

Research
Report

NOx Reduction under Oxidizing Conditions by Plasma-assisted Catalysis

Yoshihiko Itoh, Matsuei Ueda, Hirofumi Shinjoh, Kiyomi Nakakita,
Miyao Arakawaプラズマアシスト触媒による酸素過剰雰囲気下でのNO_x浄化

伊藤由彦, 上田松栄, 新庄博文, 中北清己, 荒川宮男

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 NO_x 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 NO_x reduction were measured. Then, an appropriate catalyst for PAC was developed; the catalyst properties dominating NO_x reduction and improvement of the NO_x 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

NO_x reduction, was developed. The following results were obtained:

(1) NO₂ and CH₃CHO generated by the plasma resulted in significant reduction of NO_x on γ -alumina.

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

(3) A high NO_x 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, NO_x reduction, Hydrocarbon, Aftertreatment, Oxidizing condition, Diesel engine, Lean-burn gasoline engine

要 旨

ディーゼルエンジンおよびリーンバーンガソリンエンジンの排気後処理における、プラズマアシスト触媒(PAC)システムの可能性を調査するため、炭化水素によるNO_x選択還元型触媒を用いたPACに関して、酸化雰囲気模擬排ガスでの検討を行った。まず、非熱プラズマの効果として、ガス組成、NO_x還元触媒への効果およびプラズマ反応器と触媒反応器の距離の効果を調べた。次に、PACに適した触媒として、NO_x還元の支配する触媒特性と添加元素による活性向上について検討した。最終的に、これらの結果に基づき、3段階触媒としてNO_x浄化の温度ウインドウが異なる触媒

の組み合わせを検討した。その結果、以下に示す結論が得られた。

(1) プラズマによりNO₂とCH₃CHOが生成し、 γ -アルミナ上でNO_x還元活性が大幅に向上した。

(2) 酸量の多い γ -アルミナは高いNO_x浄化率を示し、さらにInを添加することによりNO_x浄化活性は向上し、定常温度条件での活性低下が抑制された。

(3) 3段階触媒を用いたPACにより、実際のエンジン運転条件を模擬した過渡温度条件下で、NO_xのみでなく、HCおよびCOに関しても高い浄化率が得られた。

キーワード

非熱プラズマ, 触媒, NO_x浄化, 炭化水素, 後処理, 酸素過剰雰囲気, ディーゼルエンジン, リーンバーンガソリンエンジン

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 NO_x 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 NO_x reduction performance of these catalysts has been insufficient. Recently, systems that perform NO_x 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 NO_x 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 NO_x conversion, the difference of NO_x 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 NO_x conversion for PAC was surveyed. We then focused on γ -alumina, and investigated the catalyst properties dominating NO_x

reduction and attempted to improve the NO_x 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

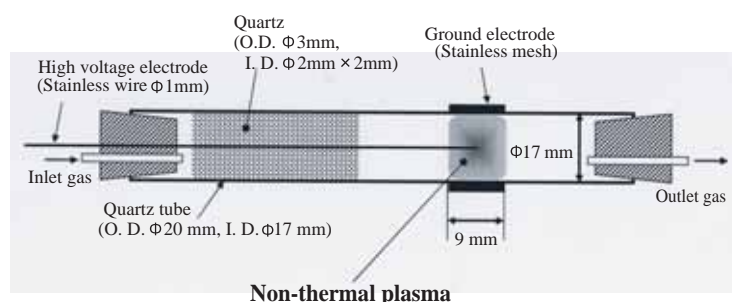


Fig. 1 Plasma reactor.

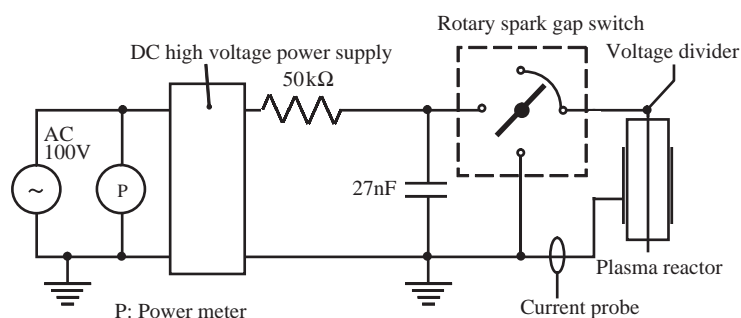


Fig. 2 Pulsed high voltage power supply.

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)**. γ -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 m²/g. α -alumina with a SSA of 9.5 m²/g was obtained by calcinating γ -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 γ -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 Ga₂O₃, 20 wt% for In₂O₃.

