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NOx Removal Using Nitrogen Gas Excited by Dielectric Barrier Discharge at Atmospheric Pressure

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ABSTARCT

The NO removal was carried out using injection of the nitrogen gas, which was excited by the dielectric barrier discharge with a one-cycle sinusoidal-wave power source. The discharge was intermittently formed between coaxial cylindrical electrodes with a space of 1.5 mm at an applied peak-to-peak voltage of 20-45 kV. The measured NO reduction was discussed on the basis of the electrical characteristics of the intermittent dielectric barrier discharge. Different from the NO reduction by ammonia radicals, NO was reduced at the measured lowest temperature, 300 ℃. NO reductions at 25 and 30 kV are nearly proportional to the repetition rate, while the increase in reduction at an applied voltage above 35 kV decreases with increasing repetition rate.

KEYWORDS: NOx, Dielectric barrier discharge, Radical, Lissajous figure

1. INTRODUCTION

NOx emission from thermoelectric power plants, diesel automobiles and so forth is an urgent problem that must be solved. For large-scale NOx removal using ammonia radicals, the electrical discharge methods have been utilized in addition to the electron-beam irradiation method[1,2]. The plasma processes have attracted attention because of their low equipment costs and simple process. In most NOx removal systems using the plasma process, the plasma is generated in a mixed state of NOx and a reaction gas such as ammonia, in which the generated radicals efficiently convert NOx into harmless gases such as N_2, O_2 and H_2O[3-5]. The mixed state production of the plasma is disadvantageous for scaling up the equipment.

Harmless reaction gas instead of ammonia is desirable from the viewpoint of environmental protection. As the plasma process, the dielectric barrier discharge (DBD, silent discharge)[5,6], the corona discharge[4.6] and the surface discharge have been reported.

In this study, the radicals were generated in a separate chamber and injected to the mixing zone of the reaction chamber[7]. Nitrogen gas was used as a radical source, because harmless nitrogen gas requires no treatment after nitric oxide (NO) reduction. The nitrogen plasma was generated by dielectric barrier discharge at atmospheric pressure[6], which was driven by self-extinguishing very short pulses of high voltage, thus creating short-lived discharge. The discharge consists of energetic electrons, which efficiently produce the radicals for the NOx removal. Additional advantages of the dielectric barrier discharge are that the durable years of the apparatus are prolonged, because the materials, which are inert to NOx, can be used as dielectric materials.

In the binary N_2-NO mixture, it is often believed that NO is reduced to N_2 through collisions with N atoms produced during the discharge by electron excitation collisions of the nitrogen molecule. This result has been deduced from experiments on NO removal using corona or dielectric barrier discharge, i.e., filamentary discharges, and comparison of measurements to results of models that treat all quantities as volume averaged. Recently, Rozoy et al.[8] showed that the N density analytically estimated from the electrical parameters are about a factor of four lower than those deduced from laser induced fluorescence measurements on NO.

According to Fresnet et al.[9] the main reaction pathways for NO removal are

$$NO + N_2(a'^1 \Sigma^- u) \rightarrow N + O + N_2 \qquad (1)$$

and

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

where $N_2(a'^1 \Sigma^- u)$ represents N_2 in metastable state, It has potential energy (8.52 eV), which is lower than dissociation energy of N-N combination (9.76 eV) but is higher than the dissociation energy of N-O combination (6.54 eV).

2. EXPERIMENTAL

Figure 1 shows a schematic diagram of the NOx reduction system using nitrogen plasma by intermittent dielectric barrier discharge. NO was diluted with nitrogen gas. It flowed through the process chamber, which was externally heated by two electric heaters. The concentrations and flow rates of NO and N_2 were adjusted in the gas blender by mixing with nitrogen. The adjusted NO gas was fed to the reaction chamber, and the adjusted N_2 gas was fed to the radical injector. The reaction temperature was varied from 300 to 800 ℃. It was measured at the mixing zone in the reaction chamber by a thermocouple.

