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Reduction of nitrogen oxide in N₂ by NH₃ using intermittent dielectric barrier discharge

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NO in N₂ gas was removed by injecting ammonia radicals, which were externally generated by flowing the NH₃ gas diluted with Ar gas through dielectric barrier discharge with a one-cycle sinusoidal-wave power source. The NO reduction for changes in both the applied voltage and the repetition rate was well correlated with the discharge power, which was proportional to the total discharge time per unit time. There was an optimum NH₃ concentration in the narrow concentration window for the energy efficiency of NO reduction at a fixed discharge power. The maximum energy efficiency was obtained at small values of the NH₃ concentration and the discharge power. The low NH₃ concentration effectively increased the energy efficiency by drastically decreasing the discharge-firing voltage. © 2001 American Institute of Physics. [DOI: 10.1063/1.1394902]

I. INTRODUCTION

The thermal reduction and elimination of the nitrogen oxide (NOₓ) from postcombustion gases via ammonia (NH₃) addition have been used in burning technology. Modeling results of the thermal de-NOₓ process are particularly sensitive to the branching ratio:

\[
\begin{align*}
\text{NH}_2 + \text{NO} & \rightarrow \text{N}_2 + \text{H}_2 \text{O}, \\
\text{NH}_2 + \text{NO} & \rightarrow \text{NH}_3 + \text{OH}.
\end{align*}
\]

Equation (1) gives a termination reaction, while Eq. (2) indicates a source of OH as well as H (from NHN dissociation). These radicals are key to sustaining the chain reaction. Recently, nonthermal plasma processes were proposed to use for the NOₓ removals at lower temperatures. The plasma processes have attracted attention because of their low instrumental costs and simple process, where the plasma-induced radicals efficiently convert NOₓ into harmless gases such as N₂, O₂, and H₂O. Nonthermal plasmas can be produced either by electron-beam irradiation or by electrical discharge method. Concerning electrical discharge methods, the plasma is produced in the discharge volume, where the reaction gas molecules were externally generated in a separate chamber of a small volume through electron-impact dissociation and ionization, and were injected in NOₓ gas to reduce/or oxidize the NOₓ molecules. Therefore, the method of radical injection is efficient in large-scale NOₓ removal.

This study concerns the removal via reduction process, while the reported studies have mainly concerned about the NOₓ removal via oxidation process. Kinetic modeling by Zhou et al. indicated that the NH₃ radicals, which are externally generated and injected into flue gas, were capable of reducing a large amount of NOₓ at temperatures well below the limit of the thermal de-NOₓ process. In their experiments NOₓ was reduced by injecting ammonia radicals, which were externally generated by flowing the NH₃ gas diluted with Ar gas through inductively coupled plasma system. Penetrante et al. compared the electrical energy consumption of different kinds of nonthermal plasma reactors with regards to the electron-impact dissociation of N₂ and the subsequent reduction of NO by the nitrogen atom. They showed that the energy cost for reduction of NO, 240 eV, was simply the energy cost for production of N radical.

In this study, NO in N₂ gas was reduced by the ammonia
radicals, which were generated by flowing the NH$_3$ gas diluted with Ar gas through dielectric barrier discharge with a one-cycle sinusoidal (OCS)-wave power source. Ar gas was used to minimize generation negative ions near the discharge zone and to maximize electron impact ammonia dissociations. The ammonia radicals were injected to a reaction chamber, and were mixed with the NO gas diluted with N$_2$. Among the ammonia radicals, NH$_2$, NH, and N, the NH$_2$ radical is considered the primary reducing agent. The NO reduction and its energy efficiency are discussed based on the experimental results for wide ranges of the ammonia concentration and the discharge power of the plasma.

II. EXPERIMENT

Figure 1 shows schematic diagrams of the nitric oxide (NO) reduction system and the radical injector. The system consists of two chambers: one used as an unheated radical injector for producing ammonia radicals, and the other as a heated reaction chamber for decomposing the NO gas by mixing it with the ammonia radicals generated in the radical injector. In this system, the ammonia radicals were produced from ammonia gas without directly exposing the NO gas to the plasma. The NO removal reaction was initiated by injecting the ammonia radical into the reaction chamber.

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, 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 metallic electrodes covered both the outer side of the outer glass tube and the inner side of the inner glass tube. The grounded outer electrode is made of a mesh steel sheet, and the inner electrode is made of stainless steel. The inner electrode can be cooled by tap water during the application of the high voltage. In this study, however, the cooling of the electrode was not needed because of the use of the intermittent power source.

NO gas was diluted with nitrogen, and ammonia was diluted with argon gas. The concentration and flow rate of NO and NH$_3$ were adjusted in the gas blender by mixing with nitrogen and argon gas. The NO concentration was 1000 ppm by volume, and the gas flow rates were 1.5, 2, and 4 l/min. The NH$_3$ concentration was in a range of 0.1%–3% by volume, and the gas flow rates was 0.5 l/min. The adjusted NO gas was fed in the reaction chamber of 50 mm in diameter and 1.3 m long, and the adjusted NH$_3$ gas was fed to the radical injector. The concentrations of NO, NO$_2$, and O$_2$ were measured before and after plasma processing. The concentration of the de-NO$_x$ gas after flowing through the reaction chamber was measured with a NO$_x$ meter (Shimadzu NOA-7000) set at the exit. The data were single point measurements. The NO reduction is defined as the ratio of NO reduced to the initial concentration of NO. During the experiment, the reaction temperature was kept constant in the range of 350–600 °C. The temperature was measured at the mixing area.

