Research Report

# NOx Reduction under Oxidizing Conditions by Plasma-assisted Catalysis

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## Abstract

In order to investigate the feasibility of using Plasma Assisted Catalysis (PAC) for exhaust aftertreatment of the diesel engine and lean-burn gasoline engine, the application of PAC to NOx reduction by HC (HC-SCR) was studied using a simulated oxidizing exhaust gas. First, the effects of non-thermal plasma were studied, and the effect of the distance between the plasma reactor and the catalyst reactor and the dominating gas composition of NOx reduction were measured. Then, an appropriate catalyst for PAC was developed; the catalyst properties dominating NOx reduction and improvement of the NOx reduction performance by an additional element were investigated. Finally, on the basis of these results, a 3-stage catalyst, the combination of catalysts with different temperature windows for NOx reduction, was developed. The following results were obtained:

(1) $NO_2$ and $CH_3CHO$ generated by the plasma resulted in significant reduction of NOx on $\gamma$-alumina.

(2) $\gamma$-alumina with a large amount of solid acid showed high NOx conversion. In addition, indium loading on $\gamma$-alumina improved the NOx reduction activity and suppressed the degradation of the activity under steady-state temperature conditions.

(3) A high NOx conversion as well as high HC and CO conversions were achieved by the 3-stage catalyst with PAC under transient temperature conditions, which simulated the actual engine operating conditions.

Keywords: Non-thermal plasma, Catalyst, NOx reduction, Hydrocarbon, Aftertreatment, Oxidizing condition, Diesel engine, Lean-burn gasoline engine

## 1. Introduction

The need to suppress carbon dioxide emissions has increased the demand for the development of the fuel-efficient diesel engine and lean-burn gasoline engine. However, these engines have an emission control problem: the conventional three-way catalyst is not effective in NOx reduction because these engines operate under oxidizing conditions. Thus, many catalytic reduction methods with HC (HC-SCR) as reductant have been studied.[1-12)] However, the NOx reduction performance of these catalysts has been insufficient. Recently, systems that perform NOx reduction by PAC (Plasma Assisted Catalysis), which combine non-thermal plasmas and HC-SCR catalysts, have been proposed and investigated by many researchers.[13-22)]

A great deal of effort has been made to understand the phenomenon of non-thermal plasma. However, few studies have been devoted to the optimization of PAC systems for automotive aftertreatment. In order to obtain high NOx reduction performance for automotive applications, it is necessary to identify the optimum PAC system.

The purpose of the present paper is to study the PAC system to achieve proper automotive aftertreatment of the diesel engine and lean-burn gasoline engine. To optimize the PAC system, the following experiments have been performed.

(1) The effects of the non-thermal plasma were studied; the effect of the distance between the plasma reactor and the catalyst reactor on the NOx conversion, the difference of NOx reduction activity depending on whether the plasma would affect HC only, NO only, or both HC and NO in PAC, and the gas composition difference in the temperature was studied through gas analysis in order to identify the effective temperature range for PAC of automotive exhaust.

(2) An appropriate catalyst for PAC was developed; a catalyst with high NOx conversion for PAC was surveyed. We then focused on $\gamma$-alumina, and investigated the catalyst properties dominating NOx reduction and attempted to improve the NOx reduction performance by using an additional element.

(3) The PAC system was studied under the transient exhaust temperature. On the basis of these results, we proposed application of a 3-stage catalyst with PAC to automotive aftertreatment.

## 2. Experimental

### 2. 1 Plasma reactor

In order to generate a non-thermal plasma, a dielectric barrier discharge with pulsed high voltage power supply was used in our study. The plasma reactor and the power supply are shown in **Figs. 1** and **2**. As shown in Fig. 1, the plasma reactor consisted of a quartz tube (17 mm I. D.) with a straight metal wire (1.0 mm diameter) as high voltage electrode and a stainless steel mesh as ground electrode wrapped around the quartz tube barrier. The effective discharging volume was about 2 ml. The upper part of the plasma reactor was

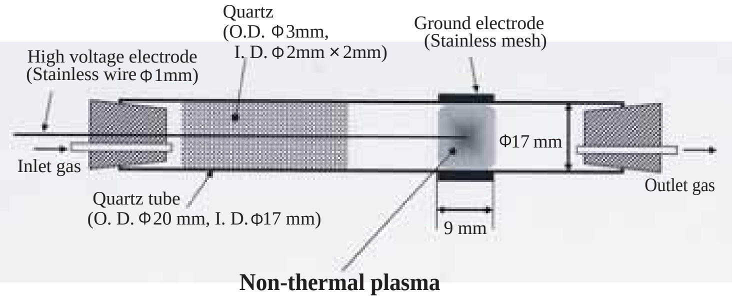


**Fig. 1** Plasma reactor.

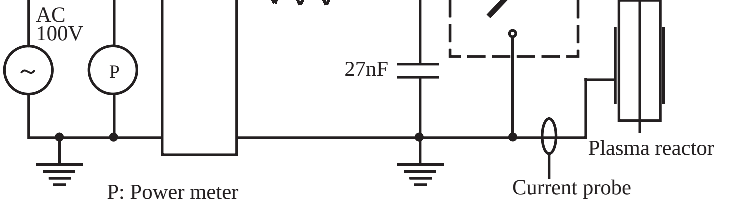


**Fig. 2** Pulsed high voltage power supply.

packed with small quartz tubes for preheating the feed gas.

In this experiment, we also used a rotary spark-gap switch for generating the high voltage pulse (see Fig. 2). Peak voltage and frequency were 10-15 kV and 230 Hz, respectively. For measurement of voltage and current waveforms, a digital oscilloscope (Tektronix, TDS3034), a voltage divider (Tektronix, P6051A), and a current probe (Tektronix, AM503) were used. The input power was 8 W, measured by a digital power meter (Yokogawa, MCP5000) inserted into the AC power input line.

### 2. 2 Catalyst preparation

The alumina catalysts used in this study are shown in **Table 1(a)**. $\gamma$-alumina, 5% La-alumina and 2.5% La-alumina were prepared by hydrolysis of aluminum hydroxide, with lanthanum nitrate in the case of 5% La-alumina and 2.5% La-alumina, followed by drying and calcination in air at 1,073 K for 5 h. La-doping was performed to improve the thermal stability of alumina. BET surface areas (Specific Surface Area, SSA) of these alumina catalysts were 130-160 $m^2/g$. $\alpha$-alumina with a SSA of 9.5 $m^2/g$ was obtained by calcinating $\gamma$-alumina at 1,473 K for 5 h in air.

