$DeNO_x$ treatment in Corona Discharge Field

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Abstract

A mechanism of NO_x reduction by a DC corona discharge was investigated experimentally. A mixture of (N_2/O_2/NO) system was used as a test gas. The compositions such as NO, NO_2 and N_2O etc. were analyzed with FT-IR and NO_x meter. It was found that the characteristics of NO reduction by corona discharge differed remarkably whether or not the oxygen was existing in the mixture. On the spectrum of light emission from corona discharge in N_2 or N_2 + O_2 mixture, some N_2 bands were detected. The ozone produced from an ozonizer was added into the mixture ([NO]=100ppm, N_2 base) to compare the characteristics of $DeNO_x$ reaction in the case of corona discharge. In the case of NO+N_2 mixture, the process of NO reduction was mainly controlled by N_2 radical excited by corona discharge. On the other hand, in the case of NO+N_2+O_2 mixture, NO was converted to NO_2 and N_2O_5 by ozone which yielded by corona discharge.

Key words: Nitrogen oxide, NO reduction, DC corona discharge, Ozone, Active nitrogen

1. Introduction

Recently, nitrogen oxide (NO_x) has been a problem as the cause of air pollution. The removal of NO_x is required urgently. Many studies on the $DeNO_x$ treatment using electric discharge are attracted. Chemical reaction schemes of $DeNO_x$ process in various gases were investigated in electric discharge field ([1], [2], [3]). By using pulsed corona discharge, Mizuno's group carried out NO_x removal test and analyzed the reaction processes in dry and wet type plasma reactor [1]. Dors and Mizeraczyk performed NO_x removal test using DC and pulsed corona discharges [2].

In this study, the effect of existence of oxygen on $DeNO_x$ reaction with a DC corona discharge was investigated. The spectrum of light emission from corona discharge was analyzed on the 90%N_2 + 10%O_2 mixture. Also, concentration of ozone yielded by corona discharge was measured in the mixing of 0-20% of oxygen concentration. On the other hand, the ozone generated by the ozonizer was added to NO mixture and the contribution of ozone for $DeNO_x$ reaction without corona discharge was investigated.

2. Experimental Apparatus and Method

A schematic diagram of the experimental set-up is shown in Fig.1. The corona discharge reactor consists of pyrex glass cylinder (27mm in inner diameter and 500 mm in length) and a straight center electrode (Cu, 0.28mm diameter) and a wire of the ground electrode (SUS304, 0.45mm diameter). A wire ground electrode is winding along the inside wall of the pyrex glass cylinder (winding pitch: 6 mm). Positive or negative DC high voltage is applied to the center electrode by power supply (SPELLMAN, SL-150 Max ± 15kV). The test gas in this experiment is the mixture of N_2 (base), O_2 and NO. O_2 concentration is 10% or 20%. The initial concentration of NO is 100ppm.

Test gas is led to the reactor passing through the mixing chamber after controlling the flow rate by flow meter (KOFLOC, RK1250 SERIES). The flow rate of test gas is fixed at Q=1.0 L/min and the residence time in the reactor is

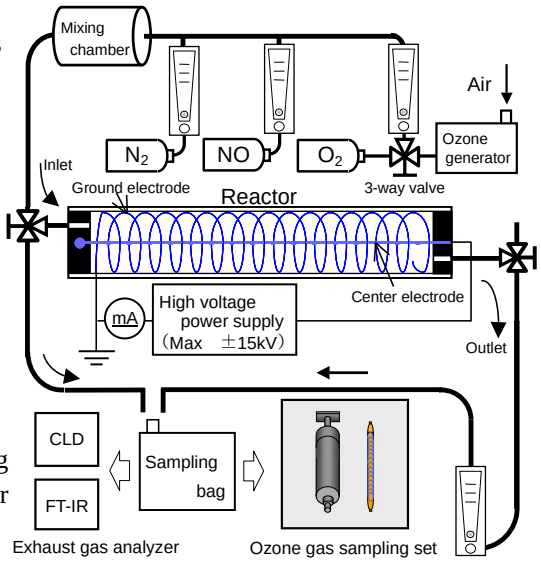

Fig. 1 Experimental set-up

17sec (Space Velocity S.V.=210 h^{-1}). The gas is collected by sampling bag after corona discharge treatment and analyzed with FT-IR (HORIBA, MEXA-4000FT) or engine exhaust gas analyzer (TOSHIBA, BECKMAN, CAREX-16EO).

