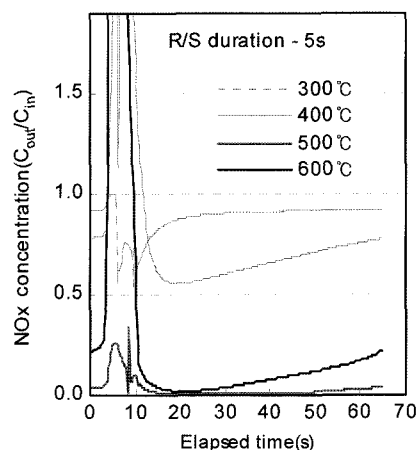


Figure 3. NOx concentration during a rich/lean cycle of air-fuel ratio variation.

a practical choice for comparing the NOx storage amounts of different catalysts. Table 2 shows time duration to reach 500 ppm NOx, which is easy to determine, and it is still a good indication of the NOx storage amount. According to the data in Table 2, catalyst C is expected to give the best performance in NOx storage, and perhaps also NOx conversion in the temperature range of 400-600°C. Catalyst B follows catalyst C in the NOx storage performance in the same temperature range, but the order of time to reach 500 ppm NOx changes in the temperature range of 300-350°C.

Figure 3 illustrates as an example of the change of NOx concentration at a downstream location of catalyst B during a lean/rich cycle of air-fuel ratio variation. The durations of the rich and lean portions of the cycle were fixed at 5 and 60 seconds, respectively. And the temperature was varied from 300°C to 600°C with step sizes of 50°C. The NOx conversion efficiency was computed on a cycle basis by using integrated quantities of incoming and outgoing NOx according to the following equation.

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 changes during a cycle due to

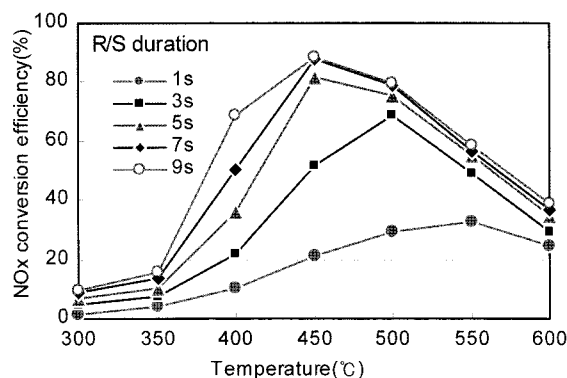
desorption during the rich period, formation and decomposition through oxidation and reduction reactions during the stoichiometric period following the rich spike (R/S), and adsorption in lean atmosphere. The NO<sub>x</sub> conversion efficiency at a moment will be determined by various contributions by these factors, which are a function of the temperature.

In the case of 300°C of Figure 3, not much NO<sub>x</sub> was either desorbed during the rich spike or reduced in the stoichiometric period, resulting in very low conversion efficiency. NO<sub>x</sub> conversion efficiency was relatively low too at 400°C despite the fact that more NO<sub>x</sub> was desorbed by the rich spike. Perhaps not enough NO<sub>x</sub> were eliminated by reduction reactions in the stoichiometric atmosphere. At 500°C, much of the adsorbed NO<sub>x</sub> were desorbed during the rich spike and reduced in the stoichiometric air-fuel atmosphere, resulting in very high conversion efficiency.

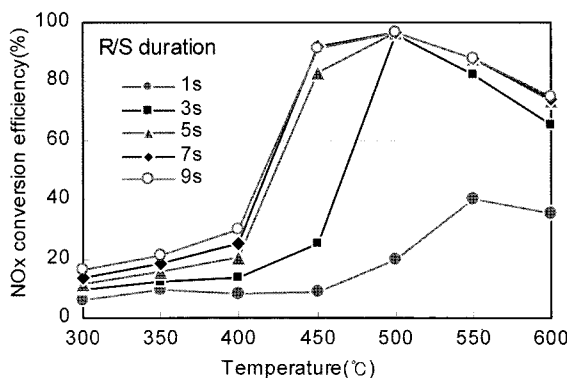
At 600°C, although the NO<sub>x</sub> reduced by reactions in stoichiometric atmosphere increased, the amount of adsorbed NO<sub>x</sub> during the lean period decreased due to the high energy requirement for desorption. Even when the length of the rich spike was varied, the obtained results for temperature variations were similar to those described above.