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 washcoat²³⁾ with γ -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)
γ -alumina	γ -alumina	162
5% La-alumina	γ -alumina with La: 5mol%	159
2.5% La-alumina	γ -alumina with La: 2.5mol%	133
α -alumina	α -alumina	9.5

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

Catalyst	Components
Cu-ZSM-5	CuO : 3.18wt%, SiO ₂ /Al ₂ O 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- γ -alumina
Ag/alumina	AgO: 10wt%, γ -alumina
Ga/alumina	Ga ₂ O ₃ : 10wt%, γ -alumina
In/alumina	In ₂ O ₃ : 20wt%, γ -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 (NO_x). 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 $23,000 \text{ h}^{-1}$. 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 NO_x conversion on γ -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 from the inlet of

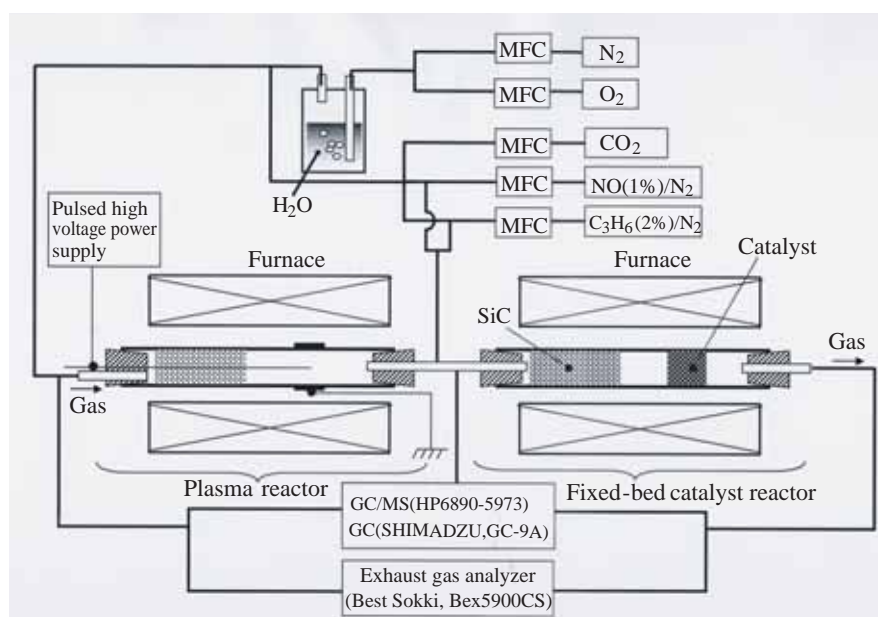


Fig. 3 Experimental apparatus used for the effects of PAC.

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	$23,000 \text{ h}^{-1}$	
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 ₃ H ₆ : 3,000 ppmC		NO : 200 ppm
NO-plasma	NO : 200 ppm		C ₃ H ₆ : 3,000 ppmC
HC/NO-plasma	C ₃ H ₆ : 3,000 ppmC NO : 200 ppm		
Base Inlet Gas (Inlet of plasma)	O ₂	10 %	
	CO ₂	4 %	
	H ₂ O	2 %	
	N ₂	Balance	
Catalyst	γ-alumina, honeycomb		
Flow rate	2L/min		
Space velocity	23,000h ⁻¹		
Temperature	673 K		
Voltage (Specific energy)	12.5 kV (30J/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. NO_x 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 NO_x and HC conversions from 673 to 423 K were evaluated for catalytic performance. NO_x 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 NO_x reduction on alumina with PAC, the amount of acid and base on the alumina catalyst was measured by CO₂ and NH₃ 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 ₃ H ₆	3,000 ppmC
	CO ₂	4 %
	H ₂ O	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 NH₃ or CO₂ adsorption occurs,
- (3) desorption: heating at a constant rate.

The number of acid sites was obtained by integrating the NH₃ concentration for the desorption process. For the number of base sites, CO₂ was used, and the value was obtained by a procedure similar to that used for the acid sites. The reaction product formed on the γ -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 ₃ H ₆	3,000 ppmC
	CO ₂	4 %
	H ₂ O	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, 15 min	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

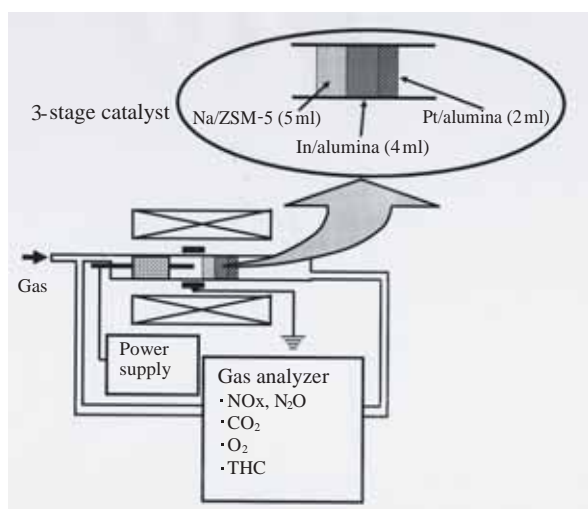


Fig. 4 Experimental setup for studying the 3-stage catalyst with PAC.