The analyzed components are NO, NO_2 and N_2O. NO_x was defined as the sum of $NO+NO_2+N_2O$ in this study. In the experiment of ozone addition without corona discharge, ozone and air mixture is supplied by an ozone generator (INPUL, ITB-IMN-BE). It was mixed with the test gas at the ratio of 50 : 50. The concentration of ozone is measured by using gas detector tube (GASTEC, 18M). The spectrum of light emission by corona discharge is analyzed by means of spectrometer (OTSUKA, PRAS-5000).

3. Results and Discussion

3.1 NO_x removal by corona discharge in $NO+N_2$ mixture

The intensity of corona discharge could be evaluated by the electric current to maintain the discharge. The onset of corona discharge was defined as imaginary point of 0 mA (I=[0]). The relationship between electric current and NO_x concentration when corona discharge is supplied on $NO+N_2$ mixture is shown in Fig.2. With an increase of the current, NO concentration decreased to 80-70 ppm, while NO_2 increased to about 10ppm and N_2O was detected slightly. From the result, more than 20% of the initial NO concentration was removed.

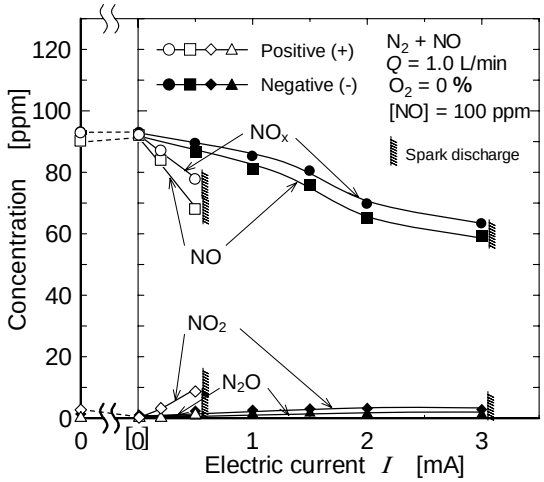

Fig.2 Variation of NO concentration by corona discharge in $NO+N_2$ mixture

3.2 NO_x removal by corona discharge in $NO+N_2+O_2$ mixture

Figure 3 shows the relation between NO_x removal and electric current in case of corona discharge in (NO=100ppm, N_2=90%, O_2=10%) mixture. (a) is the case of positive corona discharge and (b) is negative one. In the case of positive corona discharge (a), NO concentration decreased rapidly with an increase of the electric current. Conversely, NO_2 increased rapidly. N_2O was produced to the level of 10ppm. Beyond the condition of I=1.0mA, it was considered that most of NO was converted to NO_2. For this reason, the NO_x did not decreased.

On the other hand, in the case of negative corona discharge (b), NO_2 increased with the increase of electric current and then rapidly decreased at above I=0.5mA. N_2O increased gradually with increase of the current. Since N_2O was increased simultaneously with rapid reduction of NO_2, the conversion of NO_2 to N_2O was supposed. As the result, NO_x concentration decreased from 100ppm to 10ppm.

