Abatement of Nitrogen Oxides in a Catalytic Reactor Enhanced by Nonthermal Plasma Discharge

Young Sun Mok, V. Ravi, Ho-Chul Kang, and B. S. Rajanikanth, Senior Member, IEEE

Abstract—Removal of nitrogen oxides using a nonthermal plasma process (dielectric barrier discharge) combined with catalyst was investigated. In this system, selective catalytic reduction of nitrogen oxides is affected by the operating condition of the plasma process and, thus, the characteristics of the plasma process were separately examined before combining the two processes. The oxidation of NO to NO₂ in the plasma reactor easily took place at room temperature. As the temperature increased, however, the rate of the oxidation greatly decreased, which implies that an additive to increase the reaction rate is necessary. In the presence of ethylene as an additive, the oxidation of NO to NO₂ largely enhanced at a temperature range of 100 °C–200 °C. Comparison of ac with pulse voltage in terms of the energy efficiency for NO oxidation was made, and almost no difference between the two voltage types was observed. The removal of NO₅ on the catalyst (V₂O₅/TiO₂) was found to largely increase by the plasma discharge. The byproduct formaldehyde formed from ethylene in the plasma reactor could be completely removed in the catalytic reactor while significant amount of carbon monoxide and ammonia slip were observed. The plasma-catalyst system used in this study was able to remove more than 80% of NO₅ (energy yield: 42 eV/NO₅-molecule) at a temperature range of 100 °C–200 °C that is much lower than typical temperature window of selective catalytic reduction (250 °C–450 °C).

Index Terms—Catalytic reduction, NO₅, nonthermal plasma, removal, temperature window.

I. INTRODUCTION

THE REMOVAL of nitrogen oxides (NOₓ) emitted from many industrial processes has become one of the greatest challenges in environmental protection, and various NOₓ control technologies such as selective catalytic reduction (SCR), wet scrubbing, electron–beam irradiation, and nonthermal plasma process have been developed so far [1]–[4]. Among these technologies, SCR has been most widely studied due to its many advantages over other technologies [5]. One problem related to the application of SCR to manifold pollution sources may be its temperature window. It is well known that typical SCR catalyst works well around 250 °C–450 °C, whereas there are many important pollution sources that the temperatures of the exhaust gases are lower than this window. For instance, the temperature of diesel exhaust is typically 100 °C–200 °C although it depends on country and driving conditions, and typical temperature of iron-ore sintering plant is around 150 °C. Therefore, unless traditional SCR technology is modified in order that it may work well at lower temperature, it requires the heating-up of exhaust gas to a certain temperature, which leads to the increase in operation cost.

Generally, among NOₓ (NO+NO₂) emission, NO generally has a majority (95%) and the content of NO₂ is less than 5%. According to the literature in connection with SCR [6], it is reported that the performance of SCR is elevated by the increase in the ratio of NO₂ to NO. This result indicates that catalytic removal of NO₂ at relatively low temperature is possible when a part of NO is converted to NO₂. One easy method to increase the portion of NO₂ in NOₓ may be nonthermal plasma technology as its capability to oxidize NO to NO₂ has been proved elsewhere [7]–[9]. Bröer and Hammer [10], Hoard [11], and Yoon et al. [12] showed the possibility that the NOₓ removal is enhanced and the temperature window is lowered by combining nonthermal plasma with SCR technology.

Typical nonthermal plasma technologies studied so far have usually adopted such procedure as the oxidation of NO to NO₂ or HNO₃, followed by formation of fine ammonium nitrate particles which should be collected by a conventional electrostatic precipitator or a bag filter [13]–[15]. Since the formation of ammonium nitrate is a slow reaction and does not take place efficiently at higher temperatures [16], [17], most of such studies have been conducted at temperatures lower than 100 °C, and only few studies performed at high temperatures are available in the literature [18]. However, in order to combine nonthermal plasma with SCR, it is necessary to investigate the plasma discharge characteristics and the behavior of NO oxidation at high temperatures because the plasma discharge is a phenomenon related to gas ionization and the reaction mechanism of NO oxidation depends on gas temperature [19]. In this context, the study on the temperature effect on the nonthermal plasma process should be preceded before combining it with catalyst.

