

Oxygen Effect of High Concentration NO Removal Using an Intermittent DBD Generation

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ABSTRACT

The reaction schemes of oxygen to NO_x were summarized and deNO_x including oxygen was experimentally carried out. The effect of oxygen in NO/N₂ mixed gas at a NO concentration of 1000 ppm on deNO_x rate was discussed. It was found that the optimal conditions for NO reduction was performed at an oxygen concentration of 2 % and a lower temperature process became possible compared with the case without oxygen.

KEYWORDS: NO removal, DBD, Ammonia radical

1. INTRODUCTION

There are several ways to decompose nitric oxide (NO), which was exhausted from power plants and other burning system such as boilers, e.g., radical injection system into the NO gas and plasma generation of the gas including NO gas. We have developed the former system, where the ammonia radicals are produced in a dielectric barrier discharge (DBD) plasma using an intermittent one-cycle-sinusoidal power source [2]. The maximum energy efficiency was 140 g/kWh without oxygen. The system has features that the radical injector is compact in scale and scaling up is easy by multiple setting to the exhaust pipe. An intermittent one-cycle-sinusoidal power source was employed as the power source for generating DBD.

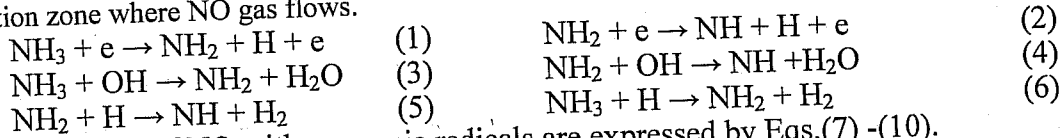
A study on de-NO_x of the NO gas, which contains oxygen (O₂), is important from the viewpoint that the real exhausted gas includes O₂ gas. This paper discusses the de-NO_x of O₂-containing NO gas. A particular emphasis is placed on the dependences of de-NO_x on gas temperature, ammonia flow rate and its concentration, and applied voltage and its repetition rate.

2. EFFECT OF O₂ IN DeNO_x

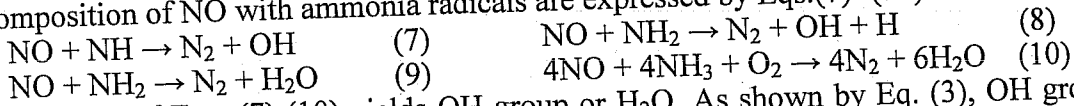
De-NO_x is carried out through reduction by ammonia (NH₃) and its radicals and through decomposition by O₂ atoms and molecules. To show the effects of O₂ in the decomposition of NO_x gas, the reactions with oxygen and ammonia radicals are briefly summarized.

The reactivity of NH₂ radical is largest among the ammonia radicals. The excessive energy generates NH radicals. Both NH radicals and the ground-state NH₃ are not expected to decompose NO_x in comparison with NH₂ radicals. First, the reaction of the NH₂ radical with NO yields N₂, OH group and

H₂O. The produced OH group effectively makes NH₂ from NH₃. These two steps form a kind of chain reaction. Equations (1)-(6) show the reactions for production of ammonia radicals. In radical injection method, the reactions of Eqs.(1) and (2) occur in the plasma and the reactions of Eqs.(3)-(6) occur in the reaction zone where NO gas flows.

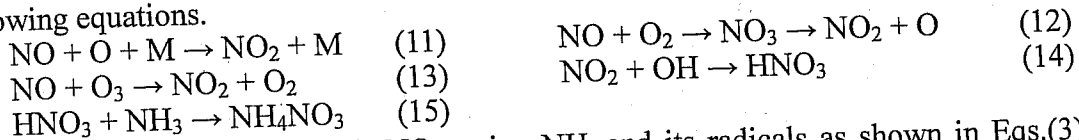


Decomposition of NO with ammonia radicals are expressed by Eqs.(7)-(10).