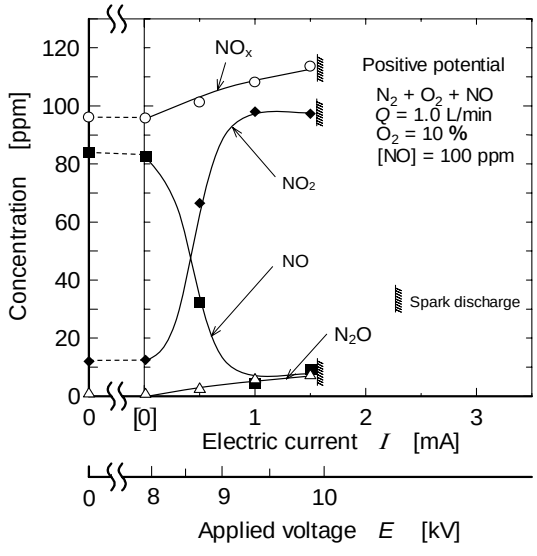

Fig.3(a) NO reduction by positive corona discharge in $NO+N_2+O_2$ mixture

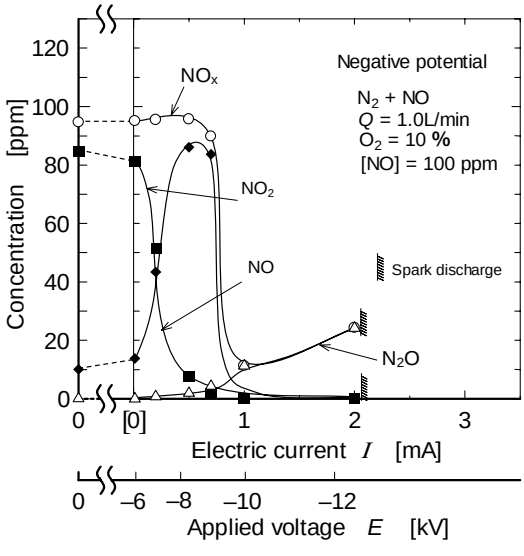

Fig.3(b) NO reduction by negative corona discharge in $NO+N_2+O_2$ mixture

3.3 Spectrum of light emission from corona discharge

The spectrum of light emission from corona discharge was analyzed to clear the mechanism of $DeNO_x$ process. Figure 4 is an example of the spectrum in the case of $90\%N_2+10\%O_2$ mixture under negative corona discharge (E= -10.5kV, I=2.0mA). Some spectrum bands of N_2 and N_2^+ were detected. It was considered that N_2 molecule in the mixture was excited by corona discharge and it might be converted to N radical. However, the spectrum band of O_2 and O radical could not be detected because O_2 band spectrum was very weak and close to N_2 band spectrum [4].

According the above discussion, the following reactions are guessed:

$$N_2 + e \rightarrow N + N + e \quad (1)$$

$$NO + N \rightarrow N_2 + O \quad (2)$$

Where e is electron. NO_2 is formed by:

$$NO + O \rightarrow NO_2 \quad (3)$$

Also, N_2O is formed from N radical as follows [5]:

$$NO_2 + N \rightarrow N_2O + O \quad (4)$$

3.4 Ozone formation by corona discharge

It is well known that ozone is formed by corona discharge in the mixture containing oxygen. The process of ozone formation is expressed as follows:

$$O_2 + e \rightarrow O + O + e \quad (5)$$

$$O_2 + O + M \rightarrow O_3 + M \quad (6)$$

Where M is a third-body collision partner. Figure 5 is the relationship between electric current of corona discharge and ozone concentration under various O_2 concentrations. When oxygen was not exist (N_2=100%), ozone was not produced at all. The higher electric current and/or oxygen concentration, the more ozone concentration increased. Further, the ozone concentration in negative corona discharge was about 10 times higher than that of the positive. It was considered for this phenomenon that the discharge range on center electrode for negative corona discharge became wide and direction of an electron motion differed by the polarity [6]. The ozone is reacted with NO as follows:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (7)$$

Also, N and O radicals produced by corona discharge are reacted as follows:

$$NO + O \rightarrow NO_2 \quad (8)$$

$$N_2 + O \rightarrow N_2O \quad (9)$$

$$NO_2 + N \rightarrow N_2 + O_2 \quad (10)$$

It was considered that the O_3, O and N were all reactive species to contribute the $DeNO_x$ reaction.

3.5 $DeNO_x$ treatment with ozone addition

The ozone produced by an ozonizer was added into the mixture of NO (NO=100ppm, N_2 base) to

