Simultaneous Reduction of Diesel Particulate and NO\textsubscript{x} Using Catalysis Combined Nonthermal Plasma Reactor

Masaaki Okubo\textsuperscript{1}, Hideaki Yamada\textsuperscript{2}, Keiichiro Yoshida\textsuperscript{3}, Tomoyuki Kuroki\textsuperscript{1}

\textsuperscript{1} Dept. of Mechanical Engineering, Osaka Prefecture University
1-1 Gakuen-cho, Naka-ku, Sakai 599-8531, Japan
e-mail: mokubo@me.osakafu-u.ac.jp

\textsuperscript{2} Railways Dept. Kanto District Transport Bureau
Ministry of Land, Infrastructure, Transport, and Tourism
Godochosya 17F, 5-57 Kitanakadori, Naka-ku, Yokohama 231-8433, Japan

\textsuperscript{3} Dept. of Electrical and Electronic Systems Engineering, Osaka Institute of Technology
5-16-1 Omiya, Asahi-ku, Osaka 535-8585, Japan

Abstract—A simultaneous reduction of particulate matter (PM) and NO\textsubscript{x} emitted from diesel engines is realized by means of a barrier-type catalyst packed nonthermal plasma (NTP) application driven by a pulse high-voltage power supply under oxygen-lean conditions. Catalysts particles having a diameter of 2-4 mm of γAl\textsubscript{2}O\textsubscript{3} and Ag/γAl\textsubscript{2}O\textsubscript{3} are used as packed pellets, and carbon PM is loaded among the pellets. NO\textsubscript{x} is reduced by N radicals, and PM is incinerated by oxygen radicals induced either by NO\textsubscript{x} or by ozone (O\textsubscript{3}) reduction under elevated local temperatures among the pellets. From the generations of CO and CO\textsubscript{2}, it can be confirmed that the carbon PM or soot is removed under the condition of lean oxygen, resulting in the simultaneous removal of the PM and NO\textsubscript{x}. An optimal value for the mass of the loaded PM exists, and when the loaded PM mass is greater than a threshold value, the effect of the NTP induced by the partial discharge is too weak to simultaneously reduce the PM and NO\textsubscript{x}. Under the optimized plasma condition, the experiment yields energy efficiencies of 0.88 g (PM)/kWh for the PM incineration and 33 g(NO\textsubscript{2})/kWh for the NO\textsubscript{x} reduction in the experiment.

I. INTRODUCTION

Diesel engines are very popular for use in automobiles, construction machines, stationary generators, ships, and trains because of their little CO\textsubscript{2} emission, compact size, and higher fuel efficiency. However, their emissions include greater amounts of harmful particulate matter (PM) and NO\textsubscript{x} (= NO +NO\textsubscript{2}) as compared to those from gasoline engines. Therefore, regulations with regard to diesel engine emissions have recently become severe; consequently, aftertreatment technologies have been extensively developed [1]–[3].

Promising technologies for overcoming these problems are nonthermal plasma (NTP) technologies, which have been developed by many researchers [4]–[9]. NTP has an extremely high electron temperature (> 10 000 K) and low gas temperatures (< 300 °C), and it
can be used to realize a higher chemical activity. However, these systems require extremely large electrical energy such that they cannot be practically implemented. In our group, PM and NOx reductions from diesel engines [10]–[21] have been investigated.

In this paper, considering these reports and other researches [22]–[26], a new technology for the simultaneous reduction of the deposited PM and NOx is investigated in a laboratory-scale experiment using NTP induced in a catalytic packed-bed plasma reactor. In the next chapter, first, the principle of the reduction is explained.