This study deals with the combination process of nonthermal plasma and SCR for the removal of NOₓ. The plasma reactor used was a coaxial dielectric barrier discharge (DBD) reactor, and the SCR catalyst used was commercial honeycomb V₂O₅/TiO₂. As previously mentioned, since the experiments at high temperatures are necessary in order to combine two processes, the study using the plasma reactor alone was conducted first and then the effect of the combined system on NOₓ removal was examined. The DBD reactor used can be operated by either ac or pulse voltage [20], [21], and the two voltage types were compared in terms of the energy efficiency for NO conversion.
II. EXPERIMENTAL

A. Description of the Experimental Setup

The schematic of the reactor system composed of nonthermal plasma reactor and catalytic reactor is presented in Fig. 1. A coaxial dielectric barrier discharge reactor made of a glass tube (inner diameter: 25.8 mm; outer diameter: 30.2 mm) and a 3/8 in stainless steel rod was used as the plasma reactor. The stainless steel rod acting as the discharging electrode was positioned in the center of the glass tube. This high-voltage electrode does not go through the catalyst. The space between the glass tube and the discharging electrode was filled with glass beads of 5 mm in diameter. The outer surface of the glass tube was wrapped with aluminum foil and grounded. The effective length of the plasma reactor where discharge occurs is 31 cm. A 1.0-μF capacitor was connected to the plasma reactor in series to measure the discharge power when ac voltage is used, which will be fully explained. In the present study, most of experiments were carried out by making use of ac voltage of 60 Hz, but a comparative study between ac and pulse energization was also made.

The SCR catalyst used was a commercial V₂O₅/TiO₂ in the form of honeycomb (20 cells per square inch). The content of vanadium in the catalyst was 5.0 wt.%, and the apparent volume of the honeycomb was 31 cm³ (1.8 × 1.8 × 9.7 cm³), which was used for the calculation of space velocity defined as the ratio of feed gas flow rate to reactor volume.

The plasma-catalyst reactor was kept in an oven to maintain the desired gas temperature, and the stainless steel tube connected to the reactor inlet was wound several times within the oven in order to ensure proper heating-up of the feed gas to a given temperature. The main components of the feed gas were nitrogen and oxygen whose flow rates were adjusted by mass flow controllers (MFC) (Model 1179A, MKS Instruments, Inc.). The flow rates of NO (5.0% (v/v) balanced with N₂), ammonia (5.0% (v/v) balanced with N₂) and ethylene (pure) were also controlled by mass flow controllers, and they were mixed with N₂ and O₂.

The experimental conditions are summarized in detail in Table I. The flow rate of the feed gas stream was 5 l/min (at room temperature), and the concentration of NOₓ (NO+NO₂) at the reactor inlet was 300 parts per million (ppm, volumetric). The concentrations of ammonia and ethylene were 300 and 750 ppm, respectively. Since the typical amount of hydrocarbon in diesel exhaust is around 750 ppm, the addition of ethylene may simulate well the real exhaust gas. A modern diesel engine may emit less hydrocarbons (measured as ppm C₁) than nitrogen oxides. The experiments were carried out at different reaction temperatures in the range of 100 °C–200 °C by a division of 50 °C, but some experiments were also conducted at room temperature to understand the phenomena related to this system.

The volume of the plasma reactor (inner diameter: 25.8 mm; length: 31 cm) is 162 cm³, and, accordingly, the residence time (reactor volume/feed gas flow rate) is calculated to be 1.9 s at a flow rate of 5 l/min. However, actual residence time should be calculated by considering the void fraction of the reactor and the volume of the electrode (22 cm³). In case of this plasma reactor packed with glass beads, the void fraction was found to be 0.37. Therefore, the real reactor volume where the reactions take place corresponds to 52 cm³. Recalculation of the actual residence time using the real reactor volume gives 0.6 s. There is one more thing that should be made clear in the calculation of residence time. The residence time (0.6 s) is based on the flow rate at room temperature, however, it should be corrected when the gas is not at room temperature, because the gas flow rate is a function of temperature.