The dielectric barrier discharge was produced with an intermittent power source. Figure 2(a) schematically shows the waveform of the applied one-cycle sinusoidal voltage. The repetition rate $R_R$ is defined as the reciprocal of the repetition time $T_T$ of the discharge. $T_T$ was approximately 10 ms, and $R_R$ was 5–50 kHz. That is, the one-cycle sinusoidal voltage was intermittently applied to the gap for a duration of 10 μs at a repetition rate of 5–50 kHz.

Figure 2(b) 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 5–20 kV. The voltage was raised by a pulse transformer (winding ratio of 1:15). The accumulated charge was obtained from the voltage across a series capacitor (16 nF) that was connected on the side of the ground in a circuit. 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. The time evolutions of source voltage, current, and accumulated charge were simultaneously monitored with an oscilloscope.
III. RESULTS AND DISCUSSION

A visual observation of the plasma in the radical injector showed no feature of the filamentary discharge, and the current waveform observed with the oscilloscope showed no series of spikes, which is characteristic of the filamentary discharge. These facts strongly suggest that the plasma is a diffused glow-like discharge. Figure 3 shows the $V-Q$ curve of the Lissajous figure for the discharge at an applied voltage of 10 kV and at a NH$_3$ concentration of 1%. 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 starting from $A$, the discharge occurs only during $B-C$, $D-E$, and $F-A$ in one cycle. The figure is not like a parallelogram, which is a typical form for dielectric barrier discharge. This is because the voltage wave is not ac but intermittent one cycle sinusoidal of a period of 10 $\mu$s. Figure 4 shows the total discharge time and the energy input per one cycle of sinusoidal as a function of the applied voltage. The total discharge time increases with increasing applied voltage, and hits the ceiling of about 8 $\mu$s at above 12 kV. The energy input per one cycle increases with increasing the applied voltage. Thus, the increase in energy input is attributable to the increase of total discharge time at an applied voltage below 12 kV due to a fixed value of energy input per one pulse of discharge, because the voltage applicable to the gap during discharge is fixed by the dielectric electrodes. When the applied voltage was further increased from 18 kV, the shining lines were frequently observed to occur in plasma, and the discharge became unstable. Thus, under the experimental conditions of this study (the applied voltage is below 18 kV) the excitation intensity of plasma is not changed, and the energy input per one cycle is increased by increasing the total discharge time.

Figure 5(a) shows the discharge power at 10 kV as a function of NH$_3$ concentration. The discharge power is approximately constant, i.e., about 23 kW, showing a weak dependence on NH$_3$ concentration. Figure 5(b) shows the discharge-firing voltage as a function of NH$_3$ concentration. The measured discharge-sustain voltage was a little less than the discharge-firing voltage. For pure Ar gas, the discharge-firing voltage is 6.8 V. When a small quantity of NH$_3$ is mixed with Ar gas, the discharge-firing voltage drastically decreases to 2 kV at NH$_3$ concentrations of 0.1%–0.3%, and then slowly increases with increasing NH$_3$ concentration. Thus, the low concentration of NH$_3$ is effective to decrease the discharge power of radical injector. This fact is attributable to the Penning ionization. That is, the excited Ar atoms in metastable state ($4^3P_2$ and $4^3P_0$) ionize NH$_3$ molecules, because the excitation energies (11.55 and 11.72 eV) of Ar($4^3P_2$) and Ar($4^3P_0$) are larger than the ionization energy (10.85 eV) of NH$_3$. It is expected that the dischargeable voltage can be further lowered by the additional mixing of a small quantity of other gas.
Figure 6 shows the NO reduction as a function of reaction temperature. NO is not reduced at a temperature below 500 °C. It is partly reduced at a temperature above 500 °C, and is completely reduced at about 600 °C. When the discharge was switched off, NO was not reduced at these temperatures. It is noted that the electron impacts efficiently dissociate NH₃ at a low temperature, although NH₃ is not thermally dissociated at a temperature below 900 °C. The measured low temperature indicates that the NO reduction reaction of this study is triggered only by plasma effect. The following results were obtained at a reaction temperature of 600 °C.