The zeolite catalysts used in this study are shown in **Table 1(b)**. Cu-ZSM-5 and H-ZSM-5 was obtained from Toso Corp. Zeolites loaded with alkali or alkaline earth metal (Li, Na, K, Mg, Ca, Sr and Ba) were prepared H-ZSM-5 with nitrate, followed by drying and calcination in air at 873 K for 5 h. The loading amount was 0.3 mol per 100 g of H-ZSM-5.

Other catalysts used in this study are shown in **Table 1(c)**. A Pt/alumina catalyst was prepared by impregnating 5% La-alumina powder with an aqueous solution of dinitrodiammine platinum. The powder was dried at 383 K for 24 h in air, followed by calcination at 873 K for 5 h in air. The loading amount of Pt was 1 wt%. Ag-, Ga- and In-loaded aluminas were prepared by impregnating $\gamma$-alumina powder with the corresponding nitrate, followed by drying and calcination in air at 873 K for 5 h. The loading amounts were 10 wt% for AgO and $Ga_2O_3$, 20 wt% for $In_2O_3$.

These powders were pressed at 98 MPa, crushed, and sieved into pellets with a diameter of 1-3 mm. The honeycomb catalyst was prepared by the conventional washcoat[23)] with $\gamma$-alumina (0.4 g) on a cordierite honeycomb (600 cpsi, 5 ml).

### 2. 3 Measurements

**Figure 3** shows the apparatus that was used to investigate the effects of PAC. The apparatus consisted of a plasma reactor located upstream in the gas flow and a catalyst reactor downstream in the gas flow. The catalyst reactor contained honeycomb or pellet catalysts and SiC balls for preheating the feed gas. Both reactors were set in a furnace to ensure that they were maintained at the same temperature. The composition of the inlet gas was chosen to simulate that of the diesel exhaust. NO and HC could be introduced into the plasma reactor

**Table 1(a)** Alumina catalysts used in this study.

| Catalyst | Components | SSA ($m^2/g$) |
|---|---|---|
| $\gamma$-alumina | $\gamma$-alumina | 162 |
| 5%La-alumina | $\gamma$-alumina with La: 5mol% | 159 |
| 2.5%La-alumina | $\gamma$-alumina with La: 2.5mol% | 133 |
| $\alpha$-alumina | $\alpha$-alumina | 9.5 |

**Table 1(b)** Zeolite catalysts used in this study.

| Catalyst | Components |
|---|---|
| Cu-ZSM-5 | CuO : 3.18wt%, $SiO_2/Al_2O_3$ : 40.6 |
| Li/ZSM-5 | Li:0.3mol per 100g of H-ZSM-5 |
| Na/ZSM-5 | Na:0.3mol per 100g of H-ZSM-5 |
| K/ZSM-5 | K:0.3mol per 100g of H-ZSM-5 |
| Mg/ZSM-5 | Mg:0.3mol per 100g of H-ZSM-5 |
| Ca/ZSM-5 | Ca:0.3mol per 100g of H-ZSM-5 |
| Sr/ZSM-5 | Sr:0.3mol per 100g of H-ZSM-5 |
| Ba/ZSM-5 | Ba:0.3mol per 100g of H-ZSM-5 |

* Cu-ZSM-5 and H-ZSM-5 were obtained from Toso Corp.

**Table 1(c)** Other catalysts used in this study

| Catalyst | Components |
|---|---|
| Pt/alumina | Pt: 1wt%, 5%La-$\gamma$-alumina |
| Ag/alumina | AgO: 10wt%, $\gamma$-alumina |
| Ga/alumina | $Ga_2O_3$: 10wt%, $\gamma$-alumina |
| In/alumina | $In_2O_3$: 20wt%, $\gamma$-alumina |

separately. The inlet and outlet gas streams of both reactors were analyzed by the exhaust gas analyzer system (Best Sokki, Bex5900CS), GC (SHIMADZU, GC-9A) and GC/MS (HP, 6890-5973). In the exhaust gas analyzer system, the water vapor was removed by a condenser prior to gas analysis. Then, the remaining components were continuously analyzed by nondispersive infrared ($CO_2$), flame ionization (HC), magnetic susceptibility ($O_2$), and chemiluminescence (NOx). GC and GC/MS were used to analyze the HC components CO and $H_2$.

The procedure for each experiment conducted to ascertain the effects of the PAC is described below.

To determine the effect of the distance between the plasma reactor and the catalyst reactor, a 8-mm silicone tube (8mm I. D.) was used to connect the two reactors. The experimental conditions are shown in **Table 2(a)**. The space velocity of the catalyst was 23,000 $h^{-1}$. Both reactors were maintained at 673 K. The effect of the distance between two reactors was studied by varying the silicone tube length.

The effective gas composition for NOx conversion on $\gamma$-alumina with PAC was determined by applying the plasma to NO and HC separately. The two reactors were connected with a glass tube (8 mm I. D.). The experimental conditions are shown in **Table 2(b)**. The experiments were performed as follows:

"HC-Plasma": $C_3H_6$ was supplied from the inlet of the plasma reactor and NO was supplied from the inlet of the catalyst reactor. The plasma was applied to HC only.

"NO-Plasma": NO was supplied from inlet of the plasma reactor and $C_3H_6$ was supplied from the inlet of the catalyst reactor. The plasma was applied to NO only.

"HC/NO-Plasma": Both HC and NO were supplied form the inlet of

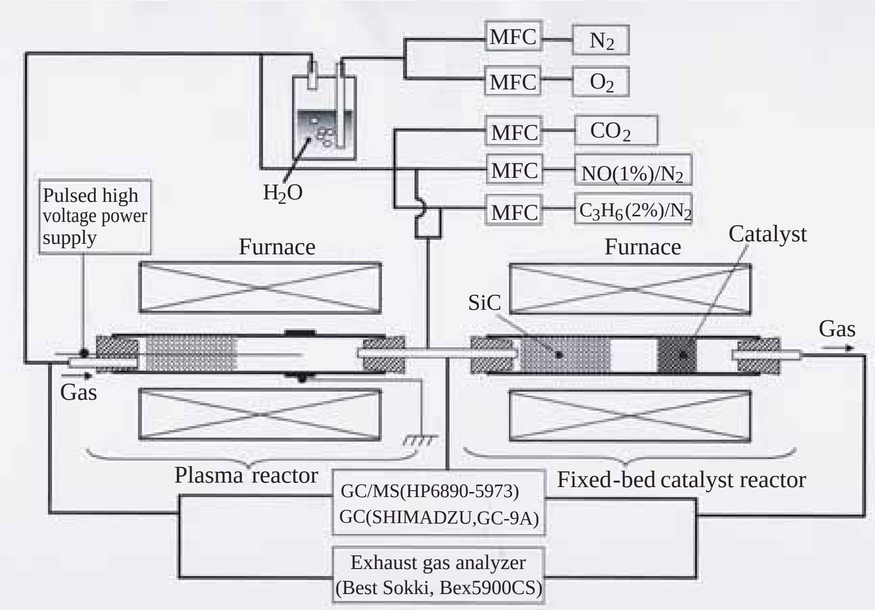


**Fig. 3** Experimental apparatus used for the effects of PAC.

**Table 2(a)** Experimental condition for the effect on the distance between the reactors.

| | | |
|---|---|---|
| Inlet gas | NO | 200 ppm |
| | $O_2$ | 10% |
| | $C_3H_6$ | 3,000 ppmC |
| | $CO_2$ | 4% |
| | $H_2O$ | 2% |
| | $N_2$ | Balance |
| Catalyst | γ-alumina, honeycomb | |
| Flow rate | 2 L/min | |
| Space velocity | 23,000 $h^{-1}$ | |
| Temperature | 673 K | |
| High voltage | 0, 10 kV(27 J/L), 15 kV(40 J/L) | |