II. PRINCIPLE OF SIMULTANEOUS REDUCTION

Figure 1 shows the principle of the plasma-activated diesel particulate–NOx reduction system. NOx adsorbents such as zeolite or alkali-earth metals are included in the DPF, and NTP can be applied to its surface. During the ordinary operation state of engines with a normal amount of fuel injection as shown in Fig. 1(a), the emission is rich in oxygen; furthermore, NO is oxidized to NO2 and adsorbed by the adsorbent. Carbon PM trapped by the filter is partially incinerated under the oxygen-rich condition. In our previous studies [11]–[13], [15], [19]–[21], the collected carbon PM was effectively incinerated by the NO2 induced by NTP according to the following chemical reactions at approximately more than 250°C.

\[
\text{Oxygen-rich condition} \\
C + NO_2 \rightarrow CO + NO \quad (1) \\
C + 2NO_2 \rightarrow CO_2 + 2NO \quad (2)
\]

According to the previously mentioned reactions, the oxidized NO2 is reduced to NO as a result of the existence of carbon PM. The following complete simultaneous reduction of the NOx and carbon PM or soot is desirable.

\[
\text{Oxygen-lean condition} \\
C + NO_2/2 \rightarrow CO + N_2/4 \quad (3) \\
C + NO_2 \rightarrow CO_2 + N_2/2 \quad (4)
\]

However, these chemical reactions rarely occur under oxygen-rich conditions (O2 ~ 10%) such as those in diesel emissions. Under these conditions, reactions (1) and (2) occur. These cannot be considered as an actual air pollution control technology because of the emission of hazardous NO. Therefore, the following lean state of oxygen is required periodically to reduce the stored NOx according to reactions (3) and (4).

When a constant amount of NOx is stored, a rich state of CO and HC and a lean state of oxygen are realized by increasing the fuel/oxygen ratio and/or the exhaust gas recirculation, as shown in Fig. 1(b). By plasma application, the stored NO2 is desorbed and reduced to N2, and the trapped PM and HC are oxidized by active oxygen into CO2 and H2O, respectively. Therefore, in the present method, a combination of CO, HC, O, and NO2 is used to assist in the emission cleanup of engines. This concept is based on the diesel particulate–NOx reduction (DPNR) technique [27], [28] proposed by Toyota Motor as a modification of the
lean NO\textsubscript{x} trap.

In this paper, plasma-enhanced DPNR is realized for diesel engine exhausts by means of oxygen-lean plasma applications. The state shown in Fig. 1 (b) where the PM is oxidized by NO\textsubscript{2} is simulated in a laboratory-scale experiment. The NO\textsubscript{2} must be obtained from NO by plasma or oxidation catalysts. The simultaneous reduction of the deposited PM and NO\textsubscript{x} can be realized according to chemical reactions (3) and (4). This process is enhanced by the catalysts such as gold (Ag) and/or alumina (Al\textsubscript{2}O\textsubscript{3}). This system does not use ammonia and urea, and it can be operated at low temperatures near the atmospheric temperature, and therefore, the aforementioned problems in the catalytic methods can be avoided.

![Fig. 1 Principle of the simultaneous reduction of PM and NO\textsubscript{x} with catalysts by NTP application](image)

**III. EXPERIMENTAL APPARATUS AND METHOD**

**A. Experimental Apparatus**

Schematic diagram of the experimental setup is shown in Fig. 2. Experiments are carried out with cylinder gases or simulated exhaust gas of diesel engines. Approximately 2000 ppm of NO\textsubscript{x} is prepared by mixing the gases of NO (2% diluted by N\textsubscript{2}), N\textsubscript{2} (purity of 99.999%), and those from synthesized air cylinders (N\textsubscript{2}: O\textsubscript{2} = 79: 21%). The flow rate is controlled by a mass flow controller in each line. The mixed gas passes through the plasma reactor, its details are explained later. The plasma reactor is placed inside the electrical oven container (Forced Convection Drying Oven, DO-600FA, AS ONE Corporation) the temperature of which is maintained as at 120°C. Both upstream and downstream of the plasma reactor, three-way valves are set in order to prepare a bypassed flow line. The simulated exhaust gas passes through the plasma reactor energized by a pulse high-voltage power supply using IGBT semiconductor switching. The waveforms of the applied voltage and current are recorded by an oscilloscope (DL1740, Yokogawa Electric Corporation) through high-voltage and high-current probes (P6015A and P6021 Tektronix Ltd.,) gas. The detail of the power supply is explained later. After the gas passes through the reactor and the treatment is performed, it passes through a tubular-type electric heater (EKR-122K, Isuzu Seisakusho Ltd.) at a constant temperature of 300°C in order to remove residual O\textsubscript{3} that often damages gas analyzers. The concentrations of NO, NO\textsubscript{x}, CO, CO\textsubscript{2}, and O\textsubscript{2} in the gas are measured by a set of gas analyzers (PG-235 and VIA-510, Horiba Ltd.). In this study, the effects of hydrocarbon and water in the exhaust gas are not investigated. Usually,
hydrocarbon inclusion may enhance the NO\textsubscript{x} reduction, and water inclusion may decrease the efficiency of the NO\textsubscript{x} reduction.

