

EVALUATION OF NO_x REDUCTION CATALYST BY MODEL GAS FOR LEAN-BURN NATURAL GAS ENGINE

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ABSTRACT—A three-way catalyst system of a natural gas vehicle (NGV) has characteristics of higher fuel consumption and higher thermal load than a lean-burn catalyst system. To meet stringent emission standards in the future, NGV with the lean-burn engine may need a catalyst system to reduce the amounts of HC, CO and NO_x emission, although natural gas system has low emission characteristics. We conducted experiments to evaluate the conversion efficiency of the NO_x reduction catalyst for the lean-burn natural gas engine. The NO_x reduction catalysts were prepared with the γ -Al₂O₃ washcoat including Ba based on Pt, Pd and Rh precious metal. In the experiments, effective parameters were space velocity, spike duration of the rich condition, and the temperature of flowing model gas. From the results of the experiments, we found that the temperature for maximum NO_x reduction was around 450°C, and the space velocity for optimum NO_x reduction was around 30,000 h⁻¹. And we developed an evaluation model of the NO_x reduction catalyst to evaluate the conversion performance of each other catalysts.

KEY WORDS : NO_x reduction catalyst, Natural gas engine, CH₄, Adsorption, Desorption

1. INTRODUCTION

Emission standards for all vehicles are becoming more stringent in most countries to reduce the amounts of harmful gases. Recently, vehicles using natural gas have gained attention because of their low emissions of CO₂ and NO_x compared with other fuels, the advanced fueling technology and the clean property of natural gas itself.

The majority of heavy-duty vehicles using natural gas have not adapted a catalyst for emission control compared with gasoline vehicles. However, to meet restricted emission standards in the future, natural gas vehicles will need a catalyst (Kim and Choi, 2000; Anderson and Cruise, 2000; Ayala *et al.*, 2003).

It is known that a three-way catalyst (TWC) system can greatly reduce emissions, such as NO_x, THC, CO, in the condition of stoichiometric air/fuel ratio. Nevertheless, this system is not suitable for the natural gas engine which operates in a lean excess air ratio mainly for improved fuel consumption and thermal load efficiency (Kowalewicz, 2001). Furthermore, the TWC system is difficult to apply to a heavy-duty engine requiring high load and power characteristics.

If the TWC system is adapted to the lean air/fuel condition, emissions of HC and CO may be purified in

high oxidation surroundings, but NO_x is hardly removed. We have developed an oxidation catalyst to remove the CO and HC, including the CH₄, in the lean condition (Yun *et al.*, 2002). It is necessary to develop de-NO_x catalyst according to the condition of combustion characteristics of the natural gas engine. In recent years, some catalysts were developed as commercial products utilizing the adsorption characteristics of NO_x on the catalyst surface (Brogan *et al.*, 1995; Takahashi *et al.*, 1996; Masumoto, 2000; Choi, 2001). In principle, if the rich spike to the catalyst is allowed to develop after the NO_x is adsorbed on the surface of the catalyst by the lean air/fuel condition, the NO_x is desorbed from the surface and then reduced in the rich atmosphere. Most of the catalysts for NO_x reduction have not been studied for use in the natural gas engine except for gasoline with a similar method.

The concentration of emitted NO_x from the natural gas engine is lower than from the gasoline engine; furthermore, the emission includes about 90% CH₄ as hydrocarbon compound. To meet the restricted emission standards in the future, a catalyst acting as NO_x adsorption type is needed for natural gas vehicles. Because vehicle load tests for catalysts are expensive, experiments for such catalysts have been performed with synthetic gas in a laboratory (Lietti *et al.*, 1998; Peyton *et al.*, 1999; Fridell *et al.*, 1999). Moreover, the experiments were performed with steady state conditions on account of the

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difficult system control and data acquisition.

In this study, we tried to present a model gas test of a novel NOx reduction catalyst that has characteristics of NOx adsorption under unsteady state conditions of lean and rich excess air ratios.

The purpose of this study was to search for a method of the model gas test that is comparable with real exhaust gases, and to evaluate relatively the catalyst performance with consideration of the optimum conditions for the effective parameters which can influence the NOx conversion efficiency.

As a result of the study findings, we have found another test method for the NOx reduction catalyst. Moreover, we could evaluate the catalyst performance for NOx conversion efficiency through the investigation of effective parameters.