**Table 2(b)** Experimental condition for the effective gas composition of PAC.

| | Inlet of plasma | Inlet of catalyst |
|---|---|---|
| HC-plasma | $C_3H_6$ : 3,000 ppmC | NO : 200 ppm |
| NO-plasma | NO : 200 ppm | $C_3H_6$ : 3,000 ppmC |
| HC/NO-plasma | $C_3H_6$ : 3,000 ppmC<br>NO : 200 ppm | |
| Base Inlet Gas (Inlet of plasma) | $O_2$ | 10% |
| | $CO_2$ | 4% |
| | $H_2O$ | 2% |
| | $N_2$ | Balance |
| Catalyst | γ-alumina, honeycomb | |
| Flow rate | 2 L/min | |
| Space velocity | 23,000 $h^{-1}$ | |
| Temperature | 673 K | |
| Voltage (Specific energy) | 12.5 kV (30 J/L) | |

the plasma reactor. The plasma was applied to both HC and NO.

The change in gas composition due to the plasma and the catalyst was monitored by GC and GC-MS analysis. The experimental conditions are shown in **Table 2(c)**. The temperature was varied from 298 to 873 K.

Appropriate catalysts for the PAC were sought using pellet, rather than honeycomb, catalysts in the catalyst reactor. NOx and HC conversions were measured as the temperature was decreased from 673 to 423 K at a rate of 30 K/min, and the average NOx and HC conversions from 673 to 423 K were evaluated for catalytic performance. NOx conversion was also measured under following conditions:

1) decreasing temperature from 773 to 373 K at a rate of 10 K/min,
2) decreasing temperature from 773 to 373 K at a rate of 24 K/min,
3) steady state conditions with the temperature fixed at 673 K,
4) steady state conditions with the temperature fixed at 573 K.

The experimental conditions are shown in **Table 3**. In order to determine the active site of NOx reduction on alumina with PAC, the amount of acid and base on the alumina catalyst was measured by $CO_2$ and $NH_3$ adsorption with TPD (Temperature Programmed Desorption) methods.

**Table 2(c)** Experimental condition for analyzing the change of gas composition with PAC.

| | | |
|---|---|---|
| Inlet Gas | NO | 200 ppm |
| | $O_2$ | 10 % |
| | $C_3H_6$ | 3,000 ppmC |
| | $CO_2$ | 4 % |
| | $H_2O$ | 2 % |
| | $N_2$ | Balance |
| Catalyst | γ-alumina, honeycomb | |
| Flow rate | 2 L/min | |
| Space velocity | 23,000 $h^{-1}$ | |
| Temperature | 298-873 K | |
| Voltage (Specific energy) | 12.5 kV (30 J/L) | |

The experimental conditions used for these measurements are shown in **Table 4**. The measurement procedure was as follows:

(1) pretreatment: purging contamination on the sample surface at high temperature,
(2) adsorption: keeping at an adequate temperature until saturation of $NH_3$ or $CO_2$ adsorption occurs,
(3) desorption: heating at a constant rate.

The number of acid sites was obtained by integrating the $NH_3$ concentration for the desorption process. For the number of base sites, $CO_2$ was used, and the value was obtained by a procedure similar to that used for the acid sites. The reaction product formed on the $\gamma$-alumina surface as a result of the PAC experiment was characterized by FT-IR analysis. The IR spectra were recorded on a Nicolet Magna 760FT-IR equipped with a Nicplan IR microscope.

For the PAC system utilizing the temperature transition of the automobile exhaust, a combination

**Table 3** Experimental condition of catalyst research for PAC.

| | | |
|---|---|---|
| Inlet gas | NO | 200 ppm |
| | $O_2$ | 10 % |
| | $C_3H_6$ | 3,000 ppmC |
| | $CO_2$ | 4 % |
| | $H_2O$ | 2 % |
| | $N_2$ | Balance |
| Catalyst | Pellet | |
| Flow rate | 2 L/min | |
| Space velocity | 60, 000 $h^{-1}$ | |
| Temperature | 673-423 K, decreasing, 30 K/min | |
| | 773-373 K, decreasing, 24, 10 K/min | |
| | 673, 573 K, fixed | |
| Voltage (Specific energy) | 12.5 kV (30 J/L) | |

**Table 4** Conditions of TPD measurements.

| | $NH_3$ TPD | $CO_2$ TPD |
|---|---|---|
| Catalyst | 2.3 g | 1 g |
| Pretreatment | $N_2$, 3.5 L/min, 873 K, 15min | He, 3 L/min, 873 K, 15 min |
| Adsorption | $NH_3$ 300 ppm - $N_2$, 3.5 L/min, 373 K, 60 min | $CO_2$ 1 % - He, 3 L/min, 373 K, 10 min |
| Desorption | $N_2$, 3.5 L/min, 373-873 K, increasing, 10 K/min | He, 3 L/min, 373-873 K, increasing, 10 K/min |

of catalysts with different temperature windows (3-stage catalyst)was studied. **Figure 4** shows the experimental device used. The catalysts and the plasma reactor were set in a quartz tube (17 mm I.D.). The catalysts were set in the order Na/ZSM-5, In/alumina and Pt/alumina in the downstream direction. A furnace controlled the temperature of the feed gas and the catalyst. The experimental conditions are shown in **Table 5**. The temperature was varied according to the profile shown in **Fig. 5**. In the beginning, the temperature was increased to 773 K and held constant for 10 min to clean the experimental device and the catalysts. Then the temperature was decreased at a rate of 40 K/min to 423 K and kept there for 1 min. After that, the temperature was increased at a rate of 40 K/min to 673 K. The temperature profile simulated that of the diesel engine exhaust in the Japanese 10-15 mode. However, the temperature ramp rate in a real engine exhaust is higher than that in the present experiment. The fastest possible temperature ramp rate achievable by the present setup was used. NOx conversion was measured from 673 K down to 423 K, and from 423 K back up to 673 K, including a temperature hold at 423 K.