A schematic diagram of the radical injector is shown in **Fig. 2.** The electrodes are coaxial in configuration with quartz glass tubes as dielectric materials. The outer glass tube is 61 mm in diameter and 2 mm thick,

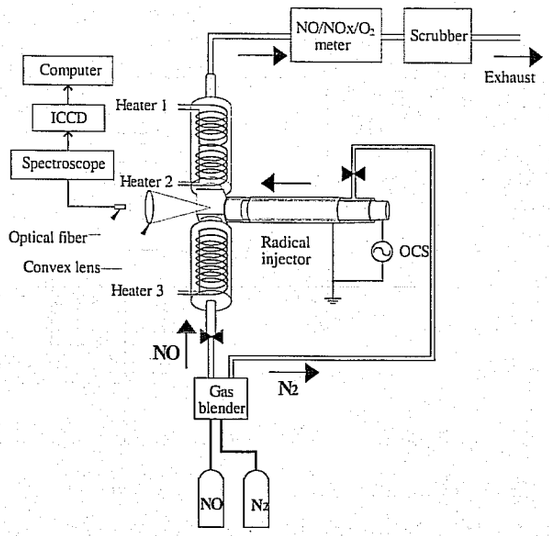


Fig.1 Schematic diagram of experimental apparatus.

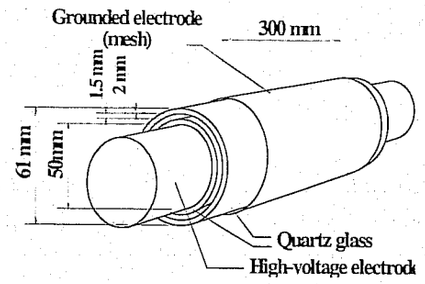


Fig.2 Radical injector and its dimensions.

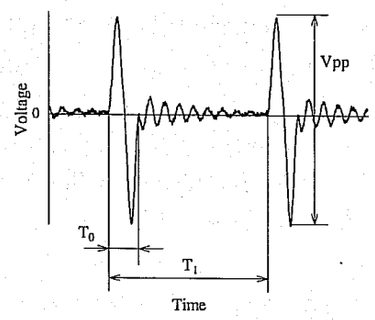


Fig.3 Waveform of voltage supplied from OCS power source.

while the inner glass tube is 50 mm in diameter and 2 mm thick. Thus, the gap between the outer and inner glass tube is 1.5 mm. The dielectric barrier discharge occurred at the gap. The grounded outer electrode is made of a mesh steel sheet, and the inner electrode made of stainless steel. **Fig. 3** schematically shows the waveform of the applied one-cycle sinusoidal (OCS) voltage. The repetition rate R_R is defined as the reciprocal of the repetition time T_1 of the discharge. T_0 was approximately 10 μs, and R_R was varied from 3 to 14 kHz. That is, the OCS voltage was intermittently applied to the gap for a duration of 10 μs at a repetition rate of 3 to 14 kHz.

Figure 4 shows a schematic diagram of the electric circuit for producing a dielectric barrier discharge and for measuring electric characteristics. The output peak-to-peak voltage of the power supply was 20 to 45 kV. The voltage was raised by a pulse transformer (winding ratio of 1:15). The time evolutions of source voltage, current and accumulated charge were simultaneously monitored with an oscilloscope.

The energy input during one cycle of the dielectric barrier discharge was estimated from the accumulated charge and voltage across the output windings of the transformer using the *V-Q* curve of the Lissajous figure. In general, the plasma discharge power *P(t)* is obtained from the product of the instantaneous current *I(t)* and the applied voltage *V(t)*,

$$P(t) = I(t)V(t) \tag{3}$$

The accumulated charge was obtained from the voltage $V_c(t)$ across a series capacitor C_0 = 16 nF (C_0 >> C_d and C_{gap}) that was connected on the side of the ground in a circuit.