Figure 4 shows the NO<sub>x</sub> conversion efficiencies of catalysts A, B and C determined under the test conditions of various temperatures and rich spike durations. Figure 4-(a) shows the conversion efficiency of Catalyst A, which has a peak lower than either that of Catalyst B in Figure 4-(b) or the Catalyst C in Figure 4-(c). Further comparison of the graphs reveals that Catalyst A also has lower conversion than that of Catalyst B or Catalyst C over the high temperature range, whereas Catalyst A has higher values near 400°C. This implies that increased Ba deposition will generally enhance the NO<sub>x</sub> conversion efficiency except in the low temperature range. With more Ba deposition, the conversion efficiency will be high in most of the temperature ranges of tested due to the increased adsorption sites and NO<sub>x</sub> storage amount. On the contrary, the reduced number of Pt sites caused by the increased deposition of Ba seems to lower the NO-to-NO<sub>2</sub> conversion and hence, the NO<sub>x</sub> conversion in low temperature range. Hydrothermal aging cycle significantly decreased the NO<sub>x</sub> conversion efficiency of the catalyst with heavy Ba deposition.

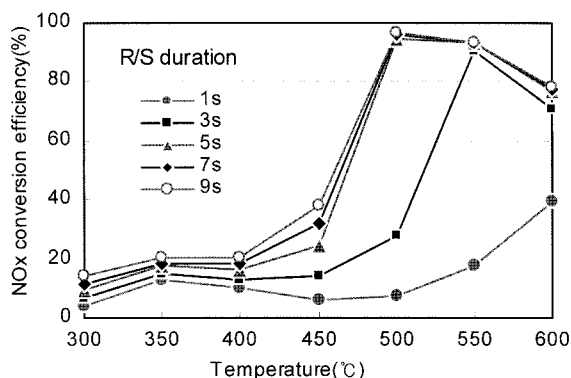
It is postulated that the low melting point of Ba causes catalytic metal to easily sinter under hydrothermal aging conditions. From these results, it became apparent that good NO<sub>x</sub> storage catalysts require sufficient number of Pt sites to convert NO to NO<sub>2</sub> at a low temperature. Moreover, Ba deposition should be minimized once appropriate number of NO<sub>x</sub> adsorption sites is secured. With these evaluation criteria for optimal NO<sub>x</sub> storage



(a) Catalyst A



(b) Catalyst B



(c) Catalyst C

Figure 4. NO<sub>x</sub> conversion efficiency of the catalysts A, B, and C.

catalyst 29 g/L of Ba deposition (catalyst A) is insufficient while 46 g/L of Ba (catalyst C) may be excessive.

### 3.2. Effects of Precious Metal Composition

Pt is an essential element in NO<sub>x</sub> storage catalysts because it plays a critical role in converting NO to NO<sub>2</sub>. Pd is an effective material for removal of carbon monoxide and hydrocarbons. Figure 5 depicts the NO<sub>x</sub> conversion efficiency of catalysts D and E during a rich-lean test cycle. These catalysts contain the same weights

of Ba and the noble metals, but in different ratios of Pt and Pd. Performances of these catalysts are to be compared with that of catalyst B in Figure 4-(b), which also has the same weights of Ba and total precious metals.

As is specified in the Table 1, catalyst D has the largest deposition of Pd while catalyst E has the least. On the other hand, catalyst E has the largest loading of Pt while catalyst D has the least. Catalyst B stands in the middle having equal amounts of Pt and Pd. All of these catalysts contain the same amount of Rh in addition to Ba and Pt. Conversion efficiencies of these three catalysts seem to be similar, except in the cases tested with rich spike durations of 3s or 5s. Catalyst B, loaded with the intermediate amount of Pt, showed the best overall conversion performance over most of the temperature range, while catalyst D the poorest among the three. Catalyst B performed even better than catalyst E, which had the highest loading of Pt. Pt directly influenced the NO<sub>x</sub> conversion efficiencies of the catalysts, but there existed an upper limit on quantity of Pt deposition due to the dispersion and aging of the catalytic materials during high temperature operations.