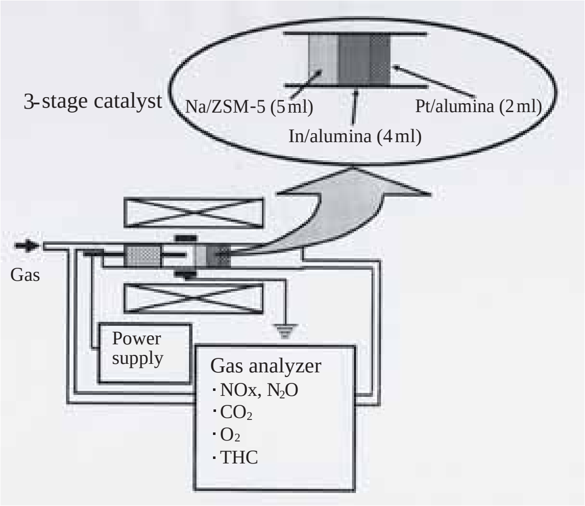


**Fig. 4** Experimental setup for studying the 3-stage catalyst with PAC.

**Table 5** The experimental condition for studying the multi catalysts with PAC.

| | | |
|---|---|---|
| Inlet Gas | NO | 200 ppm |
| | $O_2$ | 10 % |
| | $C_3H_6$ | 3,000 ppmC |
| | $CO_2$ | 6.7 % |
| | $H_2O$ | 5 % |
| | $N_2$ | Balance |
| Flow rate | 5 L/min | |
| Space velocity at catalyst | 30,000 $h^{-1}$ | |
| Temperature | 423 -773 K | |
| Voltage (Specific energy) | 14.5 kV (16 J/L) | |

## 3. Results and discussions

### 3. 1 Effects of PAC

In this study, which focuses on the effects of PAC under oxidizing conditions, the effect of the plasma on NOx, HC and the affected gas composition reacting with $\gamma$-alumina were investigated as a function of the temperature and position of reactor and catalysts for automotive exhaust aftertreatment.

Temperature dependence of the conversions of NO into $NO_2$ and the conversions of HC with and without the non-thermal plasma are shown in **Fig. 6**. Here, the non-thermal plasma showed a high NO conversion to $NO_2$, especially below 573 K. On the other hand, the Pt/alumina catalyst showed a high NO conversion to $NO_2$ only above 473 K. Above 573 K, the NO conversions for both the plasma and the Pt/alumina approached the thermal equilibrium value. Similar phenomena have been reported by other researchers.[13-22] In this reaction system, when HC was added to the oxidizing gas containing NO, the oxidation of NO to $NO_2$ was significantly enhanced and NO conversion with HC was three

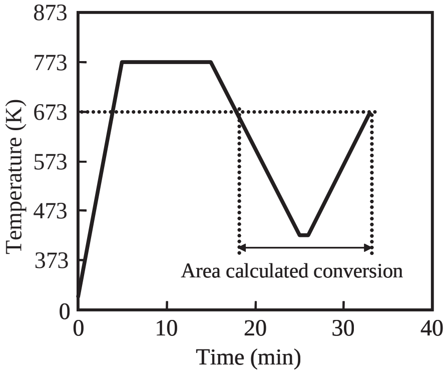


**Fig. 5** Temperature profile versus time for studying the multi catalysts with PAC.

times higher than that without HC at 673 K. This is consistent with the chemical kinetics model of Penetrante et al., which suggested that NO oxidation occurs with the non-thermal plasma containing HC through the following process:

(1) high energy electrons in the discharging non-thermal plasma generate O radicals,
(2) HC + O radicals → $HO_2$ radicals,
(3) NO + $HO_2$ radicals → $NO_2$ + OH radicals and HC suppresses the reduction of $NO_2$ back to NO by O radicals and further oxidation of $NO_2$ to nitric acid by the OH radicals by consuming these excess radicals.[14)]

When PAC is used in an automobile, the positions of the plasma reactor and the catalyst are important factors. The effect of the distance between the plasma reactor and the catalyst reactor on NOx conversion was studied. **Figure 7** illustrates the effect of the distance between the plasma reactor and the catalyst reactor on NOx conversion. According to Fig. 7, NOx conversion was not affected by the distance. It took about 10 s for the gas to pass through the 7-m-long tube. If the radical compositions generated by the plasma affected NOx conversion, the distance between the plasma reactor and the catalyst reactor would affect NOx conversion because the lifetime of the radical compositions are generally extremely short compared with the time it takes the gas to cover the distance between the reactors. On the basis of these results, the compositions that affect NOx conversion are thought to be stable, and those lifetimes were long. As far as the compositions generated by the plasma, the distance between the plasma reactor and the catalyst reactor was not an important factor.

In order to determine the dominant gas component for NOx reduction with PAC, the NOx conversion on $\gamma$-alumina was measured when the plasma was applied to NO and HC separately. **Figure 8** shows the NOx and HC conversion when the plasma was applied to HC only (HC-plasma), NO only (NO-plasma) and both HC and NO (HC/NOx-plasma). According to the figure, the conversions of HC-

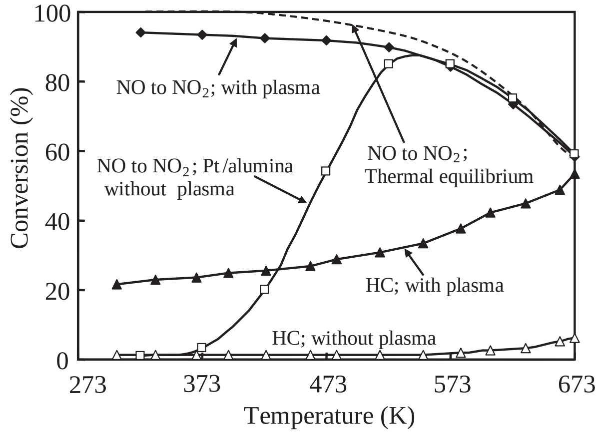


**Fig. 6** Temperature dependence of the conversions of NO into $NO_2$ and the conversions of HC with and without non-thermal plasma. The inlet gas without HC was used for Pt-alumina.

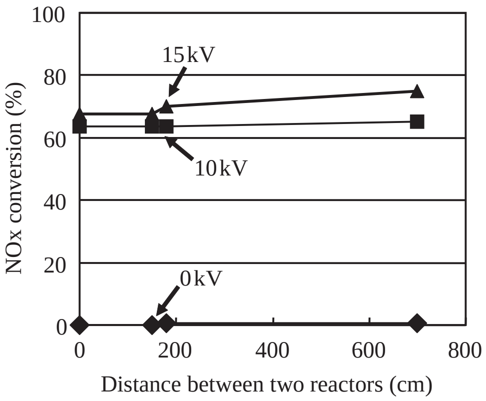


**Fig. 7** The effect on the distance between the plasma reactor and the catalyst reactor ( $\gamma$-alumina with PAC, 673 K, steady state).