![Fig. 2 Schematic diagram of experimental setup](image)

**B. Plasma reactor**

The plasma reactor used in the present experiment is shown in **Fig. 3**. It is a coaxial-type reactor made with quartz glass. It has a total length of 450 mm, an inner diameter of 22 mm and an outer diameter of 25 mm. It consists of a stainless discharge wire at the center (diameter = 2.0 mm) and a quartz glass tube around which an aluminum tape electrode is wrapped. A high voltage is applied to the discharge electrode, and the tape electrode is grounded. Either activated alumina $\gamma$Al\textsubscript{2}O\textsubscript{3} pellet (NKHD-24, Sumitomo Chemical Industry Co., diameter = 2 ~ 4 mm, pore volume density = 0.6 mL/g, and relative surface area =330 m\textsuperscript{2}/g) or Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3} (Ag added alumina) pellet is used for experiments. Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3} pellets are prepared by adding Ag with a mass concentration of 1.74 mass\% to $\gamma$Al\textsubscript{2}O\textsubscript{3} ones. The preparation method is as follows: Aqueous solution of AgNO\textsubscript{3} (concentration = 39 g/L) is prepared and activated alumina pellets are immersed in it. After 1 hour drying at reduced pressure, 12 hours and 120°C drying followed by 3 hours and 450°C baking in the air are performed. Prepared pellets are packed inside the plasma reactor. The height of the pellet layer is 50 mm, which is the same as that of the tape electrode. The pellet layer is supported by a perforated Teflon (PTFE) plate.

The carbon PM sampled from diesel engine is attached to these pellets. NTP is induced among the pellets inside the plasma reactor. The experimental conditions are as follows. The gas flow rate is 2 L/min, the initial concentration of NO\textsubscript{x} is 2000 ppm, O\textsubscript{2} concentration is either O, 0.5, or 2% balanced with nitrogen gas. The mass of pellets are approximately 10.3 g and that of attached PM is approximately 50 mg.
For IGBT switching pulsed-high voltage power supply, (PPCP Pulse, SMC-30/1000), the electric circuit is shown in reference [10]. In the circuit, the condenser C0 is energized by the DC power source (the voltage is 1500-1900 V). After that, IGBT works and switching is performed. The voltage is increased using pulse transformer (1:20). Simultaneously saturated reactor SR is energized and the current is supplied through LD1 inductor and RD1 resistance. When the power supply to C1 is finished, SR (magnetic compression) becomes saturated and the discharge current flows to the load from the condenser C1. Although the pulse high voltage is changed according to the impedance of the external load, the peak voltage of approximately 30 kV is induced when a pure capacitance load of 170 pF.

Voltage $V$, current $I$, and instantaneous power $P = V \times I$ waveforms for the NTP reactor is obtained from the display of a digital oscilloscope. The time-averaged discharge power is calculated to be 9.3 W from the product of the positive area (surround by the $V \times I$ curve and the horizontal axis), conversion factors of the $V$ and $I$ divider probes, and the pulse frequency. The peak voltage is 31.7 kV, and pulse frequency $f$ is 315Hz.
IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Case without Catalysts