$$I = C_0(dV_c / dt) \tag{4}$$

Therefore,

$$P(t) = C_0 (dV_c / dt) V(t) \qquad (5)$$

When $V(t)$ is independent of time and is constant V^*, an integration of Eq. (5) from $t = 0$ to the half period τ yields,

$$\int_0^{\tau} P(t)dt = V^* \int_0^{\tau} dQ = V^* Q . \qquad (6)$$

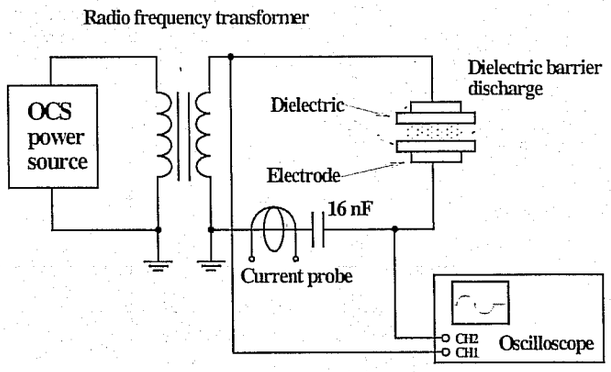


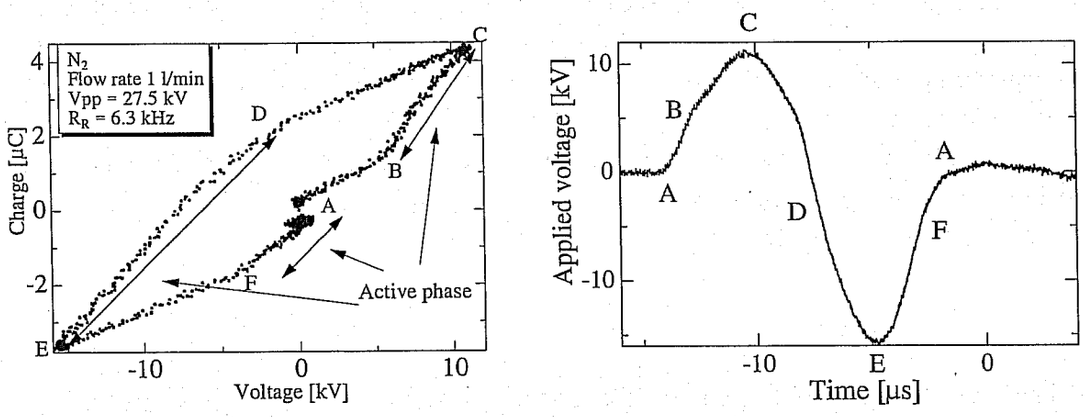
Fig.4 Circuit for measurements of electric characteristics.

Thus, the energy consumed by plasma, E, which is expressed by the first term of Eq.(6), is equal to the product of the minimum dischargeable voltage V^* and the charge Q accumulated in a series capacitor C_0 Therefore, E multiplied by 2, which is equal to the area enclosed by the charge-voltage curves in the Lissajous figure, indicates the input energy during one cycle of the dielectric glow-like discharge. The input energy multiplied by the repetition rate yields the power consumed by the discharge.

3. RESULTS AND DISCUSSION

3.1 Lissajous Figure

A visual observation of the plasma in the radical injector showed no feature of the filamentary discharge, and the current waveforms observed with the oscilloscope showed no series of spikes, which are characteristic of the filamentary discharge. These facts strongly suggest that the plasma is a diffused glow-like discharge. **Fig. 5** shows a *V-Q* curve of Lissajous figure for the discharge in N_2 at an applied voltage of 27.5 kV and at a N_2 flow rate of 1 l/min. The slope of the curve represents the composite capacitance of both the dielectric material and the gap. Thus it becomes small when discharge occurs. During the cycle



(a) Lissajous figure (b)Voltage waveform

Fig.5 *V-Q* Lissajous figure and the voltage waveform.

starting from point A corresponding to the point A in voltage waveform, the discharge occurs only during active phases in one cycle, as shown by B-C, D-E and F-A. The Lissajous figure is not like a parallelogram, which is a typical form for dielectric barrier discharge. This is because the voltage wave is not a stationary ac waveform but intermittent one cycle sinusoidal one with a period of 10 μs. The area enclosed by the charge-voltage curves in the Lissajous figure indicates the input energy during one cycle of the dielectric glow-like discharge. The input energy per one cycle of discharge in **Fig. 5** was about 60 mJ, and the discharge power was about 380 W at the repetition rate of 6.3 kHz.