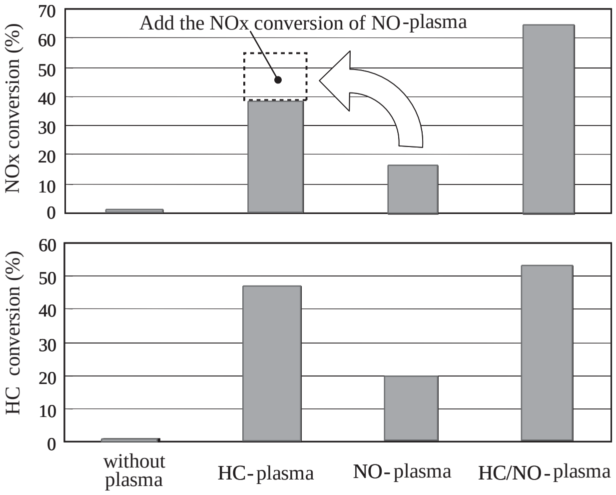
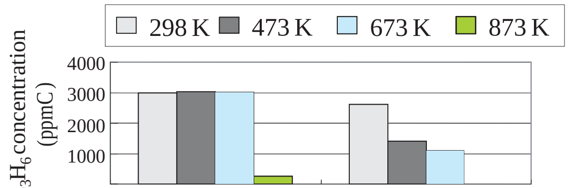


**Fig. 8** NOx and HC conversion when the plasma affect the NOx and the HC respectively ( $\gamma$-alumina with PAC, 673 K, steady state).

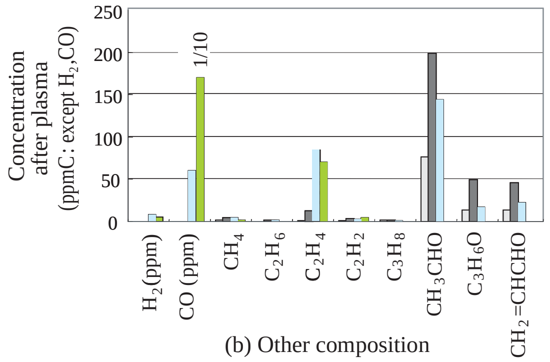
plasma were higher than those of NO-plasma. It is reported that HC was partially oxidized by the plasma and the products of partial oxidation, in particular $CH_3CHO$, strongly influenced the NO reduction.[13, 15, 17, 19] In the case of NO-plasma, NO was converted into $NO_2$ and the $NO_2$ was reduced by $C_3H_6$ on $\gamma$-alumina. However, the effect of $NO_2$ was weaker than that of the partially oxidized HC. Furthermore, NOx conversion in the case of the plasma affecting both NO and HC (HC/NO-plasma) was higher than the sum of the NOx conversion in HC-plasma and that in NO-plasma (see dot level in Fig. 8). There is a multiplier effect for NOx reduction. These results suggest that the partially oxidized HC must have been dominant in increasing NOx conversion on $\gamma$-alumina with PAC and the NOx conversion was higher due to the multiplier effect when the plasma affected HC and NOx simultaneously.

To study the gas component change in detail, GC and GC/MS analysis were performed. **Figure 9** shows the gas analysis results downstream of the plasma reactor. Figure 9(a) shows the change in $C_3H_6$ and Fig. 9(b) shows the change in other components. According to Fig. 9(a), $C_3H_6$ was decomposed by the plasma even at 298 K. Figure 9(b) shows that the main product of plasma-assisted decomposition of $C_3H_6$ at 298 K was $CH_3CHO$. At 673 K, the $C_3H_6$ decomposition produced not only $CH_3CHO$ but also $C_2H_4$ and CO. While $CO_2$ is also expected to be generated from $C_3H_6$, this could not be checked due to the presence of $CO_2$ in the initial mixture. At 873 K, $C_3H_6$ decomposition produced CO (and perhaps undetected $CO_2$, see above). $CH_3CHO$ was not observed at 873 K. From these results, we can conclude that $C_3H_6$ decomposition produced partially oxidized HC from 298 to 673 K; at 873 K, the main decomposition products were CO and $CO_2$. For $\gamma$-alumina with PAC at fixed temperature, NOx conversion at 673 K was larger than that at 423 and 873 K. **Figure 10** shows the change in gas composition through $\gamma$-alumina with PAC at 673 K. According to this figure, $CH_3CHO$ and $C_3H_6$ decreased, while CO, $H_2$ and $C_2H_4$ increased. It is known that $CH_3CHO$ can reduce NOx on $\gamma$-alumina.[15, 17] Thus, the generated $CH_3CHO$ is expected to reduce the NOx.

On the basis of these results, the effects of PAC in NOx reduction with $\gamma$-alumina can be summarized as follows. Below 673 K with plasma-assist, $C_3H_6$ is converted into $CH_3CHO$, and NO is converted into $NO_2$. These components are stable so that NOx conversion is not affected by the distance between the plasma reactor and the catalyst. Furthermore, the amount of $CH_3CHO$ produced strongly influenced NOx conversion on the $\gamma$-alumina catalyst. A larger amount of $CH_3CHO$ produced by HC-plasma would be more effective for higher NOx conversion compared to $NO_2$ by NO-plasma.



(a) $C_3H_6$



(b) Other composition

**Fig. 9** Gas analysis results downstream of the plasma reactor.

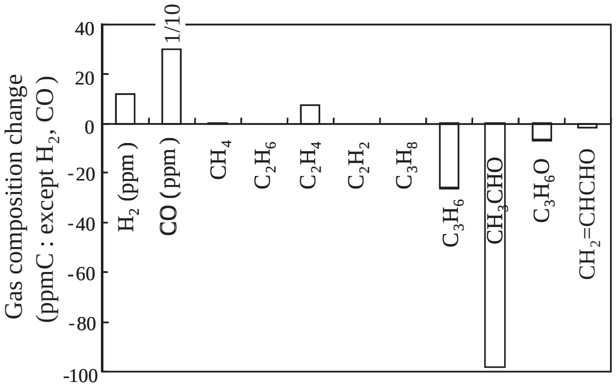


**Fig. 10** Gas composition change between the upstream of catalyst and the downstream ($\gamma$-alumina with PAC, 673 K, steady state).

### 3. 2 Appropriate catalysts for PAC

Several catalysts have been reported to show high NOx reduction activity with PAC under oxidizing conditions. However, the details of the differences between the catalysts and the relationship between the catalyst properties and the NOx reduction activity have remained unclear. Thus, the present study seeks appropriate catalysts and investigates their NOx reduction properties with PAC.