First, the experiments are carried out when the catalysts pellets are not included in the reactor. The effect of oxygen concentration and SE value on the NOx removal efficiency, where SE is defined as the ratio of plasma power (W) to the gas volumetric flow rate (m$^3$). For example, for the case of $P = 9.3$ W and $Q = 2$ L/min, SE becomes 0.0775 (kWh/m$^3$). The experimental conditions are as follows: The flow rate of simulated exhaust gas is 2.0 L/min, and the initial concentration of NOx is 2000 ppm balanced with nitrogen gas. Either 0%, 0.5%, or 2% of oxygen concentrations are adopted. Either 105 Hz, 210 Hz, 315 Hz, 420 Hz, and 525 Hz of the high voltage frequency are adopted. In the present experiments, the applied voltage is adjusted in order to make the discharge energy per a single pulse which is calculated as the integral of the applied voltage and the discharge current the same value. The atmospheric temperature is kept constant at 120°C using an electrical controlled oven.

The relations between gaseous concentrations and SE for various oxygen concentrations are measured. In these results, both NO and NOx concentrations decrease with increase in SE, while the concentration of NO2 almost remain the same. The values increase with increase in the oxygen concentration. The concentration of N2O is maximum 10 ppm in all cases. These tendencies are explained as follows: NOx reduction is mainly caused by N radical (N*) induced by the NTP, the reaction is as follows:

$$\text{NO} + \text{N}^* \rightarrow \text{N}_2 \tag{5}$$

The production of N* increases with increase in SE. As a result, the reduction of NOx proceeds. The reduction of NOx decreases with increase in the oxygen concentration, because O$_2$ dissociate to O more easily by the plasma application. The induced O radicals react with NO and NO2 as follows:

$$\text{NO} + \text{O} \rightarrow \text{NO}_2 \tag{6}$$
$$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \tag{7}$$

Because the reaction (5) is trapped with the oxidation reactions of (6) and (7), it occurs less easily. As a result, the NOx reduction declines with increasing oxygen concentration. The concentration of NO2 slightly decreases with increase in SE according to the oxidation reaction (7) and the reduction reaction (8).

$$\text{NO}_2 + \text{N} \rightarrow 2\text{NO} \tag{8}$$

N$_2$O slightly increases according to the reactions

$$\text{NO} + \text{N} \rightarrow \text{N}_2\text{O} \tag{9}$$
$$\text{NO}_2 + \text{N} \rightarrow \text{N}_2\text{O} + \text{O} \tag{10}$$
Only small amount of O₃ and HNO₃ are detected in all experiments. As a result, NOₓ reduction is confirmed in the experiments.

**B. Case with Catalysts and PM for O₂= 0%**

Next, experiments are carried out when either γ-Al₂O₃ (γ-alumina) catalyst or Ag/γ-Al₂O₃ catalyst pellets are packed inside the reactor. The concentration of oxygen is 0% and the case with PM among pellet is investigated. **Figures 4 (a), (b)** show the time-dependent gaseous concentrations for γ-Al₂O₃ catalyst and Ag/γ-Al₂O₃ catalyst. In 60 min, the NOₓ concentration is 680 ppm with the removal efficiency of 66% for γ-Al₂O₃ catalyst and it is 882 ppm with the removal efficiency of 56% for Ag/γ-Al₂O₃ catalyst. From these graphs, it takes fairly long time to achieve steady-state NOₓ removal. The concentrations of NO₂ are almost steady and constant approximately 70 ppm for both cases. The concentrations of N₂O are 28 ppm for γ-Al₂O₃ and 14 ppm for Ag/γ-Al₂O₃. The N₂O concentration reaches maximum immediately after the plasma is turned on. Afterward, gradual decreases of several ppm are observed. The generations of O₃ and HNO₃ are very small in both cases. It is known from no HNO₃ generation that NOₓ reduction is successfully achieved in all cases.