2. THE EXPERIMENTAL APPARATUS AND TEST PROCEDURE

Figure 1 shows the experimental apparatus used in this study. The chemiluminescence detector (CLD, Data test Model 501) can sample NOx in sequence at a flow rate of 80 mL/min. Excess air ratio was controlled by a spike timer (Autonics, FX4-2P) calibrated in one hundredths of a second. A mass flow controller was 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 temperature controller. A data-logger (Yokogawa DR1400) was used to measure the temperature from the reactor, and to sample the NOx concentration from the NOx analyzer.

The catalyst was prepared with a coating at a Pt/Pd/Rh ratio of 9/3/1 on ceramic monolith. Ba and La were mixed more to the γ -Al₂O₃ washcoat as an assistant metal.

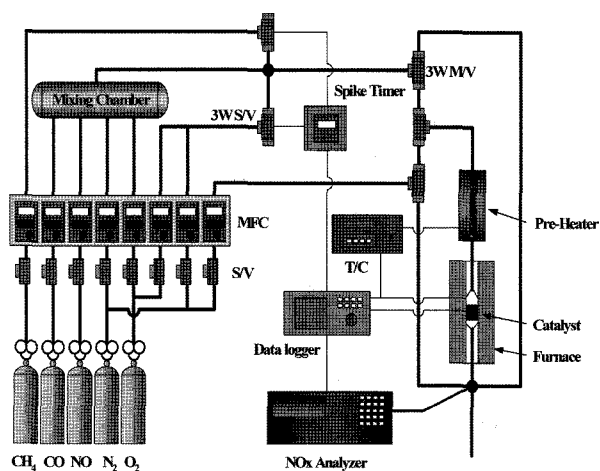


Figure 1. Schematic diagram of experimental apparatus.

The cell density of the catalyst was 600 cpsi (93 cell/cm²).

First, the sample core was flushed with nitrogen gas at a rate of 1 L/min at 400°C, for 30 min, after it had been inserted to a reactor. After flushing, the gas temperature was increased to a set point at a flow rate of 2.5 L/min. The nitrogen gas of the fluid was exchanged with the mixing gas when the temperature reached the set point. The mixing gas was released into the reactor until the NOx concentration reached the set point under the condition of rich excess air ratio. If the NOx concentration continued with the same value, the excess air ratio of the fluid was exchanged to the lean condition. This condition was maintained until the NOx concentration reached the saturation point under the condition of lean excess air ratio. If the NOx concentration continued with the same value, the cycle of rich spike and lean fluid of 60s was repeated until the NOx 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. SV was varied by the catalyst volume, with a range of 20,000 h⁻¹ to 50,000 h⁻¹. The temperature of model gas, through the catalyst, was varied from 400°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 $\lambda=1.5$ and $\lambda=0.7$, respectively. The duration of the rich spike was varied from 1s to 9s.

3. RESULTS AND DISCUSSION

3.1. Optimum Duration of Rich Spike

Figure 2 shows an example curve for NOx variation as a

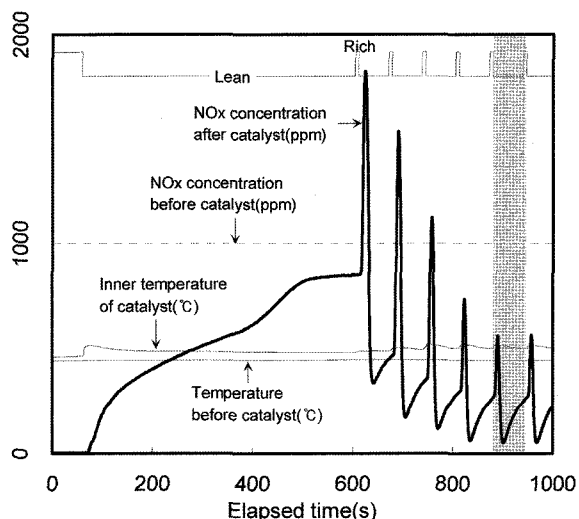


Figure 2. A shape of NOx variation according to the rich spike duration.

result of the rich and lean, excess air ratio in the catalyst. The conditions specified for this test were $SV=20,000\text{ h}^{-1}$, gas temperature 450°C , lean excess air ratio $\lambda=1.5$, and rich spike $\lambda=0.7$. NO, CO and CH₄ of 1000 ppm were supplied into the reactor. The entrance and inner temperatures of the catalyst were demonstrated for the reaction temperature. The upper and lower teeth of the lean/rich curve indicate the duration of the rich and lean conditions, respectively.