In case of ac, the variation in the applied voltage can change the discharge power, and it was varied from 4 to 14 kV. When pulse voltage was employed to compare it with ac voltage, the spark gap switch depicted in Fig. 2 was used. In this circuit, the pulse-forming capacitor (396 pF) is charged through 20-kΩ resistor by a negative dc high-voltage power supply (Korea Switching Company). As the voltage on the capacitor reaches the spark-over voltage of the spark gap electrode, the capacitor is discharged, producing narrow positive high-voltage pulses. The pulse frequency is changed by adjusting the charging time of the pulse-forming capacitor, by which way it was varied from 5 to 30 Hz (pulses/s).

The voltage applied to the discharging electrode was measured by a 1000:1 high voltage probe (PVM-4, North Star Research, Corporation) and a digital oscilloscope (TDS 3032, Tektronix). For the measurement of the voltage between both ends of the 1.0-μF capacitor, a 10:1 voltage probe (Tektronix P6139A) was used. The current in case of using pulse voltage was measured by a current transformer (Pearson Electronics) having the ratio 0.25 V/A. The measurement of input power was carried out using a digital power meter (Model WT 200, Yokogawa).

The concentrations of NO and NO₂ were analyzed by a chemiluminescence NO-NO₂-NOₓ analyzer (Model 42C, Thermo Environmental Instruments, Inc.). This kind of NO-NO₂-NOₓ analyzer has a problem in measuring NO₂ concentration when ammonia is present, and thus, in some cases, a portable flue gas analyzer (Eurotron) was utilized to analyze NO₂ concentration. This portable flue gas analyzer was also used for the measurement of carbon monoxide (CO). Ethylene concentration was detected using a gas chromatograph equipped with a flame ionization detector and a thermal conductivity detector (GC-14B, Shimadzu) and a capillary column (CBP10-M25-025, Shimadzu). Ammonia and formaldehyde concentrations were measured by chemical detectors (Gastec Company, Japan).
TABLE I

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<th>EXPERIMENTAL CONDITION</th>
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<tr>
<td>Gas flow rate</td>
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<td>Oxygen content in feed gas</td>
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<td>Ethylene concentration</td>
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<td>NOx concentration</td>
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**B. Discharge Power Measurement**

The method adopted to measure the discharge power when the ac voltage was applied to the reactor is as follows [22]–[24]. A 1.0-μF capacitor was connected in series with the reactor as shown in the Fig. 1. Since the dielectric barrier discharge reactor can be considered as a capacitor, the charge stored in the capacitor (1.0-μF) is equal to that in the reactor. The charge stored in the capacitor \(Q\) is the product of capacitance and voltage \((CV, C: \text{capacitance}; V: \text{voltage})\), which can be directly read by the voltage between both ends of the capacitor. In other words, the charge stored in the capacitor is equal to \(10^{-6}\) times the voltage. Fig. 3(a) shows an example of the voltage waveforms measured at the discharging electrode and at the 1.0 μF capacitor, and Fig. 3(b) shows the charge–voltage plot at the corresponding voltage. The area of the parallelogram in Fig. 3(b) conforms to the discharge energy per one cycle, and the average discharge power can be obtained by multiplying the discharge energy per one cycle by the ac frequency (i.e., 60 Hz). For example, in Fig. 3(b), the discharge energy per cycle at 12 kV was found to be 7.33 mJ/cycle. Hence, the average discharge power is \(7.33 \times 10^{-3} \text{ J/cycle} \times 60 \text{ Hz} = 0.44 \text{ W}\). A mathematical formula is available for calculating the area of the parallelogram [22]–[24]. For convenience, in the present case, the area of parallelogram was calculated by comparing the total mass of the graph with that of the parallelogram. It was assumed that the thickness of the paper was uniform throughout. We compared both methods of calculating the area of the parallelogram and the results were found to agree well within 5%.