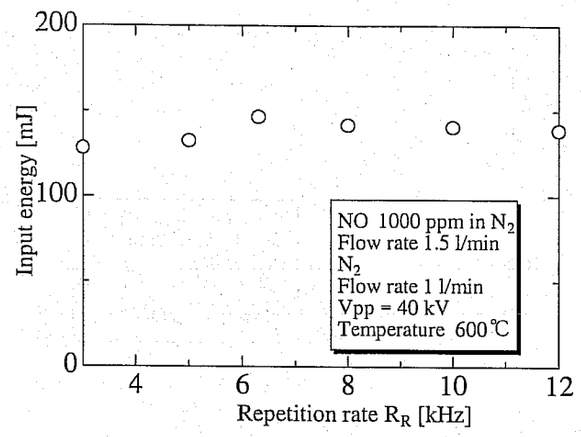


Fig.6 Input energy per one cycle as a function of repetition rate.

Figure 6 shows the input energy per one pulse as a function of the repetition rate R_R. The input energy is independent of the repetition rate and is about 130 mJ. Thus, the discharge power, which is obtained by multiplying the repetition rate by the input energy, is proportional to the repetition rate.

3.2 NO Reduction

Figure 7 shows the NO reduction as a function of reaction temperature. NO is reduced at the measured lowest temperature, 300 ℃. When the discharge was switched off, NO was not reduced at these temperatures. The measured low temperature indicates that NO reduction reaction of this study is triggered only by plasma effect. In addition, the variation of NO reduction with reaction temperature suggests that the reduction reaction; Eq. (2) weakly dependent on reaction temperature. It is contrary to the reduction reaction with ammonia radicals[10].

The ammonia radicals do not reduce NO at a temperature below 500 ℃; it is partly reduced at a temperature above 500 ℃, and is completely reduced at about 600 ℃. The nearly constant reduction at temperatures above 700 ℃ suggests that the reaction is limited by the quantity of $N_2(a'^1\Sigma^-u)$ and N. Work is in progress to increase the quantity of $N_2(a'^1\Sigma^-u)$ and N in the experiments. The following results were obtained at a temperature of 600 ℃.

Figure 8 shows the NO reductions for various applied voltages as a function of repetition rate. For each applied voltage, the NO reduction increases with increasing repetition rate. The NO reductions at 25 and 30 kV are nearly proportional to the repetition rate, while the increase in reduction at an applied voltage above 35 kV decreases with increasing repetition rate. The results at 45 kV indicate the existence of the upper limit of NO reduction at about 40 %.

4. CONCLUSIONS

NO can be removed by injection of the nitrogen gas, which is excited by the dielectric barrier discharge with a one-cycle sinusoidal-wave power source. Different from the NO reduction by ammonia radicals, NO can be reduced at a temperature of 300℃. NO reductions at 25 and 30 kV are nearly proportional to

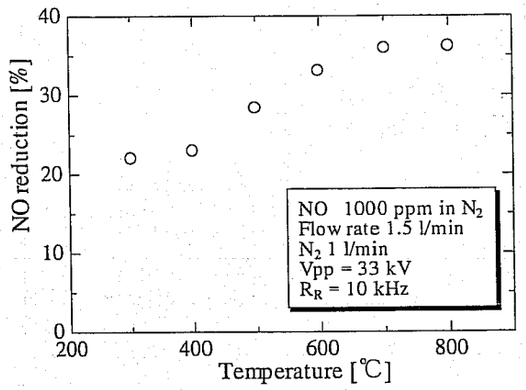


Fig.7 NO reduction as a function of reaction temperature.

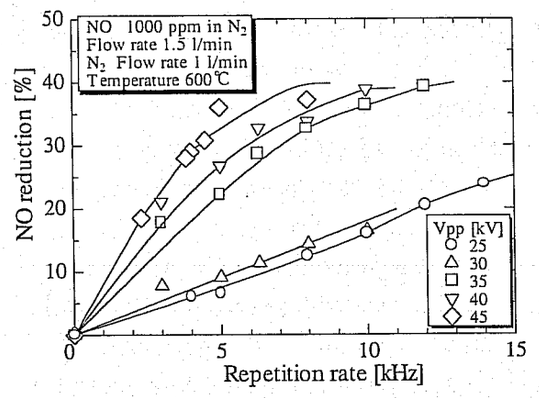


Fig.8 NO reduction as a function of repetition rate.

the repetition rate, while the increase in reduction at an applied voltage above 35 kV decreases with increasing repetition rate.

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