As shown in Figure 2, NO_x increased during the lean condition, and reached the saturation point after around 540s. If the outlet NO_x concentration reached the saturation point, the cycle of 60s of lean and 5s of rich spike was repeated until the shape became regular.

The surface of the catalyst was varied to excessive oxygen atmosphere from the rich atmosphere when the rich spike was finished. From the results, we could estimate that the reactions of desorption and reduction for NO_x were being reduced until the next rich spike, instead of the adsorption increment. After the concentration reached NO_x saturation, the shape of the NO_x variation curve became regular with repeating lean/rich spikes. The regular shape of the NO_x variation curve by gas temperature and rich spike duration can be summarized into the following 3 types.

The first shape features by some repetition of the lean/rich spike, as shown in Figure 2. As result of some repetition, the peak point of the NO_x concentration cycle slowly comes down with reducing desorption, and the trough point on the NO_x concentration curve comes down with increasing reduction. As result of some repetition, the shape becomes regular.

The second shape forms when the gas temperature is not high enough to react, even though the rich spike duration is long enough, or when the rich spike duration is not long enough to react, even though the gas temperature is high enough. The peak point and the trough point on the NO_x concentration curve are maintained at the first level without reducing to the same shape, because of the short rich spike duration and low gas temperature for the reaction.

The third shape occurs when the gas temperature and rich spike duration have opposite conditions to those above. Although there is only one rich spike, the peak point and the trough point on the NO_x concentration curve immediately drop to the lowest level because the rich spike duration is sufficient with the higher gas temperature for the reaction. Moreover, the points stay at the lowest level sequentially due to the repetition of the same lean/rich spike conditions.

As a result of these experiments, we estimated that the rich spike duration of the first case was optimum for maximizing the efficiency of the NO_x adsorption catalyst. The rich spike duration of the second case was

evaluated to be too short, because the repeated rich spike could not reduce the NO_x emission sufficiently due to lower temperature, and that of the third case to be too long, because it could increase the fuel consumption from after the second lean/rich cycle repetition.

The rich spike duration of the actual automotive system could be controlled automatically within the NO_x feedback system which is affected by the catalyst temperature and NO_x concentration as variables.

3.2. Effects of Temperature

Figures 3 to 5 show the NO_x variation per cycle according to the rich spike duration when the gas temperature varied from 400°C to 600°C in the study of the effect of the average concentration due to temperatures. The figures indicated a part of the curve as a hatched section of Figure 2.

As shown in the figures, the elapsed time of cycle is indicated from the finish point of the previous rich spike to next start point. Because of the differential distance of the spike timer and the catalyst in the reactor, the entrances of the sampling probe and NO_x analyzer, the effect of the rich spike is reflected to the NO_x analyzer after 10 seconds from the rich spike finish point.

The average conversion efficiencies of the NO_x were 33%, 61%, and 27% at 400°C , 500°C , and 600°C , respectively. In addition, the average conversion efficiencies at 450°C and 550°C were 54% and 46%, respectively.

These results indicated that the average conversion efficiency of the NO_x decreases with increasing temperature, or decreases from the center of 500°C . This behavior indicates that the characteristics of the catalyst for NO_x adsorption are different as a factor of

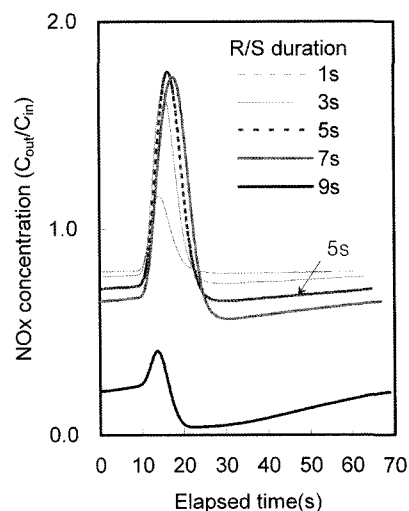


Figure 3. NO_x variation per cycle according to rich spike duration at 400°C , $SV=20,000\text{ h}^{-1}$.