When pulse voltage was applied, the average discharge power was obtained with the voltage and current forms. Fig. 4 shows the pulse voltage and current waveforms measured at the discharging electrode and the grounded aluminum foil.
respectively. The rise time of the pulse voltage (10%–90%) was 11 ns, and the pulselength (full width at half maximum) was about 200 ns. The integration of the product of these voltage and current waveforms corresponds to the discharge energy per pulse. In this case, the discharge energy per pulse was calculated to be \(86.7 \text{ mJ/pulse}\). The average discharge power was obtained by multiplying the discharge energy per pulse by the pulse repetition rate.

III. RESULTS AND DISCUSSION

A. Plasma Reactor

Fig. 5 shows the discharge power curves as a function of applied voltage at different temperatures. The occurrence of discharge ignition shifted toward lower voltages and the discharge power largely increased with the increase in temperature. The discharge ignition voltage that gives nonzero discharge power was calculated by extrapolating each curve. At 27 °C, 100 °C, 150 °C, and 200 °C, the respective discharge ignition voltages were found to be 7.4, 6.7, 5.5, and 4 kV. This lower discharge ignition voltage and higher discharge power at higher temperature can be explained as follows. When pressure is constant, the gas density \(n\) decreases with the increase in temperature, which leads to the increase in the reduced electric field \(E/n\) [25]. Since the dielectric breakdown of the gas discharge occurs at a certain reduced electric field, the increase in temperature results in the decrease in discharge ignition voltage. Therefore, the gas at high temperature can be more easily ionized. As the extent of ionization increases, the discharge current increases because of decreased gas resistance, and the discharge powers increases. The discharge power data in Fig. 5 were used for the calculation of energy density that is defined as the ratio of discharge power to gas flow rate.

Fig. 6 shows the concentration profiles of NO as a function of energy density at different temperatures. In a gas mixture of the present case, the NO removal takes place mainly by its oxidation to \(\text{NO}_2\) [7], [8], [26]. At room temperature, NO was easily depleted. As the temperature increased, however, the rate of NO conversion largely decreased. The decrease in NO conversion with temperature can be explained with the rates of the relevant reactions. Main reactions for this case of NO oxidation are as follows [27], [28]:

\[
\text{NO} + \text{O} \rightarrow \text{NO}_2 \quad k_1 = 5.0 \times 10^{-33} \exp(900/T) [\text{M}] \tag{1}
\]

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad k_2 = 1.0 \times 10^{-31} (300/T) 1.6 [\text{M}] \tag{2}
\]

\[
\text{O} + \text{O}_2 \rightarrow \text{O}_3 \quad k_3 = 5.6 \times 10^{-34} (300/T) 2.23 [\text{M}] \tag{3}
\]

\[
\text{O} + \text{O}_3 \rightarrow 2\text{O}_2 \quad k_4 = 8.0 \times 10^{-12} \exp(-2060/T) \tag{4}
\]

According to the previous results, ozone was proved to play an important role in the oxidation of NO at room temperature [26]. As can be understood in (3) and (4), however, generation of ozone decreases much with the increase in temperature and, moreover, the decomposition into molecular oxygen becomes significant as the temperature increases. As a result, (2) cannot contribute to the oxidation of NO at high temperatures, which can explain why the oxidation rate is lowered. At relatively high temperatures in the range of 100 °C–200 °C, the key reaction for the oxidation of NO is, thus, (1). Since this reaction is in inverse proportion to the temperature, higher temperature gives rise to lower oxidation efficiency of NO. Moreover, the lower oxidation efficiency of NO at higher temperature can
also be attributed to the back reaction of NO to NO by O radical (NO$_2$ + O → NO + O$_2$) [29]. Meanwhile, the NO$_2$ level (NO+NO$_2$) was kept almost constant regardless of the oxidation of NO although the data were not presented in Fig. 6, which means that NO was simply converted to NO$_2$.