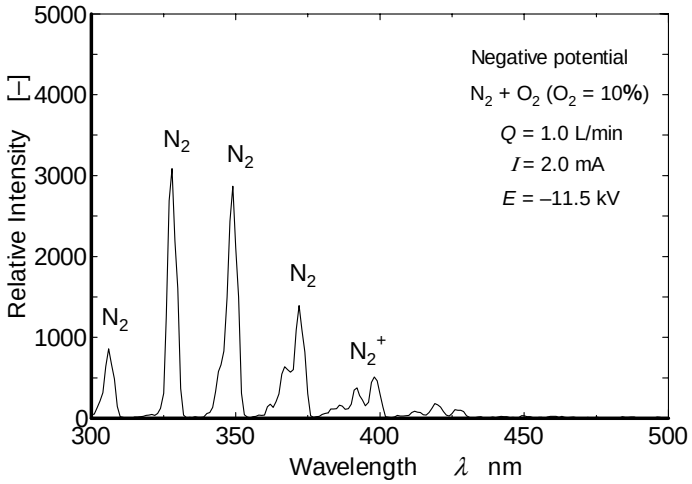

Fig.4 Spectrum of light emission in corona discharge field

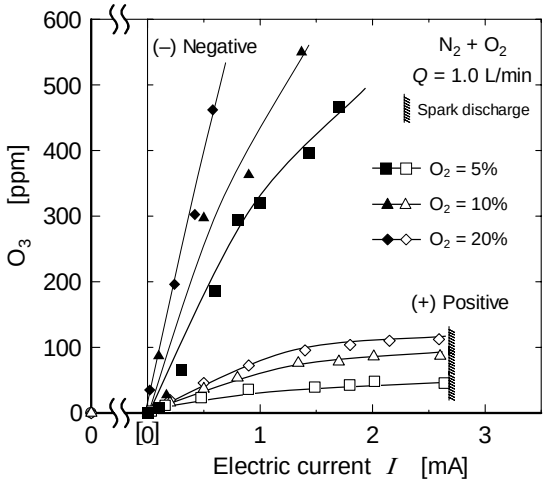

Fig.5 Effect of polarity on ozone produced by corona discharge

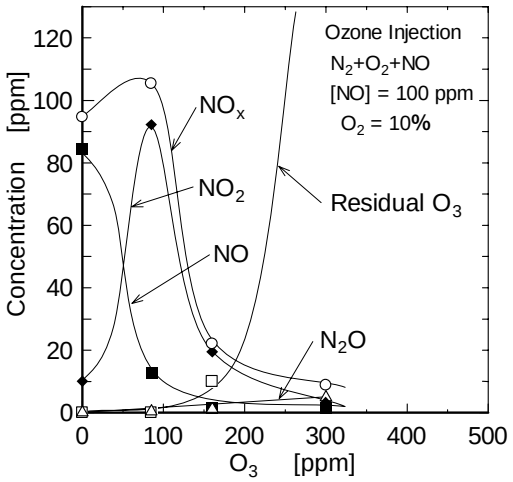

Fig.6 Effect of ozone produced by ozonizer on NO removal

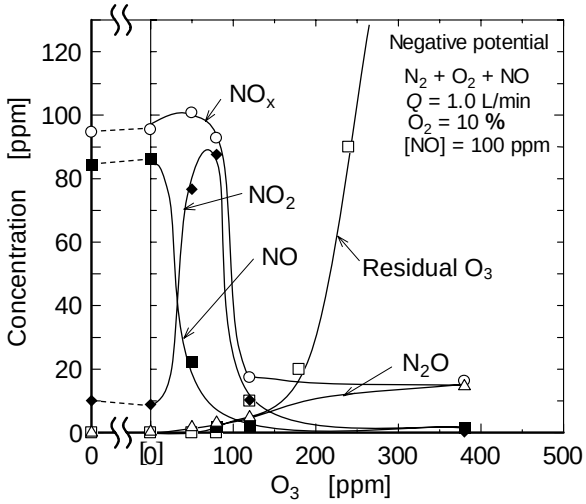

Fig.7 Effect of ozone produced by negative corona discharge on NO removal

separate the effect of pure ozone from the effect of discharge. Figure 6 shows the effect of ozone concentration on NO removal. When the ozone concentration was less than 100ppm, the conversion from NO to NO_2 was enhanced with an increase of the ozone concentration. Farther increase of ozone concentration, the reduction NO_2 concentration was started at the point that the ozone concentration increased over 100 ppm, and it continued until 150ppm. When the ozone concentration increased over 150ppm, residual ozone increased rapidly. From the result, when ozone concentration increased, NO was oxidized by ozone and then NO_2 continued to increase in proportion to the in ozone concentration until NO was completely vanished. Furthermore, it was supposed that NO_2 was decreased by the following reactions:

$$2NO_2 + O_3 \rightarrow N_2O_5 \qquad (11)$$

In this study, however, N_2O_5 could not be measured.

Characteristics of NO removal with ozone produced by corona discharge was compared with that of NO removal with ozone produced by ozonizer. Figure 7 shows the NO_x concentration vs O_3 concentration, in which the horizontal axis of Fig.5 was replaced into the ozone concentration. Comparing Figs 6 and 7, the tendencies of NO removal were almost the same. The residual ozone concentration in the case of NO removal by corona discharge was slightly higher than the case of NO removal by using the ozonizer. It was considered that N radical contributed to the reduction of NO_2 through chemical reaction (10). Consequently, in case of corona discharge with in the mixture of $90\%N_2+10\%O_2$, ozone and N radical acted significantly to $DeNO_x$ reaction.

4. Conclusions

The $DeNO_x$ treatment using DC corona discharge for mixture of $NO+N_2+O_2$ was studied experimentally, and the following results were obtained.

1. The mechanism of NO removal by corona discharge differed by the existence of oxygen in the mixture.
2. In the spectrum of light emission from corona discharge, the strong bands of N_2 and N_2^+ were detected.
3. The large amount of ozone was produced by negative corona discharge in the oxygen containing mixture.
4. In $NO+N_2+O_2$ mixture, N_2 radical and ozone produced by corona discharge contributed to NO removal dominantly.

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