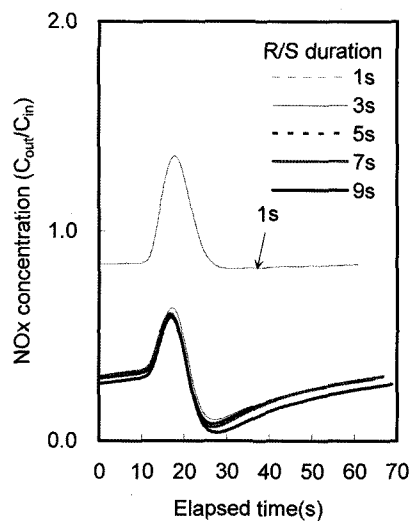


Figure 4. NOx variation per cycle according to rich spike duration at 500°C, SV=20,000 h⁻¹.

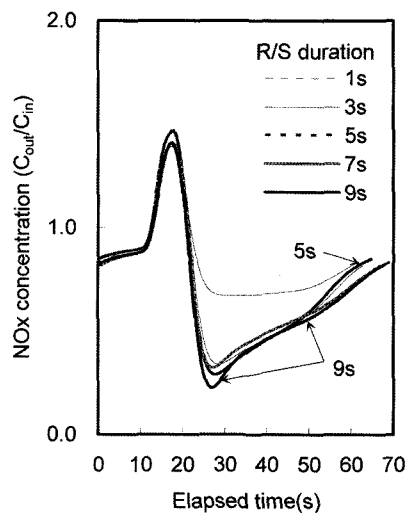


Figure 5. NOx variation per cycle according to rich spike duration at 600°C, SV=20,000 h⁻¹.

temperature for the TWC systems that the conversion efficiency of NOx increases with increasing temperature. In addition, a further reason is that the degree of NOx adsorption on the catalyst surface varies due to the temperature.

As shown in Figure 5, the concentration of the emitted NOx increases at 600°C even faster than that other case after desorption of NOx by the rich spike in the lean atmosphere. In the result, the emitted NOx concentration at the end point of the cycle was higher than that for the cases at 400°C and 500°C. This phenomenon can be interpreted to suggest that NOx adsorption is difficult at high temperature.

On the contrary, the average conversion efficiency of NOx at a temperature range under 500°C increased with increasing temperature because the reduction of NOx led to a preponderance of NOx conversion efficiency instead of the NOx being decreased by the adsorption process.

These results indicated that there is a window of temperature, which influences the conversion efficiency of NOx in the catalyst. The study results confirmed that the temperature range for maximum NOx conversion efficiency was 450°C to 500°C.

3.3. Effects of Space Velocity

The average conversion efficiency of the NOx per cycle

Table 1. Average NOx conversion efficiency (%) per cycle at SV=20,000 h⁻¹.

Gas temp. (°C)	R/S duration (s)				
	1	3	5	7	9
400	18	16	20	25	85
450	16	21	77	78	78
500	10	73	74	74	77
550	18	49	52	54	55
600	17	28	28	30	31

Table 2. Average NOx conversion efficiency (%) per cycle at SV=30,000 h⁻¹.

Gas temp. (°C)	R/S duration (s)				
	1	3	5	7	9
400	19	19	28	86	88
450	18	22	85	90	84
500	12	78	79	79	78
550	20	53	56	55	57
600	15	23	24	26	28

Table 3. Average NOx conversion efficiency (%) per cycle at SV=50,000 h⁻¹.

Gas temp. (°C)	R/S duration (s)				
	1	3	5	7	9
400	18	18	17	16	17
450	16	20	66	69	69
500	12	55	57	57	58
550	10	47	46	49	48
600	13	16	18	20	21

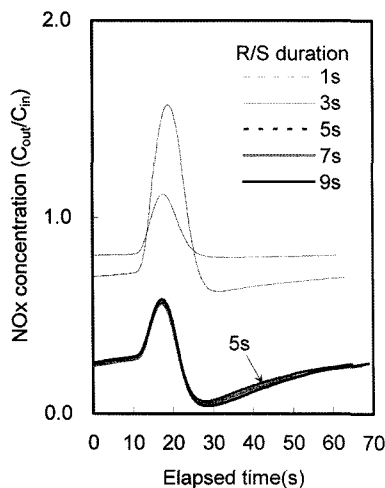


Figure 6. NO_x variation per cycle according to rich spike duration at 450°C, SV=20,000 h⁻¹.

according to the rich spike duration and gas temperature is summarized in Tables 1 to 3. The conversion efficiency was converted into a percentage after the value during a cycle was integrated, and divided by the initial entrance value.