$\gamma$-alumina and zeolites loaded with alkali or alkaline earth metals were selected and compared with Pt-loaded catalysts$^{1-3)}$ and Cu-zeolite,$^{4, 5)}$ which have been proposed as HC-SCR catalysts under oxidizing conditions. Average NOx conversions of the catalysts from 673 to 423 K with and without PAC are shown in **Fig. 11**. As shown in Fig. 11, ZSM-5 catalysts loaded with alkali or alkaline earth metals (Li, Na, K, Mg, Ca, Ba and Sr) showed higher NOx conversions than those of Pt/alumina and Cu-ZSM-5 with PAC. Difference in NOx conversions for loaded elements was within 15 %, and $\gamma$-alumina and these zeolites hardly showed NOx reduction activity without PAC. H-ZSM-5 showed low NOx conversion (less than 10 %, does not show in Fig. 11) with and without PAC. On the other hand, Cu-ZSM-5 and Pt/alumina showed slightly lower NOx conversion than that without PAC. Among these catalysts, $\gamma$-alumina showed the highest NOx conversion with PAC.

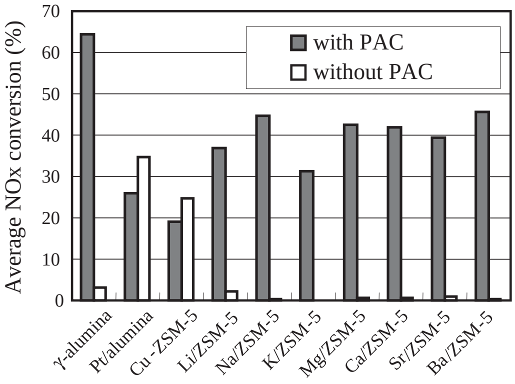


**Fig. 11** Average NOx conversions of the catalysts from 673 to 423 K with and without PAC (decreasing temperature, 30 K/min).

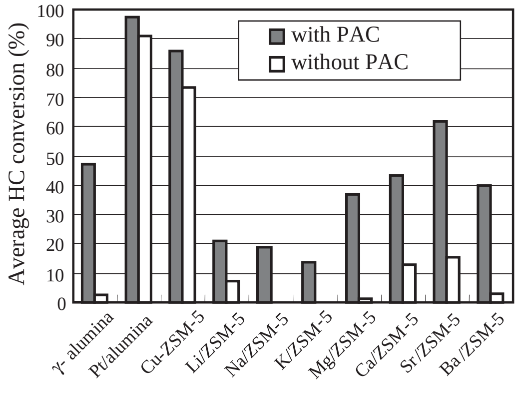


**Fig. 12** Average HC conversions of the catalysts from 673 to 423 K with and without PAC (decreasing temperature, 30 K/min).

Average HC conversions of the catalysts with and without PAC are shown in **Fig. 12**. As shown in Fig. 12, the HC conversions on $\gamma$-alumina and zeolites were significantly increased by PAC. By contrast, Pt/alumina and Cu-ZSM-5 showed only a slight increase by PAC and higher HC conversions compared to $\gamma$-alumina and zeolites. It was established in the previous section that partially oxidized HCs from $C_3H_6$ and $NO_2$ produced by the non-thermal plasma played an important role in HC-SCR. This suggested that PAC enhanced the rate-determining step on alumina or zeolite catalysts. In contrast, high oxidation activity of HC for Cu-ZSM-5 and Pt/alumina could promote the HC-SCR reaction without PAC and lead to ineffective PAC for these catalysts.

NOx conversions of several alumina catalysts with PAC are shown in **Fig. 13**. The order of the NOx reduction activities was as follows: $\gamma$-alumina > 5% La-alumina > 2.5% La-alumina > $\alpha$-alumina. Here,

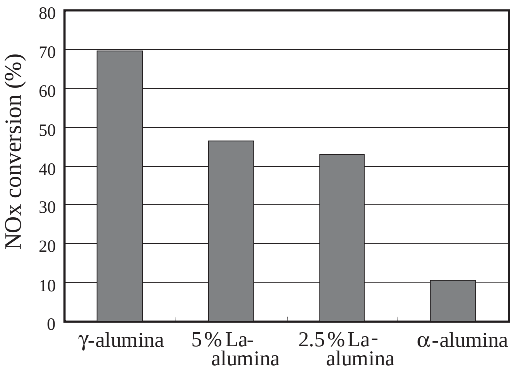


**Fig. 13** NOx conversions of several alumina catalysts with PAC (673 K, steady state).

the NOx reduction activities with PAC were strongly influenced by the type of alumina catalyst. This also suggests that La-doping inhibits the NOx reduction activity of $\gamma$-alumina catalyst with PAC. In order to determine the relationship between the NOx reduction activity of the alumina catalysts with PAC and their properties, the NOx conversion was plotted as a function of SSA, adsorption amount of $NH_3$, and adsorption amount of $CO_2$. The results are shown in **Fig. 14**, in which the catalyst properties are normalized with respect to the maximum value. Actual and the normalized values of the catalyst properties are also shown in **Table 6**. As shown in Fig. 14, the order of the NOx conversion did not correspond to the order of the SSA or the amount of $CO_2$ adsorption. On the other hand, the NOx conversion of the alumina catalysts was in proportion to the adsorption amount of $NH_3$, that is, the amount of acid on the alumina. These results support the idea that the solid acid on the alumina acts as active sites for NOx reduction. Ingelsten et al. reported that the NOx reduction activity of alumina, silica, and alumina-silica clearly correlate with the Brϕnsted acid site density and that the NOx reduction for alumina occurred via the following steps: (1) $NO_2$ and partially oxidized HC formed isocyanate on the Brϕnsted acid sites of the alumina, and (2) isocyanate decomposed into $N_2$, $CO_2$ and $H_2O$.[24] On the other hand, Burch et al. reported that the adsorption amount of both $NO_2$ and partially oxidized HCs increased relative to that of NO and HCs and that the formation of $NO_2$ and the partial oxidation of HC were the rate-determining reaction steps of the NOx reduction for alumina.[25] In summary, it is believed that the active sites of NOx reduction of alumina with PAC are the acid sites on the alumina and that a high NOx reduction activity is obtained due to the following reasons: (1) partially oxidized HCs, particularly $CH_3CHO$ from $C_3H_6$ and $NO_2$, form the compounds on the acid sites of the alumina and promote the adsorption of the alumina, (2) the non-thermal plasma promotes the slow reaction step of the alumina for the formation of $NO_2$ and partially oxidized HCs.