Since the oxidation of NO was very slow at high temperatures as previously examined, it was necessary to use a hydrocarbon additive. In this study, the hydrocarbon additive was ethylene. The hydrocarbon plays an important role in enhancing the oxidation of NO [7], [9], [18]. In real flue gases such as diesel exhaust and iron-ore sintering flue gas, some amount of hydrocarbon exists, and they may have similar effect to ethylene on NO conversion. Under plasma discharge, ethylene is decomposed into several fragments such as CH$_3$ and CH$_2$O radicals [9], [26], and these radicals can enhance the oxidation of NO via several reactions. Methyl radical (CH$_3$) can react with oxygen which is one of the major constituents of the feed gas as follows [27]:

$$\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 \quad k_5 = 7.56 \times 10^{-31} \frac{(T/298)^{-3.64}}{[\text{M}]}.$$  

This intermediate CH$_3$O$_2$ converts NO to NO$_2$ by changing its oxidation state as below [27]

$$\text{NO} + \text{CH}_3\text{O}_2 \rightarrow \text{NO}_2 + \text{CH}_3\text{O} \quad k_6 = 2.8 \times 10^{-12} \exp(285/T).$$  

Methoxy radical (CH$_3$O) formed in (6) reacts with oxygen to generate formaldehyde (HCHO) and HO$_2$ radical. HO$_2$ is a strong oxidizing radical capable of oxidizing NO to NO$_2$ [27]

$$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \quad k_7 = 7.2 \times 10^{-14} \exp(-1080/T)$$  

$$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \quad k_8 = 3.4 \times 10^{-12} \exp(270/T).$$  

Formaldehyde reacts with OH radical to form HCO, which, in turn, gives rise to carbon monoxide and carbon dioxide as [27], [28]

$$\text{HCHO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O} \quad k_9 = 1.66 \times 10^{-11} \exp(-86/T)$$  

$$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2 \quad k_{10} = 3.5 \times 10^{-12} \exp(140/T)$$  

$$\text{HCO} + \text{O} \rightarrow \text{CO} + \text{OH} \quad k_{11} = 5 \times 10^{-11}$$  

$$\text{HCO} + \text{O} \rightarrow \text{H} + \text{CO}_2 \quad k_{12} = 5 \times 10^{-11}.$$  

The other important scheme leading to the oxidation of NO to NO$_2$ are as follows [9]:

$$\text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{C}_2\text{H}_5\text{OH} \quad (13)$$  

$$\text{C}_2\text{H}_4\text{OH} + 2\text{O}_2 + 2\text{NO} \rightarrow 2\text{HCHO} + 2\text{NO}_2 + 2\text{OH} \quad (14)$$

Since these reactions are initiated by OH radical, they are more pronounced when water vapor is present in the feed gas stream.

As explained in (5)–(14), the addition of ethylene can promote the oxidation of NO, and the results obtained in the presence of ethylene are shown in Fig. 7. The presence of ethylene dramatically increased the NO oxidation. Despite the addition of ethylene, however, no reduction in NO$_2$ level was observed just as the case in the absence of it. In Fig. 7, the difference between NO$_2$ and NO concentrations corresponds to NO$_2$ concentration. As mentioned, the changes in the ratio of NO$_2$ to NO may affect the performance of SCR catalyst. In this sense, it can be said that the increase in NO$_2$ portion by the oxidation of NO is important when nonthermal plasma is combined with SCR catalyst. In the meantime, the increase in temperature decreased the oxidation of NO, and accordingly, more energy was required to convert the identical amount of NO at higher temperature. For example, the energy density required to obtain equimolar composition of NO and NO$_2$, i.e., to make both NO and NO$_2$ 150 ppm, were 15, 35, and 45 J/l at 100°C, 150°C, and 200°C, respectively. In the present study, the effect of water vapor on the conversion of NO was not investigated, but in the presence of water vapor much smaller influence of the temperature on the conversion of NO was reported [30].