The conversion efficiency of the NO_x at SV=30,000 h⁻¹ was better than that at other SVs, generally. And the efficiency peaked at 450°C. A rich spike of 1s did not influence the efficiency.

Figures 6 to 8 show the NO_x variation per cycle according to the rich spike duration when SV was varied from 20,000 h⁻¹ to 50,000 h⁻¹, and the temperature was set to 450°C to investigate the average concentration due to SV. SVs are changed by varying the catalyst volume. The average conversion efficiency of NO_x was increased

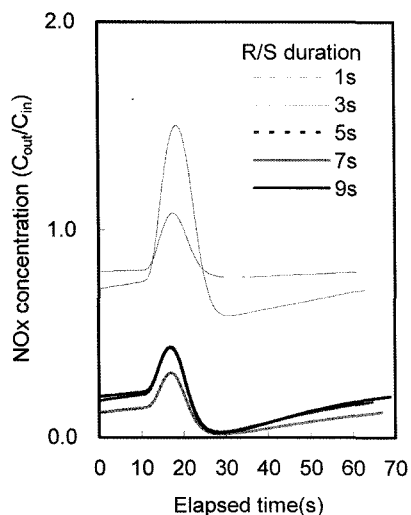


Figure 7. NO_x variation per cycle according to rich spike duration at 450°C, SV=30,000 h⁻¹.

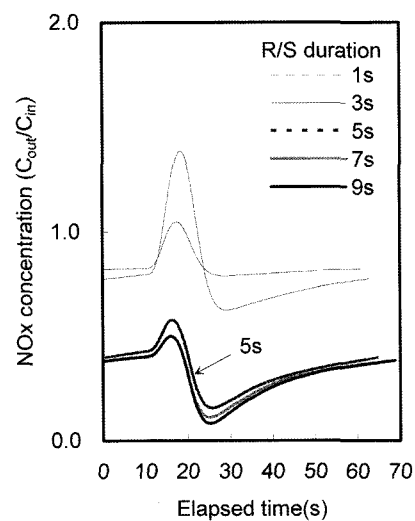


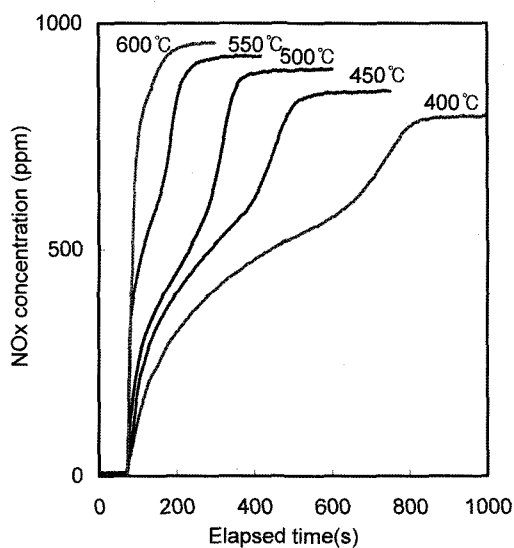
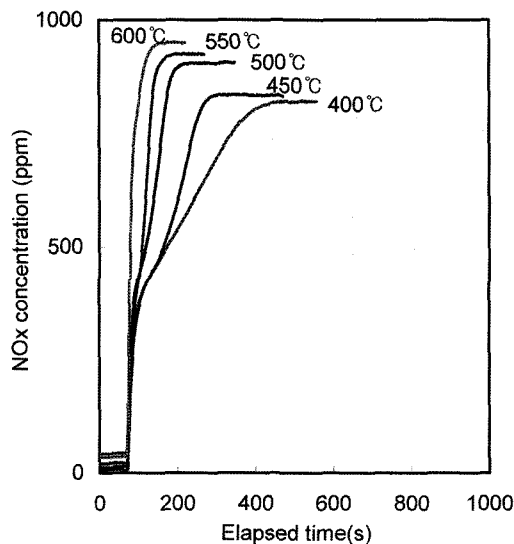
Figure 8. NO_x variation per cycle according to rich spike duration at 450°C, SV=50,000 h⁻¹.

when the SV of 20,000 h⁻¹ was increased to 30,000 h⁻¹, but was decreased at SV=50,000 h⁻¹. For rich spikes of 1s and 3s, the NO_x conversion efficiency was much the same as the low value. However, the average values of the rest of the cases were 78%, 85%, and 57%, at SV values of 20,000 h⁻¹, 30,000 h⁻¹, and 50,000 h⁻¹, respectively, with the highest value occurring when SV=30,000 h⁻¹.