In order to elucidate the performance of $\gamma$-alumina with PAC, temperature dependence of the NOx conversion was measured for different cooling rates. Using the lower rate, NOx conversion approaches that of the steady-state temperature condition and is strongly influenced by reactant formation on the catalyst surfaces. The results are shown in **Fig. 15**.

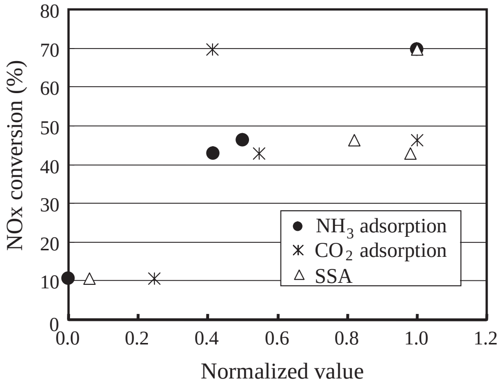


**Fig. 14** Relationship between the NOx conversion of alumina catalysts with PAC (673 K, steady state) and their properties.

**Table 6** Actual and the normalized values of alumina catalysts properties and NOx conversion with PAC.

| Catalyst | NOx conversion (%) | $NH_3$ adsorption |  | $CO_2$ adsorption |  | SSA |  |
|---|---|---|---|---|---|---|---|
|  |  | ( μmol/g) | Normalized value | ( μmol/g) | Normalized value | ($m^2$/ g) | Normalized value |
| γ-alumina | 69.5 | 488.3 | 1 | 55.0 | 0.414 | 162 | 1 |
| 5% La-alumina | 46.4 | 244.9 | 0.502 | 132.8 | 1 | 133 | 0.821 |
| 2.5% La-alumina | 42.9 | 202.6 | 0.415 | 72.8 | 0.548 | 159 | 0.981 |
| α-alumina | 10.6 | 0 | 0 | 32.5 | 0.245 | 9.5 | 0.059 |

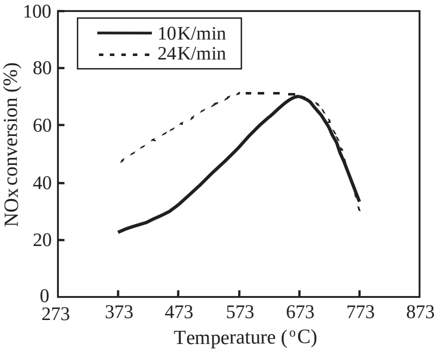


**Fig. 15** Temperature dependence of the NOx conversion for $\gamma$-alumina with PAC in different cooling temperature rates.

As shown in the figure, NOx conversion for the rate of 24 K/min was about 70 % as the maximum conversion value at about 673 K and gradually decreased below 573 K. The maximum NOx conversion for 10 K/min was the same as that for 24 K/min, and was independent of the rate. However, the NOx conversion for 10 K/min rapidly decreased below 673 K. Thus, the NOx reduction activity of $\gamma$-alumina with PAC below 673 K decreased for the higher rate. After the measurement, the color of $\gamma$-alumina changed from white to brownish yellow. The NOx reduction activity of $\gamma$-alumina with PAC and the color of the catalyst was recovered by calcination in air. Furthermore, to investigate the steady-state NOx reduction performance of $\gamma$-alumina with PAC below the temperature of maximum NOx conversion, the NOx conversion was measured as a function of time at a fixed temperature of 573 K. The results are shown in **Fig. 16**. The NOx conversion decreased from 67 % at the outset to 38 % 30 min later. FT-IR analysis was performed to characterize the surface of the alumina catalyst. **Figure 17** shows FT-IR spectra of $\gamma$-alumina with PAC and fresh catalyst and the differential spectrum of the two curves. Alkyl groups (R-) and the R-$NO_2$ structure were observed in the differential spectrum in Fig. 17. These results suggest that nitro-alkyl compounds were formed on the catalyst surface by reactants from the non-thermal plasma and that these decreased the NOx conversion for $\gamma$-alumina with PAC below 673 K.

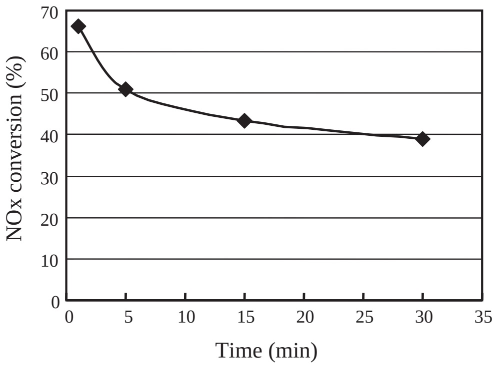


**Fig. 16** NOx conversion as a function of time for $\gamma$-alumina with PAC at fixed temperature of 573 K.

By suppressing the formation of the deposited materials, we investigated the loading effect of the elements that promote oxidation. It is reported that Ag, Ga and In are active elements for HC-SCR(8-12) and that loading of alumina with Ag and In is also effective in PAC.(22) Thus, we investigated the loading effect of these elements on the steady-state NOx reduction activity of $\gamma$-alumina with PAC at 573 K. **Figure 18** shows the NOx conversions of $\gamma$-alumina, Ag/alumina, Ga/alumina and In/alumina catalysts with PAC at a fixed temperature of 573 K. Here, In/alumina showed the highest NOx conversion during the first 30 min of conversion. It

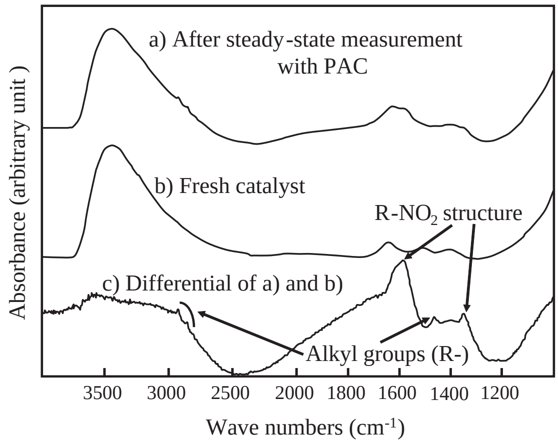


**Fig. 17** FT-IR spectra of $\gamma$-alumina with PAC (573K, steady state) and fresh catalyst.

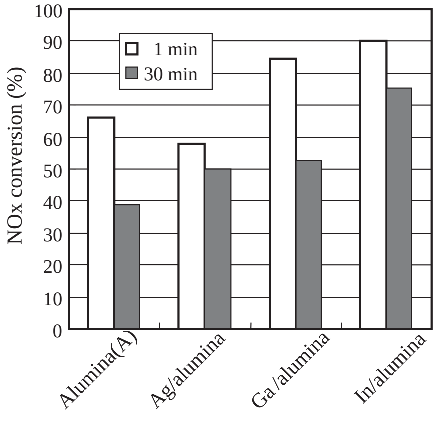


**Fig. 18** NOx conversions of $\gamma$-alumina, Ag/alumina, Ga/alumina and In/alumina catalysts with PAC at fixed temperature of 573 K.