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

Inlet Gas	NO	200 ppm
	O ₂	10 %
	C ₃ H ₆	3,000 ppmC
	CO ₂	6.7 %
	H ₂ O	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)	

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. NO_x 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.

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 NO_x, HC and the affected gas composition reacting with γ -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 NO₂ 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 NO₂, especially below 573 K. On the other hand, the Pt/alumina catalyst showed a high NO conversion to NO₂ 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 NO₂ was significantly enhanced and NO conversion with HC was three

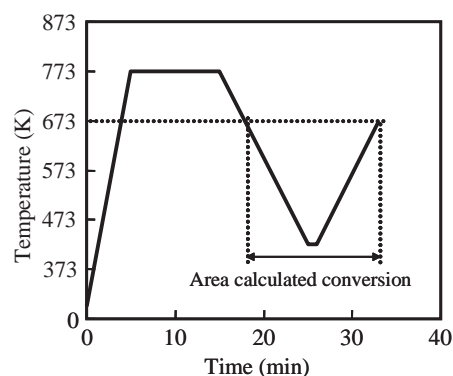


Fig. 5 Temperature profile versus time for studying the multi catalysts with PAC.

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) $\text{HC} + \text{O radicals} \rightarrow \text{HO}_2 \text{ radicals}$,
- (3) $\text{NO} + \text{HO}_2 \text{ radicals} \rightarrow \text{NO}_2 + \text{OH radicals}$ 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

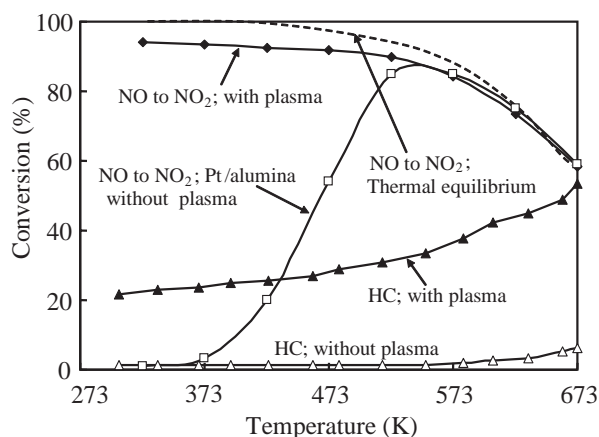


Fig. 6 Temperature dependence of the conversions of NO into NO_2 and the conversions of HC with and without non-thermal plasma. The inlet gas without HC was used for Pt-alumina.

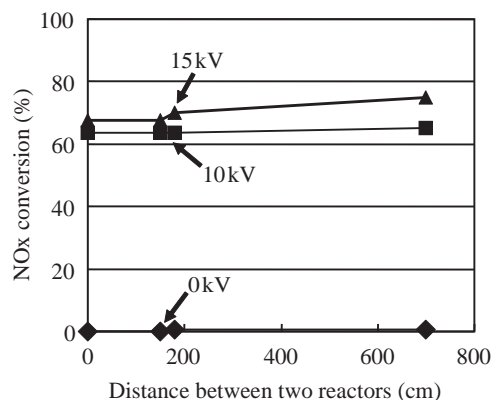


Fig. 7 The effect on the distance between the plasma reactor and the catalyst reactor (γ -alumina with PAC, 673 K, steady state).

of the plasma reactor and the catalyst are important factors. The effect of the distance between the plasma reactor and the catalyst reactor on NO_x conversion was studied. **Figure 7** illustrates the effect of the distance between the plasma reactor and the catalyst reactor on NO_x conversion. According to Fig. 7, NO_x 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 NO_x conversion, the distance between the plasma reactor and the catalyst reactor would affect NO_x 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 NO_x 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 NO_x reduction with PAC, the NO_x conversion on γ -alumina was measured when the plasma was applied to NO and HC separately. **Figure 8** shows the NO_x and HC conversion when the plasma was applied to HC only (HC-plasma), NO only (NO-plasma) and both HC and NO (HC/NO-plasma). According to the figure, the conversions of HC-