The time-dependent CO₂ and CO concentrations are shown in **Fig. 4 (c)**. For the experiment with PM included, CO₂ and CO are generated by the combustion of PM. The concentration of CO₂ and CO increases for PM included more than those for PM not included. It is observed that CO₂ increases slightly at the initial stage (< 5 min) and decreases down to the background gas level (= 100 ppm) this slight increase may be caused by the some hydrocarbon material at the surface of the catalyst pellets. It is difficult to remove this effect completely. The mass of incinerated carbon in PM is calculated as 5.00 mg for γ-Al₂O₃ and 4.58 mg for Ag/γ-Al₂O₃. They correspond to 9.8% and 9.0% masses of total packed PM masses, respectively. CO₂ generation occurs mainly at initial stage (< 10 min) while the concentrations of CO are steady and almost constant.

![Graph](image_url)
C. Case with Catalysts and PM for $O_2 = 0.5\%$

Next, similar experiments are carried out with oxygen concentration of 0.5%. In the result, in 60 min, the NO$_x$ concentration is 950 ppm with the removal efficiency of 52% for $\gamma$Al$_2$O$_3$ catalyst and it is 879 ppm with the removal efficiency of 66% for Ag/$\gamma$Al$_2$O$_3$ catalyst. Compared with the case of $O_2 = 0\%$, NO$_x$ removal efficiency tend to decrease because oxidation reaction (3) occurs more. The concentrations of NO$_2$ are approximately 140 ppm for $\gamma$Al$_2$O$_3$ catalyst and 90 ppm for Ag/$\gamma$Al$_2$O$_3$ catalyst. The NO$_2$ concentration
gradually increases while total NO\textsubscript{x} decreases. The concentrations of N\textsubscript{2}O are 25 ppm for $\gamma$Al\textsubscript{2}O\textsubscript{3} and 27 ppm for Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3}. The concentration reaches maximum immediately after the plasma is turned on. Afterward, gradual decreases of several ppm are observed. The generations of O\textsubscript{3} and HNO\textsubscript{3} are very small in both cases. It is known from no HNO\textsubscript{3} generation that NO\textsubscript{x} reduction is successfully achieved in all cases.

The time-dependent CO\textsubscript{2} and CO concentrations are measured. The mass of incinerated carbon in PM is calculated as 6.30 mg for $\gamma$Al\textsubscript{2}O\textsubscript{3} and 7.59 mg for Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3}. They correspond to 12.7\% and 15.3\% masses of total packed PM masses, respectively. CO\textsubscript{2} generation occurs mainly at initial stage (< 10 min) while the concentrations of CO are steady and almost constant.

D. Case with Catalysts and PM for O\textsubscript{2} = 2\%

Next, similar experiments are carried out with oxygen concentration of 2\%. In the result, in 60 min, the NO\textsubscript{x} concentration is 1263 ppm with the removal efficiency of 37\% for $\gamma$Al\textsubscript{2}O\textsubscript{3} catalyst and it is 1282 ppm with the removal efficiency of 36\% for Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3} catalyst. Compared with the case of O\textsubscript{2} = 0\%, NO\textsubscript{x} removal efficiency tend to decrease because oxidation reaction (3) occurs more. The concentrations of NO\textsubscript{2} are approximately 150 ppm for $\gamma$Al\textsubscript{2}O\textsubscript{3} catalyst and 140 ppm for Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3} catalyst. The NO\textsubscript{2} concentration is almost steady. The concentrations of N\textsubscript{2}O are 19 ppm for $\gamma$Al\textsubscript{2}O\textsubscript{3} and 20 ppm for Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3}. The concentration reaches maximum immediately after the plasma is turned on. Afterward, gradual decreases of several ppm are observed. The generations of O\textsubscript{3} and HNO\textsubscript{3} are very small in both cases. It is known from no HNO\textsubscript{3} generation that NO\textsubscript{x} reduction is successfully achieved in all cases.

The time-dependent CO\textsubscript{2} and CO concentrations are measured. The mass of incinerated carbon in PM is calculated as 8.18 mg for $\gamma$Al\textsubscript{2}O\textsubscript{3} and 7.93 mg for Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3}. They correspond to 16.2\% and 15.6\% masses of total packed PM masses, respectively. CO\textsubscript{2} generation occurs mainly at initial stage (< 10 min) while the concentrations of CO are steady and almost constant.