Because the specific contact area of gas for the catalyst is expanded when SV decreases, we can suppose that the conversion efficiency at SV=20,000 h⁻¹ will be higher than that at SV=30,000 h⁻¹. However, the result does not have as much equivalence as expected. Because of the exothermic reaction in the catalyst from the rich spike of 5–9s, the inner temperature of the catalyst is maintained at 500–520°C, 470–500°C and 440–470°C at SV = 20,000 h⁻¹, 30,000 h⁻¹ and SV=50,000 h⁻¹, respectively. The generation of high temperature by exothermic reaction may have been due to the increased specific contact area of the gas for the catalyst at low SV. The degree of exothermic reaction influences the catalyst temperature, and this variation in temperature affects the NO_x conversion efficiency. For this reason, we can estimate that the average conversion efficiency of NO_x at SV=30,000 h⁻¹ is higher than that at SV=20,000 h⁻¹, due to the reduction of NO_x adsorption. These results indicate that there is a window for SV, which influences the conversion efficiency of NO_x in the catalyst.

3.4. Adsorption and Storage Capacity of NO_x

Because the NO_x storage catalyst is mainly used in lean conditions, an investigation into the variation of emitted NO_x concentration is important for the evaluation of adsorption capacity.

Figure 9. NOx storage capacity at $\lambda=1.6$, $SV=20,000 \text{ h}^{-1}$.Figure 10. NOx storage capacity at $\lambda=1.6$, $SV=50,000 \text{ h}^{-1}$.

Figures 9 and 10 show the variation of the emitted NOx concentration when the catalyst was continuously exposed to the lean condition ($\lambda=1.6$) with $SV=20,000 \text{ h}^{-1}$ and $SV=50,000 \text{ h}^{-1}$. The concentration remains near zero until before the excess air ratio exchange because of the initial rich condition. After the condition is changed to a lean excess air ratio, the concentration slowly increases to the saturation point. The increasing shapes of these concentration curves are different from each other for the SV and gas temperature.

The elapsed time to the saturation point was reduced when SV and temperature were increased. The reduction of the elapsed time to the saturation point with increasing SV may have been due to the relative reduction of NOx

Table 4. NOx saturation at $\lambda=1.6$, $SV=20,000 \text{ h}^{-1}$.

Temperature ($^{\circ}\text{C}$)	400	450	500	550	600
Duration for saturation (s)	1000	660	500	280	200
Concentration of saturation (ppm)	800	850	900	930	960
Integrated concentration (ppm/s)	560	600	650	740	820

Table 5. NOx saturation at $\lambda=1.6$, $SV=50,000 \text{ h}^{-1}$.

Temperature ($^{\circ}\text{C}$)	400	450	500	550	600
Duration for saturation (s)	450	390	210	190	110
Concentration of saturation (ppm)	820	830	910	930	950
Integrated concentration (ppm/s)	640	680	700	750	820

adsorption amount, which occurred, with the increment of specific contact area for the flowing gas.

In addition, the reduction of the elapsed time to the saturation point with the increasing temperature may have been due to the difficulty of NOx adsorption on the surface of the catalyst. Moreover, the results may show that the adsorption energy is reduced under these conditions (Jun *et al.*, 2002).

Tables 4 and 5 summarize the duration for NOx saturation, the concentration of saturation and the specific concentration for unit time at $SV=20,000 \text{ h}^{-1}$ and $SV=50,000 \text{ h}^{-1}$.

At a specific concentration for unit time, we observed the increment of NOx concentration with increasing temperature. This increment may have been due to reduction of the NOx adsorption on the catalyst surface. Because the storage capacity of NOx at 400°C is relatively greater than that at other temperatures, the conversion efficiency of NOx can be expected to be higher. However, the efficiency is not high at this temperature due to the lower degree of reduction according to the temperature.

The experimental results indicated that more vigorous adsorption and reduction activity of NOx are required in the catalyst to increase NOx conversion.