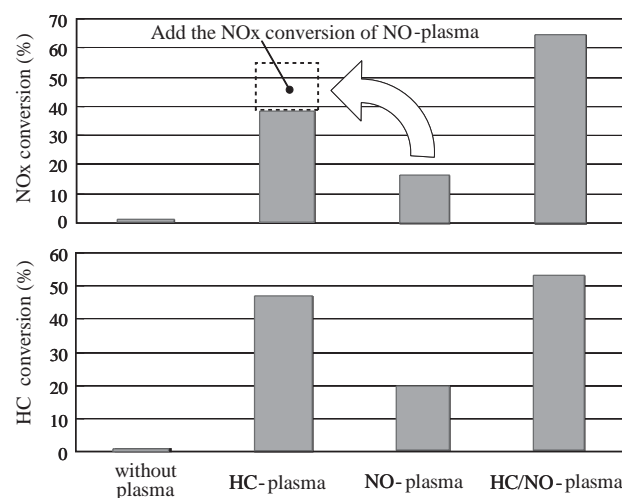


Fig. 8 NO_x and HC conversion when the plasma affect the NO_x and the HC respectively (γ -alumina with PAC, 673 K, steady state).

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 γ -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 γ -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

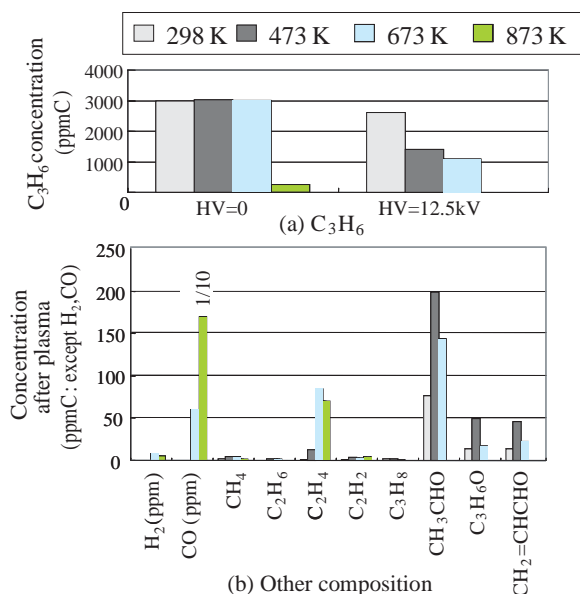


Fig. 9 Gas analysis results downstream of the plasma reactor.

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 γ -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 γ -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 γ -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 γ -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 γ -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.

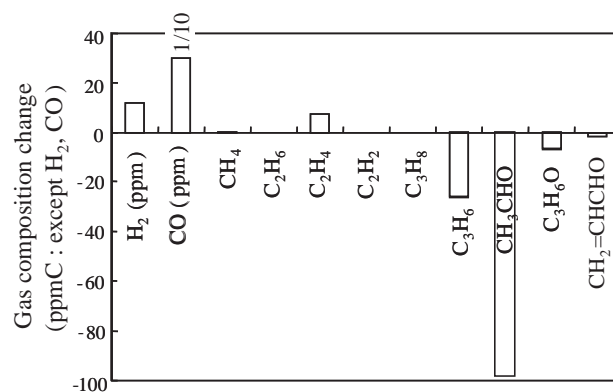


Fig. 10 Gas composition change between the upstream of catalyst and the downstream (γ -alumina with PAC, 673 K, steady state).

3.2 Appropriate catalysts for PAC

Several catalysts have been reported to show high NO_x 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 NO_x reduction activity have remained unclear. Thus, the present study seeks appropriate catalysts and investigates their NO_x reduction properties with PAC.

γ -alumina and zeolites loaded with alkali or alkaline earth metals were selected and compared with Pt-loaded catalysts¹⁻³⁾ and Cu-zeolite,^{4, 5)} which have been proposed as HC-SCR catalysts under oxidizing conditions. Average NO_x conversions of the catalysts from 673 to 423 K with and without PAC are shown in Fig. 11. As shown in Fig. 11,

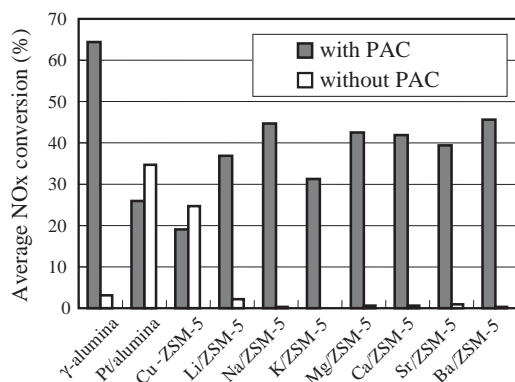


Fig. 11 Average NO_x conversions of the catalysts from 673 to 423 K with and without PAC (decreasing temperature, 30 K/min).