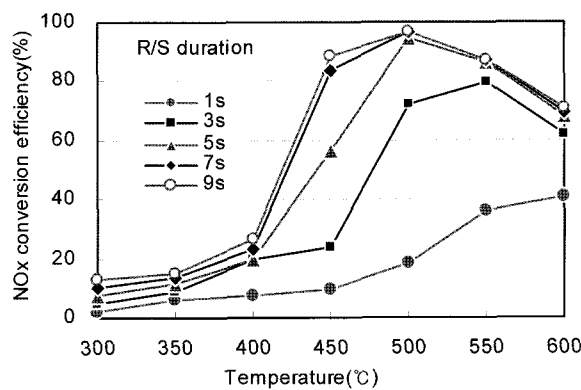
Catalysts with high loadings of Pt suffered significant loss of NO<sub>x</sub> conversion efficiency as a result of aging at high temperature. Based on the results of this investigation, catalyst B seemed to have the proper amount of deposited Pt, and also the appropriate ratio of Pt, Pd and Rh for yielding the best conversion efficiency.

Ratio effects of precious metal loadings on CO and CH<sub>4</sub> conversions can be analyzed from Figure 6, which shows how CO and CH<sub>4</sub> concentrations decline due to catalytic conversion at various temperatures under lean air-fuel conditions. Expected LOT (light-off temperature) of catalyst D for CO and CH<sub>4</sub> was lower than that of either catalysts B or E because of the high Pd loading. However, the test result in Figure 5 showed the opposite. CO and CH<sub>4</sub> reactions by Pd were not very effective maybe because Pd had been deposited on the bottom layer of the catalyst where there was a lot of Ba.

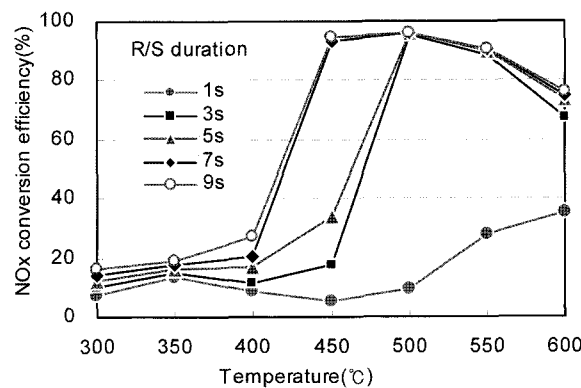
It was assumed that the 65% deposition of Ba on the bottom layer exceeded the appropriate level. It was also speculated that CH<sub>4</sub> conversion was effected more by the Pt on the upper layer rather than by the Pd on the bottom layer. A high level of Ba deposit either on the bottom or upper layers may reduce the Pd reaction sites for CO and CH<sub>4</sub>.

### 3.3. Effects of Reductants

Indicating fairly low conversion in the low temperature range (below 400°C) in Figures 4 and 5, high NO<sub>x</sub> concentration was maintained because CH<sub>4</sub> was used in these tests as the reductant, which only reacts with NO<sub>x</sub> in a theoretical air-fuel atmosphere. Figure 7 indicates the NO<sub>x</sub> conversion efficiency during a rich-lean cycle for



(a) Catalyst D



(b) Catalyst E

Figure 5. NO<sub>x</sub> conversion efficiency of the catalysts D and E.

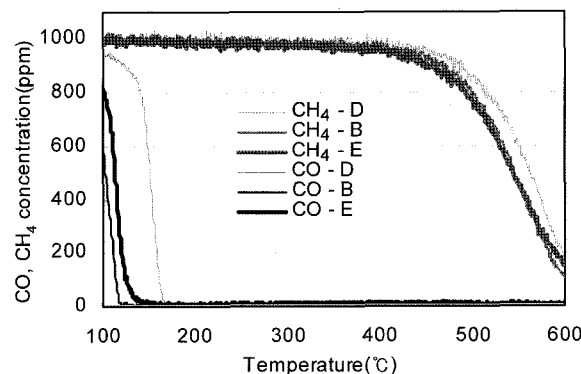


Figure 6. Concentrations change of CO and CH<sub>4</sub> due to catalytic conversion.

catalyst E, where various hydrocarbons are used as the reducing agents.