3.5. Characteristics of NOx Reduction Catalyst

From these results of the investigation into the adsorption and desorption of NOx with the catalyst, we determined that the variation of NOx concentration has a regular shape according to the duration of rich spike, temperature and SV. Figure 11 shows the reaction characteristics of NOx reduction catalyst with the variation of lean and rich

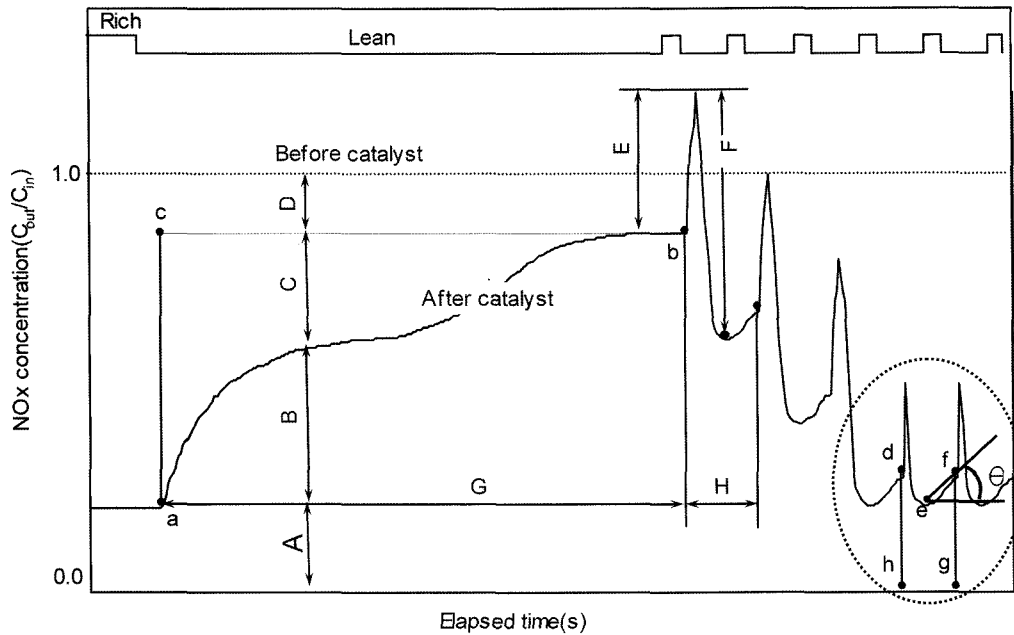


Figure 11. Reaction characteristics of NO_x reduction catalyst on the variation of air excess ratio.

excess air ratio.

The conversion efficiency and performance of NO_x in the catalyst can be varied with the position and magnitude of the factors as described below.

- A : Emitting NO_x concentration without the reduction
- B : Emitting NO_x concentration without the reduction and adsorption
- C : Storing NO_x concentration with the reduction and adsorption
- D : Reducing NO_x concentration with reduction
- E : Emitting NO_x concentration with the desorption by rich spike
- F : Reducing NO_x concentration with the reduction
- G : Duration for saturation of NO_x
- H : Cycle duration

To obtain superior performance from the NO_x reduction catalyst, the values of A, B, E and G must be relatively greater than those of other catalysts. In particular, the average slopes of the segments "ab" and "ef", which affect the conversion efficiency of NO_x, must be maintained low. If the average slope of segment "ab" is built up at a lower value, the emitted NO_x concentration per unit time has a reducing effect, and the NO_x concentration influences the next cycle.

With repetitions of the lean/rich spike cycle, the position "e" of minimum concentration and the average slope angle "ε" of segment "ef" affect the area "defgh" directly, which indicates the integrated NO_x per cycle. This is because the position of point "e" changes the

angle "ε", and angle "ε" affects the NO_x concentration at the finish and start points of the cycle.

4. CONCLUSIONS

We obtained the following study results from an investigation on the NO_x reduction catalyst for the lean burn natural gas engine.

- (1) The optimum duration of the rich spike was 3–5s under equivalent conditions of gas temperature and SV.
- (2) The temperature window for maximum NO_x conversion was between 450°C and 500°C.
- (3) The SV window for optimum NO_x conversion was near SV=30,000 h⁻¹.
- (4) The NO_x storage capacity was reduced with increasing SV and temperature under the condition of lean excess air ratio.
- (5) From the high and low level NO_x concentration in the reaction characteristics curve, the relative NO_x conversion efficiency of the catalysts can be determined.

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