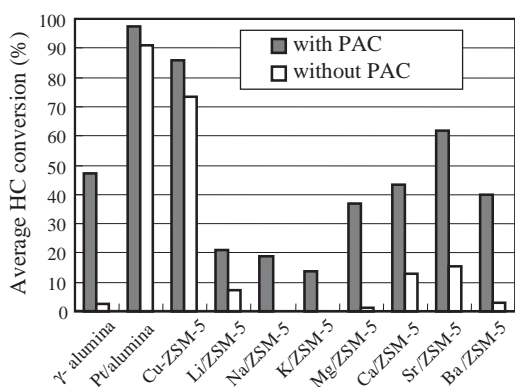


Fig. 12 Average HC conversions of the catalysts from 673 to 423 K with and without PAC (decreasing temperature, 30 K/min).

ZSM-5 catalysts loaded with alkali or alkaline earth metals (Li, Na, K, Mg, Ca, Ba and Sr) showed higher NO_x conversions than those of Pt/alumina and Cu-ZSM-5 with PAC. Difference in NO_x conversions for loaded elements was within 15 %, and γ -alumina and these zeolites hardly showed NO_x reduction activity without PAC. H-ZSM-5 showed low NO_x 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 NO_x conversion than that without PAC. Among these catalysts, γ -alumina showed the highest NO_x conversion with PAC.

Average HC conversions of the catalysts with and without PAC are shown in Fig. 12. As shown in Fig. 12, the HC conversions on γ -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 γ -alumina and zeolites. It was established in the previous section that partially oxidized HCs from C₃H₆ and NO₂ 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.

NO_x conversions of several alumina catalysts with PAC are shown in Fig. 13. The order of the NO_x reduction activities was as follows: γ -alumina > 5% La-alumina > 2.5% La-alumina > α -alumina. Here,

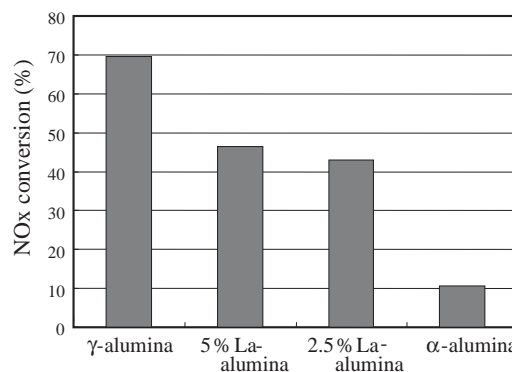


Fig. 13 NO_x conversions of several alumina catalysts with PAC (673 K, steady state).

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 γ -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

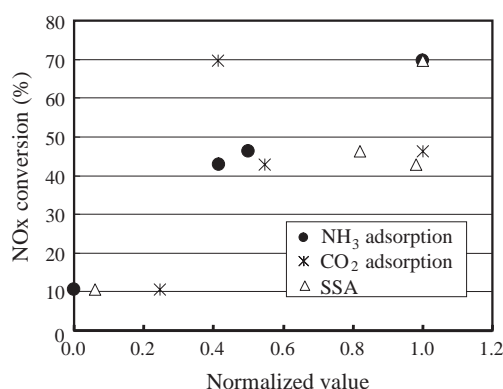


Fig. 14 Relationship between the NOx conversion of alumina catalysts with PAC (673 K, steady state) and their properties.

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	
		($\mu\text{mol/g}$)	Normalized value	($\mu\text{mol/g}$)	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

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 Brønsted 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 Brønsted 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 γ -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.

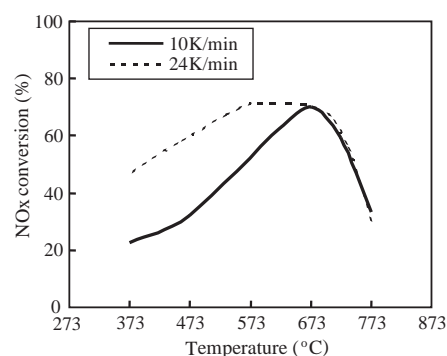


Fig. 15 Temperature dependence of the NOx conversion for γ -alumina with PAC in different cooling temperature rates.

As shown in the figure, NO_x 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 NO_x conversion for 10 K/min was the same as that for 24 K/min, and was independent of the rate. However, the NO_x conversion for 10 K/min rapidly decreased below 673 K. Thus, the NO_x reduction activity of γ -alumina with PAC below 673 K decreased for the higher rate. After the measurement, the color of γ -alumina changed from white to brownish yellow. The NO_x reduction activity of γ -alumina with PAC and the color of the catalyst was recovered by calcination in air. Furthermore, to investigate the steady-state NO_x

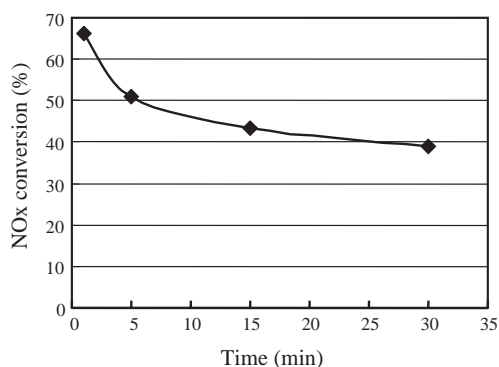


Fig. 16 NO_x conversion as a function of time for γ -alumina with PAC at fixed temperature of 573 K.