E. Case with Catalysts and PM for O\textsubscript{2} = 5\%

Next, similar experiments are carried out with oxygen concentration of 5\%. Figures 5 (a), (b) show the time-dependent gaseous concentrations with PM included. In 60 min, the NO\textsubscript{x} concentration is 1408 ppm with the removal efficiency of 30\% for $\gamma$Al\textsubscript{2}O\textsubscript{3} catalyst and it is 1396 ppm with the removal efficiency of 30\% for Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3} catalyst. Compared with the case of O\textsubscript{2} = 0\%, NO\textsubscript{x} removal efficiency tend to decrease because oxidation reaction (3) occurs more. The concentrations of NO\textsubscript{2} are approximately 180 ppm for $\gamma$Al\textsubscript{2}O\textsubscript{3} catalyst and 210 ppm for Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3} catalyst. The NO\textsubscript{2} concentration is almost steady. The concentrations of N\textsubscript{2}O are 11 ppm for $\gamma$Al\textsubscript{2}O\textsubscript{3} and 3 ppm for Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3}. The concentration reaches maximum immediately after the plasma is turned on. Afterward, gradual decreases of several ppm are observed. The generations of O\textsubscript{3} and HNO\textsubscript{3} are very small in both cases. It is known from no HNO\textsubscript{3} generation that NO\textsubscript{x} reduction is successfully achieved in all cases.

The time-dependent CO\textsubscript{2} and CO concentrations are shown in Fig. 5 (c). The mass of incinerated carbon in PM is calculated as 7.18 mg for $\gamma$Al\textsubscript{2}O\textsubscript{3} and 8.33 mg for Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3}. They correspond to 14.3\% and 16.7\% masses of total packed PM masses, respectively.
CO$_2$ generation occurs mainly at initial stage (< 10 min) while the concentrations of CO are steady and almost constant.

(a) NO, NO$_x$, NO$_2$, and N$_2$O (PM 50.1 mg)

(b) NO, NO$_x$, NO$_2$, and N$_2$O (PM 49.9 mg)
The effects of catalyst type and PM inclusion on the NO\textsubscript{x} removal efficiency are investigated. Note that the highest NO\textsubscript{x} removal efficiency in each condition is considered plotted. It is known in these data that the effect of Ag inclusion to the catalyst is small in the present experiments. In the present experiments as well as previous study [10] without catalyst, the PM inclusion improved the reduction efficiency of NO\textsubscript{x} or NO\textsubscript{2}. The process of the improvement is explained as follows: NO and NO\textsubscript{2} reductions by the PM or dry soot are caused according to the reactions (3) and (4). These reactions can assist NO reduction in the reaction (5). As a result, NTP energy can be reduced compared with the direct reduction with (5). Therefore, improvement of NO\textsubscript{x} reduction by PM addition scarcely occurs in the present experiment.

Under the optimized plasma condition, the experiment yields energy efficiencies of 0.88 g (PM)/kWh for the PM incineration and 33 g(NO\textsubscript{2})/kWh for the NO\textsubscript{x} reduction in the experiment.

V. CONCLUSION

Experiments are carried out on the simultaneous removal of NO\textsubscript{x} and particulate matter using catalysts assisted by NTP. The main results are summarized as follows:

1. The removal efficiencies of both NO\textsubscript{x} and NO decrease with increase in oxygen concentration.
2. The generation of O\textsubscript{3} and HNO\textsubscript{3} is small.
3. The plasma assisted $\gamma$Al\textsubscript{2}O\textsubscript{3} and Ag/$\gamma$Al\textsubscript{2}O\textsubscript{3} catalysts increase the energy efficiency of NO\textsubscript{x} removal.
(4) The inclusion of PM among catalysts pellet increases the NO\textsubscript{x} removal efficiency. Further, Concentrations of CO and CO\textsubscript{2} increases when PM exists. As a result, simultaneous NO\textsubscript{x} and PM removals are possible.

(5) With increase in oxygen concentration, NO\textsubscript{2} increases and N\textsubscript{2}O decreases on the contrary.

(6) PM combustion increases with increase in oxygen concentration.

REFERENCES