When CH<sub>4</sub> was the reductant, the conversion proceeded slower than when C<sub>3</sub>H<sub>6</sub> or C<sub>3</sub>H<sub>8</sub> were used. Having a stable molecular structure, CH<sub>4</sub> was neither oxidized by NO<sub>x</sub> nor decomposed at low temperature. This implies that NO<sub>x</sub> conversion efficiency of a NO<sub>x</sub> storage catalyst for natural gas vehicles will be lower than those for

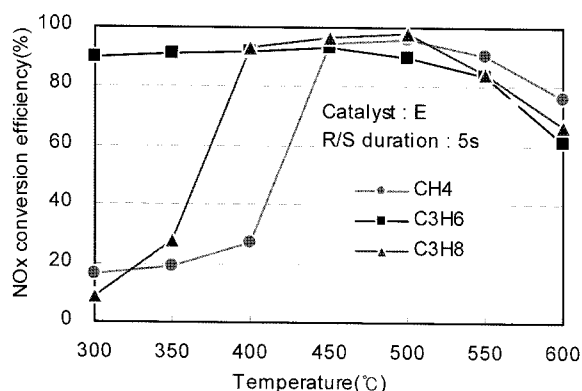


Figure 7. NO<sub>x</sub> conversion efficiency of the catalyst E with various reductants.

vehicles with other fuels. Therefore, if some other hydrocarbons (like as C<sub>3</sub>H<sub>6</sub>) other than CH<sub>4</sub> are introduced as reductants in the exhaust stream, lean de-NO<sub>x</sub> catalysts for natural gas vehicles will be improved in reducing NO<sub>x</sub> emission.

#### 4. CONCLUSIONS

Several kinds of NO<sub>x</sub> storage type reduction catalysts were formulated for application to natural gas fueled lean-burn vehicles, and tested on a model gas test bench. The main findings from this experimental study can be summarized as follows.

- (1) When Ba loading of a catalyst was increased, the quantity of NO<sub>x</sub> stored in the catalysts increased in the high temperature range over 350°C.
- (2) With more Ba deposition, the NO<sub>x</sub> conversion efficiency as well as its peak value increased in the high temperature range, but decreased in the low temperature range.
- (3) The best of de-NO<sub>x</sub> catalyst tested in this study was catalyst B, which was loaded with 42.8 g/L of Ba in addition to Pt, Pd and Rh in the ratio of 7:7:1.
- (4) In the low temperature range under 450°C, the NO<sub>x</sub> conversion efficiencies of the catalysts with CH<sub>4</sub> used as the reductant were lower than those with either C<sub>3</sub>H<sub>6</sub> or C<sub>3</sub>H<sub>8</sub> as the reductant.