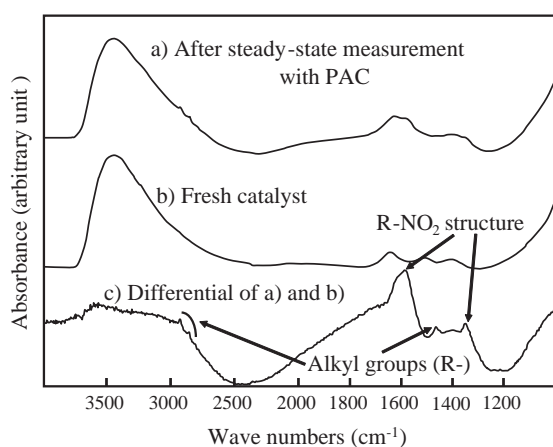


Fig. 17 FT-IR spectra of γ -alumina with PAC (573K, steady state) and fresh catalyst.

reduction performance of γ -alumina with PAC below the temperature of maximum NO_x conversion, the NO_x conversion was measured as a function of time at a fixed temperature of 573 K. The results are shown in **Fig. 16**. The NO_x 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 γ -alumina with PAC and fresh catalyst and the differential spectrum of the two curves. Alkyl groups (R-) and the R-NO₂ 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 NO_x conversion for γ -alumina with PAC below 673 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-SCR⁸⁻¹²⁾ 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 NO_x reduction activity of γ -alumina with PAC at 573 K. **Figure 18** shows the NO_x conversions of γ -alumina, Ag/alumina, Ga/alumina and In/alumina catalysts with PAC at a fixed temperature of 573 K. Here, In/alumina showed the highest NO_x conversion during the first 30 min of conversion. It

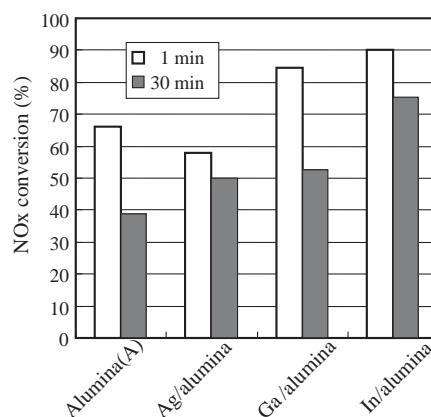


Fig. 18 NO_x conversions of γ -alumina, Ag/alumina, Ga/alumina and In/alumina catalysts with PAC at fixed temperature of 573 K.

is demonstrated that In-loading is effective in improving NO_x reduction activity and suppressing the degradation of γ -alumina with PAC under steady-state temperature conditions. Upon In-loading of γ -alumina, an increase in HC conversion (about 10 %) was observed. This might promote the oxidation or decomposition of the deposits and improve the NO_x reduction activity of the In-loaded γ -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 NO_x conversion on γ -alumina, In/alumina, Na/ZSM-5 and Pt/alumina with PAC under steady-state temperature conditions. Figure 19 shows that the maximum NO_x conversion on γ -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 NO_x 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. NO_x 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 NO₂ 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 NO_x and HC at higher temperature, NO_x was reduced by In/alumina in the middle region and HC and CO were oxidized by Pt/alumina further downstream. **Figure 20** shows the NO_x and HC conversion of the 3-stage catalyst with PAC under transient temperature conditions. As can be seen in this figure, high NO_x conversion was achieved by this system over a wide temperature range. NO_x conversion was higher during cooling than during heating. This is presumably the result of NO_x and HC adsorption on the catalysts. During the temperature decrease, there were two peaks on the NO_x conversion curve. The first peak was attributed to the NO_x reduction by In/alumina and Na/ZSM-5, which was consistent with the peak temperature of the NO_x conversion of these catalysts (see Fig. 20).

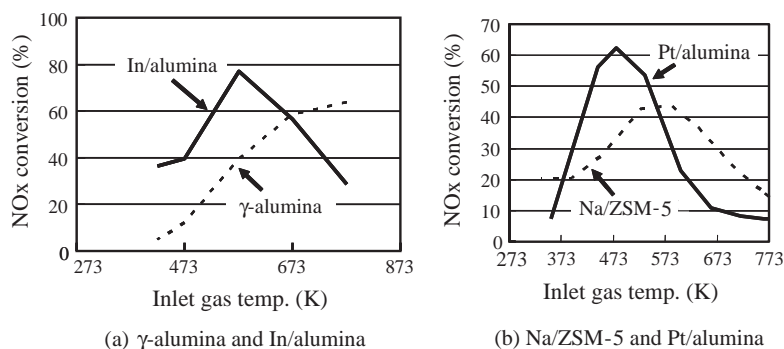


Fig. 19 NO_x conversion of γ -alumina, In/alumina, Na/ZSM-5 and Pt/alumina with PAC under steady state temperature condition.