Fig. 8 shows the concentrations of unreacted ethylene emitted from the plasma reactor. As observed, the concentration of ethylene was higher at higher reaction temperature. According to
the previous results, the decomposition of ethylene is mainly caused by the active species such as \( O, OH, \) and \( O_3 \). However, since this temperature range is too high to form ozone and in addition there is no water vapor, the reaction of ethylene with \( O \) radical dominates the decomposition. Since this reaction decreases with temperature [27], higher concentration of ethylene was observed at higher temperature. From (7) to (14), it can be seen that ethylene, while taking part in NO oxidation reactions, gives rise to some byproducts such as \( CO, CO_2, \) and \( HCHO \). Among these byproducts, \( CO \) and \( HCHO \) are known as harmful pollutants. The formation of any other byproduct was confirmed to be negligible after analyzing the treated gas by gas chromatograph. Figs. 9 and 10 show the formation of carbon monoxide and formaldehyde. The formation of these byproducts decreases with the temperature, which is in accordance with the results of ethylene decomposition (see Fig. 8).

In general, DBD reactors are energized by ac voltage, however, some researchers have employed pulse energized DBD reactors [20]–[22]. In order to compare the performances of ac and pulse voltages in terms of NO conversion, experiments were carried out using both voltage sources. Fig. 11 compares ac with pulse voltage in terms of NO conversion efficiency as a function of energy density. It was found that the NO conversion efficiencies were almost equal regardless of the type of the voltage applied. Since both voltages perform equally, choice can be made depending on cost, reliability, and compatibility. In the present study, further experiments were conducted using ac voltage only.

**B. Plasma Catalytic Reactor**

Fig. 12 shows the concentration profiles of NO and \( NO_2 \) at the outlet of the plasma–catalytic reactor when 300 ppm of ammonia was added. The experimental reproducibility for the plasma reactor was very good. When the catalyst was combined with plasma reactor, however, each experiment conducted at identical condition gave a slightly different result in the NO and \( NO_2 \) concentration. The maximum concentration discrepancy was 10 ppm, corresponding to about 3% removal efficiency (initial \( NO_2 \) concentration: 300 ppm). Although the data in Fig. 12 are the average values of the data repeated several times, they may include some experimental errors. Referring to the literature [6], [11], the gas mixture should contain \( NO_2 \) for efficient catalytic removal of \( NO_x \) because the adsorption capability of
NO\textsubscript{2} is larger than that of NO. When ammonia is added as a reducing agent, NO\textsubscript{2} not only reacts with the gas phase NO fast, but is also easily decomposed into nitrogen as follows [10], [31]:

\[
\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad (15)
\]

\[
6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}. \quad (16)
\]

Equation (15) implies that the concentrations of NO and NO\textsubscript{2} should be equal, and (16) signifies the importance of NO\textsubscript{2}, which reaches a conclusion that at least the concentration of NO\textsubscript{2} should be the same with that of NO. The results in Fig. 12 clearly show the significance of the plasma discharge in the removal of NO\textsubscript{x} on catalyst. For example, in the absence of plasma discharge, the catalyst removed 40%, 46%, and 70% of NO\textsubscript{x} at 100 °C, 150 °C, and 200 °C, respectively. In the presence of plasma discharge, NO\textsubscript{x} removal was nearly 80% at all temperatures at an energy density of 40 J/l. Since the plasma reactor alone hardly gave any reduction in NO\textsubscript{x} level as shown in Fig. 7, it can be said that the enhancement in the NO\textsubscript{x} removal efficiency in the presence of plasma discharge resulted from the increase in NO\textsubscript{2} concentration. Such synergistic effect is more significant as the temperature decreased, which indicates that the performance of SCR can largely be enhanced especially at low temperatures. The removal efficiency of 80% is tantamount to an energy yield of 42-eV/NO\textsubscript{x} molecule. Miessner et al. [31] reported that with an energy input of about 30 eV/NO\textsubscript{x}-molecule, 500 ppm NO was reduced by more than half at a temperature of 300 °C. Bröer and Hammer [10] showed that with an energy input of 20-eV/NO\textsubscript{x} molecule a NO\textsubscript{x} reduction of more than 85% was achieved at temperatures above 160 °C, and at 130 °C about 50% reduction. This value of 20-eV/NO\textsubscript{x} molecule is higher than that obtained here, but the energy yields cannot directly be compared because the catalyst, the initial concentration of NO\textsubscript{x} and the operating condition are different one another.