Figure 7 shows the NO reduction for two kinds of NO gas flow rates as a function of the NO concentration. The NO reduction decreases with increasing NO concentration, the reduction for 4 l/min being lower than that for 2 l/min. All the data, except for that at 1000 ppm for 4 l/min, are well correlated with the solid lines, which show a constant volumetric NO reduction rate of 1.2 cm³/min. That is, the molar NO reduction rate is constant, i.e., $5.36 \times 10^{-5}$ mol/min, for the NH₃ flow rate of $22.3 \times 10^{-2}$ mol/min and is independent of the flow rate and the concentration of NO gas. Thus the NO reduction is not limited by the chemistry of the process, but rather by the ability to generate ammonia radicals effectively and to provide favorable conditions for the introduc-
tion to NO gas flow and mixing with it. The following discussions are based on the results, obtained at the NO concentration of 1000 ppm and at gas flow rates of 1.5 and 2 l/min.

Figure 8 shows the NO reduction and its energy efficiency at a NH$_3$ concentration of 1% as a function of applied voltage $V_{pp}$ and repetition rate $R_R$, respectively. The energy efficiency is defined as the mass flow rate of reduced NO per input electrical power. The results obtained by changing both the applied voltage and repetition rate show the same trend, showing optimum conditions of the discharge for the decomposition of NH$_3$ into the radicals, which reduce NO efficiently. That is, the NO reduction shows the maximum values at a repetition rate of 20 kHz and at an applied voltage of 16 kV, while the energy efficiency shows the maximum values at a repetition rate of 8 kHz and at an applied voltage of 12 kV. Thus, the optimum repetition rate and the optimum applied voltage for the energy efficiency of NO reduction are lower than the corresponding for the NO reduction.

These results for the NO reduction and energy efficiency were replotted as a function of the discharge power in Fig. 9. The NO reduction and the energy efficiency are well correlated with the discharge power. This fact can be explained as follows. The discharge power increases in proportion to the repetition rate, and it increases linearly with increasing applied voltage at a constant repetition rate, as shown in Fig. 4. The former is due to a fixed value of energy input per one pulse, and the latter is attributable to the increase in the number of discharge, because the voltage applicable to the gap during discharge is fixed in dielectric barrier discharge. In other words, the NO reduction is determined by the total discharge time, because the discharge power is proportional to the total discharge time for changes in both the applied voltage and the repetition rate. Figure 9(b) shows that the energy efficiency increases with decreasing the discharge power and that the maximum value is obtained near the lowest discharge power. This fact has been reported also for the NO$_x$ removal via oxidation process, and it is generally known that the energy efficiency in plasma chemical process, such as the conventional NO reduction system, ozonizer, etc., decreases with increasing the power. Therefore, the ammonia radicals should be produced by the electron-impact dissociation of NH$_3$, which is the most energetically efficient way for producing the radicals.

Figure 10 show the NO reduction and its energy efficiency at applied voltages $V_{pp}$ of 4, 8, and 12 kV as a function of NH$_3$ concentration. At each applied voltage, the NO reduction and the energy efficiency depend strongly on NH$_3$ concentration, showing the maximum values at the same value of NH$_3$ concentration. The NH$_3$ concentration windows of effective NO reduction is narrow, suggesting that the fraction of the ammonia radicals (NH$_2$, NH, and N), which are produced by electron-impact dissociation of NH$_3$, de-
pends on the concentration of NH₃, and that the fraction of
the primary reducing agent, NH₂ radical, is larger at the ef-
fective NH₃ concentration. The maximum value of NO re-
duction at each optimum NH₃ concentration decreases but
the maximum value of energy efficiency increases with de-
creasing applied voltage, indicating that a lower applied volt-
age shows the maximum energy efficiency in a way similar
to that for a constant NH₃ concentration as shown in Fig.
9(b). Figure 11 shows the optimum NH₃ concentration for
the energy efficiency of NO reduction as a function of dis-
charge power. The optimum NH₃ concentration weakly de-
pends on discharge power, and decreases with decreasing
discharge power, indicating that a lower NH₃ concentration
is optimum for a lower discharge power.

The highest energy efficiency, 24 g/kWh, was obtained
at a NH₃ concentration of 0.3%, at an applied voltage of 5
kV, and at a repetition rate of 2.5 kHz. The corresponding
specific energy consumption is 46.6 eV per NO molecule.
Penetrante et al. reported the specific energy consumption
of 240 eV per NO molecule; the larger value is attributable to
the larger dissociation energy of N₂ compared to that of
NH₃. A similar value of the energy efficiency, 20 g/kWh, has
been reported for the NO removal via oxidation process in
NO-air mixture using corona discharge, although the disso-
ication energy of O₂ is low compared to those of NH₃.

IV. CONCLUSIONS

NO in N₂ gas can be removed by injecting ammonia
radicals, which were externally generated by flowing the
NH₃ gas diluted with Ar gas through dielectric barrier dis-
charge with a one-cycle sinusoidal-wave power source. The
NO reductions for changes in both the applied voltage and
the repetition rate are well correlated with the discharge
power, which is proportional to the total discharge time per
unit time. There is an optimum NH₃ concentration in the
narrow concentration window for the energy efficiency of
NO reduction at a fixed discharge power. The maximum en-
ergy efficiency is obtained at small values of the NH₃ con-
centration and the discharge power. The low NH₃ concentra-
tion effectively increases the energy efficiency by drastically
decreasing the discharge-firing voltage.

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