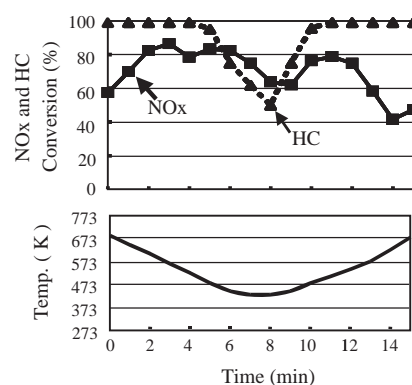


Fig. 20 NO_x and HC conversion of 3-stage catalyst with PAC under transient temperature conditions.

On the other hand, NO_x conversion during the temperature increase was presumably lowered by the desorbed NO_x. 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 NO_x reduction under oxidizing conditions. The results obtained can be summarized as follows:

(1) The gas analysis revealed that PAC used γ -alumina and C₃H₆ as a reductant, and the NO₂ and CH₃CHO that were generated by the plasma reduced NO_x on γ -alumina.

(2) The distance between the plasma reactor and the γ -alumina reactor had no effect on NO_x conversion.

(3) As CH₃CHO and NO₂ are generated from C₃H₆ and NO by the plasma, the influence of CH₃CHO on the NO_x conversion of γ -alumina with PAC was stronger than that of NO₂.

(4) The NO_x reduction activities of γ -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, γ -alumina with a large amount of solid acid showed the highest NO_x conversion.

(5) The steady-state measurements with PAC at low temperature (573 K) revealed that the NO_x conversion of γ -alumina decreased with PAC as a function of time. In-loading on γ -alumina improved the NO_x 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/ γ -alumina and a precious metal catalyst, a wide temperature window and high NO_x, HC and CO conversions were obtained under transient temperature conditions.

Acknowledgments

The authors are indebted to Mr. M. Yamamoto (Toyota Central R&D Labs, Inc.) for the GC and GC/MS analysis and Mr. E. Sudo (Toyota Central R&D Labs, Inc.) for the FT-IR analysis.

References

- 1) Zhang, G., et al. : "Selective Reduction of Nitric Oxide over Platinum Catalysts in the Presence of Sulfur Dioxide and Excess Oxygen", *Appl. Catal. B*, **1**(1992), L15
- 2) Obuchi, A., et al. : "Performance of Platinum-group Metal Catalysts for the Selective Reduction of Nitrogen Oxides by Hydrocarbons", *Appl. Catal. B*, **2**(1993), 71
- 3) Iwamoto, M., et al. : "Performance and Durability of Pt-MFI Zeolite Catalyst for Selective Reduction of Nitrogen Monoxide in Actual Diesel Engine Exhaust", *Appl. Catal. B*, **5**(1994), L1
- 4) Held, W., et al. : "Catalytic NO_x Reduction in Net Oxidizing Exhaust Gas", *SAE Tech. Pap. Ser.*, No.900496(1990)
- 5) Iwamoto, M. and Hamada, H., et al. : "Removal of Nitrogen Monoxide from Exhaust Gases through Novel Catalytic Processes", *Catal. Today*, **10**(1991), 57
- 6) Kintaichi, Y., et al. : "Selective Reduction of Nitrogen Oxides with Hydrocarbons over Solid acid Catalysts in Oxygen-rich Atmospheres", *Catal. Lett.*, **6**(1990), 239
- 7) Hamada, H., et al. : "Transition Metal-promoted Silica and Alumina Catalysts for the Selective Reduction of Nitrogen Monoxide with Propane", *Appl. Catal.*, **75** (1991), L1
- 8) Miyadera, T. : "Alumina-supported Silver Catalysts for the Selective Reduction of Nitric Oxide with Propene and Oxygen-containing Organic Compounds", *Appl. Catal. B*, **2**(1993), 199
- 9) Bethke, K. A. and Kung, H. H. : "Supported Ag Catalysts for the Lean Reduction of NO with C₃H₆", *J. Catal.*, **172**(1997), 93
- 10) Hoost, T. E., et al. : "Characterization of Ag/ γ -Al₂O₃ Catalysts and Their Lean-NO_x Properties", *Appl. Catal. B*, **13**(1997), 59
- 11) Haneda, M., et al. : "Enhanced Activity of Metal Oxide-doped Ga₂O₃-Al₂O₃ for NO Reduction by Propene", *Catal. Today*, **54**(1999), 391
- 12) Park, P. W., et al. : "In₂O₃/Al₂O₃ Catalysts for NO_x Reduction in Lean Condition", *J. Catal.*, **210**(2002), 97
- 13) Hoard, J. W. and Panov, A. : "Products and Intermediates in Plasma-catalyst Treatment of Simulated Diesel Exhaust", *SAE Tech. Pap. Ser.*, No.2001-01-3512(2001)
- 14) Penetrante, B. M., et al. : "Plasma-assisted Catalytic Reduction of NO_x", *SAE Tech. Pap. Ser.*, No.982508(1998)