As observed in Figs. 9 and 10, significant amounts of formaldehyde and carbon monoxide as a result of ethylene decomposition were emitted from the plasma reactor. These byproducts were also measured at the outlet of the plasma-catalytic reactor, and the results are shown in Fig. 13. Formaldehyde was found to be completely removed on the catalyst surface, i.e., the concentration was always zero in this experimental condition. Besides, in the gas chromatogram obtained by using the flame ionization detector, no peaks other than ethylene were observed, implying that no organic species were formed from ethylene. On the other hand, the emission of CO at the outlet of the plasma-catalytic reactor was significant, especially at high temperature. Further studies are thus required to bring down the CO level to allowable limit for practical application of this system. Otherwise, the use of another additive capable of promoting the oxidation of NO to NO\textsubscript{2} without evolving CO may be preventive measures against this problem. One candidate of chemical additive for this purpose may be hydrogen peroxide [32].

The emission of unreacted ammonia is called as ammonia slip that should be kept as low as possible. An attempt was made to minimize the NH\textsubscript{3} slip by decreasing the ratio [NH\textsubscript{3}]/[NO\textsubscript{x}] from 1.0 to 0.8 (see Fig. 14). As the concentration ratio of ammonia to initial NO\textsubscript{x} decreased, the ammonia slip decreased while retaining almost similar NO\textsubscript{x} removal efficiency. At a ratio of 0.8, for example, the NO\textsubscript{x} removal was decreased by only 4% with the corresponding decrease of 30 ppm in NH\textsubscript{3}. This drop in NH\textsubscript{3} slip without compensating much of the NO\textsubscript{x} removal efficiency suggests the existence of other removal pathways involving ethylene and formaldehyde present in the gas mixture. According to the literature [12], formaldehyde can take part in the reduction of NO\textsubscript{x} on the catalyst. It is believed that similar phenomenon took place in this system, too. If other removal pathways do not exist, negligible NH\textsubscript{3} slip should be observed because the amount of NH\textsubscript{3} added is nearly equal to that of NO\textsubscript{x} removed. The other plausible reason that may account for the ammonia slip is the release of NH\textsubscript{3} stored in the catalyst. The stored ammonia may contribute significantly to the ammonia slip and the NO\textsubscript{x} reduction. Since the results in Fig. 14 are not the values taken by allowing sufficient time, further experimental verification for an extended time should be performed.
IV. CONCLUSION

The following conclusions were drawn from the present studies on the plasma-catalyst combination system.

1) NO conversion efficiencies were found to be almost equal regardless of the applied voltage types such as ac and pulse.

2) For the effective NO oxidation using plasma reactor at high temperature, it is necessary to add an additive such as ethylene to the gas mixture.

3) The important role of plasma reactor in the plasma catalytic reactor is mainly to oxidize NO to NO2. The selective catalytic reduction of NO2 was largely enhanced when the gas mixture consisted of both NO and NO2.

4) With catalyst alone, the NO2 reduction was 40%, 46%, and 70% at 100 °C, 150 °C, and 200 °C whereas with plasma-catalytic reactor the NO2 removal efficiency was around 80% at all temperatures that are much lower than typical reaction temperature of selective catalytic reduction. With the plasma reactor alone, almost no reduction in NO2 level was observed. The differences between the summation of individual NO2 removal efficiencies of plasma and catalytic reactors, and the removal efficiencies of the plasma-catalytic reactor were 40%, 34%, and 10% at 100 °C, 150 °C, and 200 °C, respectively. The removal efficiency of 80% at an energy density of 40 J/l corresponds to an energy yield of 42 eV/NO2-molecule.

5) One of the main byproduct, formaldehyde produced in the plasma reactor was decomposed completely in the plasma-catalytic reactor. This may be an indication that the formaldehyde can take part in the NO2 removal. However, significant amount of CO emission should be properly managed for the practical application of this process.

REFERENCES


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