#### REFERENCES

- Brogan, M. S., Brisley, R. J. A., Walker, P., Webster, D. E., Boegner, W., Fekete, N. P., Kramer, M., Krutzsch, B. and Voigtlander, D. (1995). Evaluation of NO<sub>x</sub> storage catalysts as an effective system for NO<sub>x</sub> removal from the exhaust gas of leanburn gasoline engine. *SAE Paper No. 952490*.
- Centi, G. and Perathoner, S. (1996). Role and importance of oxidized nitrogen oxide adspecies on the mechanism and dynamics of reaction over copper-based catalysts. *Catalysis Today*, **29**, 117–122.
- Choi, B. C., Jeong, J., Son, G. and Jung, M. (2005). Conversion characteristics of double-layer washcoat tri-metal TWC using high cell density substrate. *JSME Int. J. B.* **48**, **4**, 874–881.
- Fridell, E., Persson, H., Westerberg, B., Johansson, S. and Smedler, G. (1999). NO<sub>x</sub> storage in barium-containing catalysts. *J. Catalysis*, **183**, 196–209.
- Holmgren, E. M., Yung, M. M. and Ozkan, U. S. (2007). Dual-catalyst aftertreatment of lean-burn natural gas engine exhaust. *Applied Catalysis B: Environmental*, **74**, 73–82.
- Jun, H. J. and Shu, G. (2002). *An Introduction to Catalysis*. Hanlimwon. Seoul. Korea. 15–54.
- Kaspar, J., Fornasier, P. and Hickey, N. (2003). Automotive catalytic converter: Current status and some perspective. *Catalysis Today*, **77**, 419–449.
- Kim, Y. K. and Choi, B. C. (2001). *Alternative Energy Engine*. Baro Press Co., Gwangju. Korea. 6–58.
- Lee, C. H. and Choi, B. C. (2005). Evaluation of NO<sub>x</sub> reduction catalyst by model gas for lean-burn natural gas engine. *Int. J. Automotive Technology* **6**, **6**, 591–598.
- Lee, C. H., Choi, B. C. and Juhng, W. N. (2004). Comparison of NO<sub>x</sub> reduction characteristics of NO<sub>x</sub> storage catalyst with TWC for lean-burn natural gas vehicles. *Trans. Korean Society of Automotive Engineers* **12**, **5**, 79–84.
- Miyoshi, N., Matsumoto, S. and Katoh, K. (1995). Development of new concept three-way catalyst for automotive lean-burn engines. *SAE Paper No. 950809*.
- Matsumoto, S., Ikeda, Y., Suzuki, H., Ogai, M. and Miyoshi, N. (2000). NO<sub>x</sub> storage-reduction catalyst for automotive exhaust with improved tolerance against sulfur poisoning. *Applied Catalysis B: Environmental*, **25**, 115–124.
- Matsumoto, S. (2004). Recent advances in automobile exhaust catalysts. *Catalysis Today*, **90**, 183–190.
- Ohtsuka, H., Tabata, T. and Hirano, T. (2000). Palladium-platinum-loaded sulfated zirconia: A highly durable catalyst for the reduction of nitrogen oxides by methane in the presence of water vapor and SO<sub>x</sub>. *Applied Catalysis B: Environmental* **28**, **2**, L73–L76.
- Ohtsuka, H. and Tabata, T. (2001). Roles of palladium and platinum in the selective catalytic reduction of nitrogen oxides by methane on palladium-platinum-loaded sulfated zirconia. *Applied Catalysis B: Environmental* **29**, **3**, 177–183.
- Rohr, F., Peter, S. D., Lox, E., Kögel, M., Sassi, A., Juste, L., Rigaudeau, C., Belot, G., Gélina, P. and Primet, M. (2005). On the mechanism of sulphur poisoning and regeneration of a commercial gasoline NO<sub>x</sub>-storage catalyst. *Applied Catalysis B: Environmental*, **56**, 201–

212.

- Ryan, R. (2006). *Surface and Nanomolecular Catalysis*. Taylor & Francis. New York. 7–11.
- Sadovskaya, E. M., Suknev, A. P., Pinaeva, L. G., Goncharov, V. B., Bal'zhinimaev, B. S., Chupin, C., Pérez-Ramírez, J. and Mirodatos, C. (2004). Mechanism and Kinetics of the selective NO reduction over Co-ZSM-5 studied by the SSITKA technique: 2. reactivity of NO<sub>x</sub>-adsorbed species with methane. *J. Catalysis* **225**, *1*, 179–189.
- Takahashi, N., Shinjoh, H., Iijima, T., Suzuki, T., Yamazaki, K., Yokota, K., Suzuki, H., Miyoshi, N., Matsumoto, S., Tanizawa, T., Tanaka, T., Tateishi, S. and Kasahara, K. (1996). The new concept 3-way catalyst for automotive lean-burn engine: NO<sub>x</sub> storage and reduction catalyst. *Catalysis Today*, **27**, 63–69.
- Theis, J. R., Ura, J. A. and Graham, G. W. (2004). The effects of aging temperature and air-fuel ratio on the NO<sub>x</sub> storage capacity of a lean NO<sub>x</sub> trap. *SAE Paper No.* 2004-01-1493.