- 15) Panov, A. G., et al. : "Selective Reduction of NO_x in Oxygen Rich Environments with Plasma-assisted Catalysis: the Role of Plasma and Reactive Intermediates", SAE Tech. Pap. Ser., No.2001-01-3513(2001)
- 16) Ebeling, A. C., et al. : "Characterization of Acid Sites in Ion-exchanged and Solid State-exchanged Zeolites", SAE Tech. Pap. Ser., No.2001-01-3571 (2001)
- 17) Miessner, H., et al. : "Plasma-enhanced HC-SCR of NO_x in the Presence of Excess Oxygen", Appl. Catal. B, **36**(2002), 53
- 18) Miessner, H., et al. : "NO_x Removal in Excess Oxygen by Plasma-enhanced Selective Catalytic Reduction", Catal. Today, **75**(2002), 325
- 19) Tonkyn, R. G., et al. : "Reduction of NO_x in Synthetic Diesel Exhaust via Two-step Plasma-catalysis Treatment", Appl. Catal. B, **40**(2003), 207
- 20) Balmer, M. L., et al. : "Diesel NO_x Reduction on Surfaces in Plasma", SAE Tech. Pap. Ser., No.982511(1998)
- 21) Hemingway, M. D., et al. : "Evaluation of a Non-thermal Plasma System for Remediation of NO_x in Diesel Exhaust", SAE Tech. Pap. Ser., No.1999-01-3639(1999)
- 22) Aardahl, C. L., et al. : "Steady-state Engine Testing of γ -alumina Catalysts under Plasma Assist for NO_x Control in Heavy-duty Diesel Exhaust", SAE Tech. Pap. Ser., No.2003-01-1186(2003)
- 23) Agrafiotis, C. and Tsetsekou, A. : "The Effect of Powder Characteristics on Washcoat Quality. Part I: Alumina Washcoats", J. Eur. Ceram. Soc., **20**(2000), 815
- 24) Ingelsten, H. H., et al. : "The Influence of Surface Acidity on NO₂ Reduction by Propane under Lean Conditions", J. Mol. Catal. A, **209**(2004), 199
- 25) Burch, R., et al. : "A Comparison of the Selective Catalytic Reduction of NO_x over Al₂O₃ and Sulphated Al₂O₃ using CH₃OH and C₃H₈ as Reductants", Appl. Catal. B, **17**(1998), 115
(Report received on Mar. 13, 2006)



Yoshihiko Itoh

Research fields : Catalysis & catalyst development
 Academic degree : Dr. Eng.
 Academic society : Surface Finishing Soc. Jpn.



Matsuei Ueda

Research fields : Control of diesel engine and diesel aftertreatment system.
 Academic degree : Dr. Eng.
 Academic society : Soc. Autom. Eng. Jpn., Jpn. Soc. Mech. Eng.
 Awards : The outstanding tech. pap. Award, Soc. Autom. Eng. Jpn., 2004



Hirohumi Shinjoh

Research fields : Catalysis & catalyst development
 Academic degree : Dr. Eng.
 Academic society : Catal. Soc. Jpn., Chem. Soc. Jpn., Soc. Chem. Eng. Jpn., Soc. Autom. Eng. Jpn.
 Awards : Technol. Prize, Jpn. Soc. Mech. Eng., 1995



Kiyomi Nakakita

Research fields : Engine combustion, Laser diagnosis, Hybrid vehicle
 Academic degree : Dr. Eng.
 Academic society : Soc. Autom. Eng. Jpn., Jpn. Soc. Mech. Eng., Combust. Soc. Jpn., Inst. Liq. Atomization & Spray Syst. - Jpn.
 Awards : The outstanding tech. pap. Award, Soc. Autom. Eng. Jpn., 1992, 2000, & 2005
 Engin Systems Memorial Award, The Engine Systems Div., Jpn. Soc. Mech. Eng., 1996
 2003 Harry L. Horning Memorial Award, SAE, 2004



Miyao Arakawa*

Research fields : R&D of powertrain control systems
 Academic society : Soc. Autom. Eng. Jpn.

*DENSO Corp.