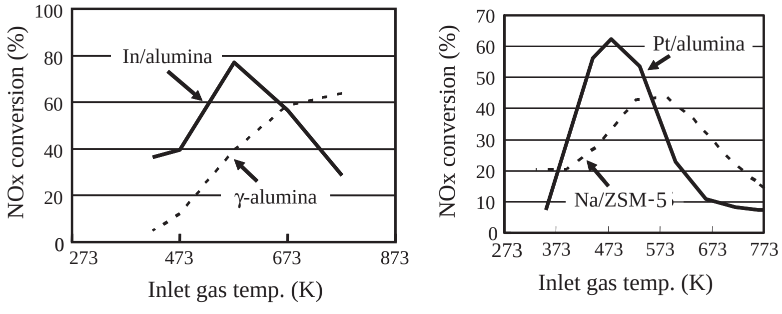
is demonstrated that In-loading is effective in improving NOx reduction activity and suppressing the degradation of $\gamma$-alumina with PAC under steady-state temperature conditions. Upon In-loading of $\gamma$-alumina, an increase in HC conversion (about 10 %) was observed. This might promote the oxidation or decomposition of the deposits and improve the NOx reduction activity of the In-loaded $\gamma$-alumina catalyst with PAC under steady-state temperature conditions. Thus, In-loaded alumina with a large amount of solid acid has been proposed as the most suitable catalyst for PAC.

### 3. 3 Three-stage catalyst with PAC under transient temperature conditions

The exhaust temperature of an automobile diesel engine generally changes from 423 to 673 K in the Japanese 10-15 mode. However, there has not been a single catalyst covering the entire range of the exhaust temperature. To achieve that, we used a 3-stage catalyst with different temperature windows. A similar study has already been reported.13) However, we used the newly discovered catalyst In/alumina. Furthermore, the more rapid temperature change used in our experiments was closer to real exhaust conditions.

**Figure 19** shows the NOx conversion on $\gamma$-alumina, In/alumina, Na/ZSM-5 and Pt/alumina with PAC under steady-state temperature conditions. Figure 19 shows that the maximum NOx conversion on $\gamma$-alumina occurred at a temperature above 673 K, which was higher than the exhaust temperature range of Japanese 10-15 mode. On the other hand, the maximum NOx conversion on In/alumina occurred at about 573 K and its temperature window covered almost the entire exhaust temperature range of Japanese 10-15 mode. NOx could be reduced by Pt/alumina from 423 to 573 K, and by In/alumina and Na/ZSM-5 from 473 to 673 K. Moreover, Na/ZSM-5 was capable of adsorption of HC and $NO_2$ at 473 K,18) and Pt/alumina can be used for oxidizing HC and CO. Thus, In/alumina, Na/ZSM-5 and Pt/alumina were chosen to achieve the wide temperature window.

For this purpose, the catalysts were set in order Na/ZSM-5, In/alumina and Pt/alumina in the downstream direction. Because Na/ZSM-5 releases the adsorbed NOx and HC at higher temperature, NOx was reduced by In/alumina in the middle region and HC and CO were oxidized by Pt/alumina further downstream. **Figure 20** shows the NOx and HC conversion of the 3-stage catalyst with PAC under transient temperature conditions. As can be seen in this figure, high NOx conversion was achieved by this system over a wide temperature range. NOx conversion was higher during cooling than during heating. This is presumably the result of NOx and HC adsorption on the catalysts. During the temperature decrease, there were two peaks on the NOx conversion curve. The first peak was attributed to the NOx reduction by In/alumina and Na/ZSM-5, which was consistent with the peak temperature of the NOx conversion of these catalysts (see Fig. 20).



(a) γ-alumina and In/alumina (b) Na/ZSM-5 and Pt/alumina

**Fig. 19** NOx conversion of $\gamma$-alumina, In/alumina, Na/ZSM-5 and Pt/alumina with PAC under steady state temperature condition.

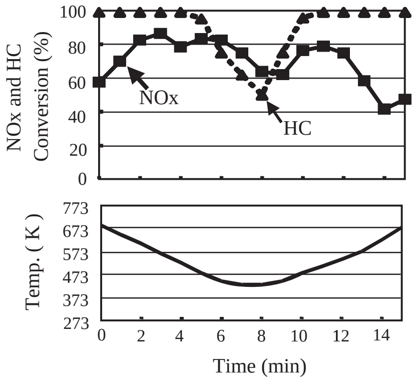


**Fig. 20** NOx and HC conversion of 3-stage catalyst with PAC under transient temperature conditions.

On the other hand, NOx conversion during the temperature increase was presumably lowered by the desorbed NOx. High HC conversion was also achieved except below 473 K. CO emission was less than 5 ppm (not shown in the figure). Thus, this 3-stage catalyst with PAC was found to be effective for an automotive aftertreatment system under oxidizing conditions over a wide temperature range under transient conditions.

## 4. Conclusions

We have studied the application of PAC to NOx reduction under oxidizing conditions. The results obtained can be summarized as follows:

(1) The gas analysis revealed that PAC used $\gamma$-alumina and $C_3H_6$ as a reductant, and the $NO_2$ and $CH_3CHO$ that were generated by the plasma reduced NOx on $\gamma$-alumina.

(2) The distance between the plasma reactor and the $\gamma$-alumina reactor had no effect on NOx conversion.

(3) As $CH_3CHO$ and $NO_2$ are generated from $C_3H_6$ and NO by the plasma, the influence of $CH_3CHO$ on the NOx conversion of $\gamma$-alumina with PAC was stronger than that of $NO_2$.

(4) The NOx reduction activities of $\gamma$-alumina and zeolites loaded with alkali or alkaline earth metals were significantly improved by PAC. By contrast, the activities on Cu-ZSM-5 and the Pt-loaded catalyst were not affected by PAC. Among these catalysts, $\gamma$-alumina with a large amount of solid acid showed the highest NOx conversion.

(5) The steady-state measurements with PAC at low temperature (573 K) revealed that the NOx conversion of $\gamma$-alumina decreased with PAC as a function of time. In-loading on $\gamma$-alumina improved the NOx reduction activity and suppressed the degradation of the activity under steady-state temperature conditions.

(6) A 3-stage catalyst with PAC for automotive exhaust aftertreatment is proposed. By using the combination of alkaline loading ZSM-5, In/$\gamma$-alumina and a precious metal catalyst, a wide temperature window and high NOx, HC and CO conversions were obtained under transient temperature conditions.

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