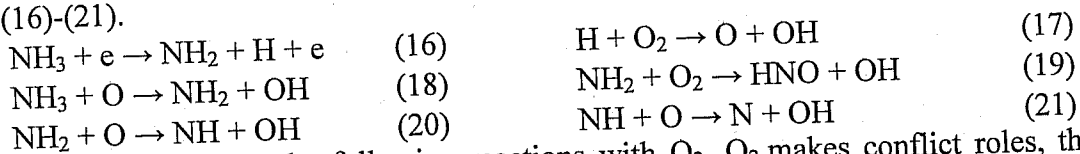


Each reaction of Eqs. (7)-(10) yields OH group or H₂O. As shown by Eq. (3), OH group again produces NH₂ radical, and changes gaseous secondary products into solid form by Eqs. (14) and (15). Thus, NO decomposes in a chain reaction, which makes the de-NO_x system efficient.

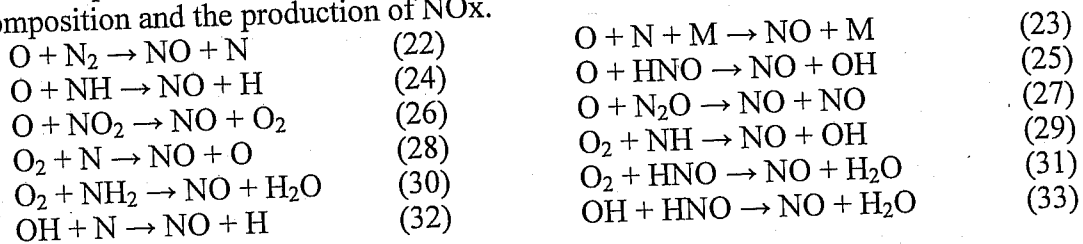
NO is oxidized to NO₂ by O₂ and its radicals. Then NO₂ reacts with OH group and NH₃, and it is removed in the form of final solid product NH₄NO₃. The reactions are expressed by the following equations.



Chain reaction works in de-NO_x using NH₃ and its radicals as shown in Eqs.(3) and (8). This means that OH group production is effective to NO decomposition. O₂ also contributes to NO_x decomposition. When both gases of O₂ and NH₃ coexist, OH group can be produced by the reaction between O₂ and NH₃, as shown Eqs.(3) and (19), which causes a reaction shown in Eq.(9), for example. However, O₂ reproduces NO as shown in Eq.(31) for example. Thus, an optimum O₂ concentration is expected to decompose NO_x. The reactions are expressed by Eqs.(16)-(21).



NO is reproduced by the following reactions with O₂. O₂ makes conflict roles, that is, the decomposition and the production of NO_x.



3. EXPERIMENTAL

Figure 1 shows a schematic diagram of the De-NO_x system. It 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 exposing the NO gas to the plasma. The NO removal reaction was initiated by injecting the ammonia radicals into the reaction chamber. The concentration and flow rate of NO and NH₃ were adjusted in the gas blender by mixing with nitrogen and argon gas. NO and O₂ gases were diluted with nitrogen, and NH₃ gas was diluted with argon gas. The nitrogen gases

contain 920 ppm NO and 20% O₂ by volume, respectively, and the gas flow rate was in a range of 0.98 - 1.48 l/min. The argon gas contains 2720 or 3000 ppm NH₃ by volume, and the flow rates were 0.78, 0.98 and 1.48 l/min. The NO containing nitrogen gas was fed into the reaction chamber of 50 mm in diameter and 1.3 m long, and the NH₃ containing argon gas was fed into the radical injector. The concentrations of NO, NO₂ and O₂ were measured before and after plasma processing. The concentration of the de-NO gas after flowing through the reaction chamber was measured with a NOx 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 gas was heated with electric heaters, which were externally wound to the chamber. As shown in Fig 1, there are three heaters: one before the mixing zone and two after the mixing zone. The temperature at the mixing zone was defined as the reaction temperature.

After the measurements, the gas was exhausted via the treatment with water shower in a gas-processing chamber. For comparison, the experiments on thermal de-NOx were also made, where the maximum temperature of NO gas was 1000 °C without DBD plasma.

A schematic diagram of the radical injector is shown in Figure 2. The details of the injector are described in a recent paper [2]. The dielectric barrier discharge was produced with an intermittent power source. Figure 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 μ s, and R_R was 5 to 50 kHz. That is, the OCS voltage was intermittently applied to the gap for a duration of 10 μ s at a repetition rate of 5 to 50 kHz. The electric circuit for producing a dielectric barrier discharge and for measuring electric characteristics is described elsewhere [2].

4.RESULTS AND DISCUSSION

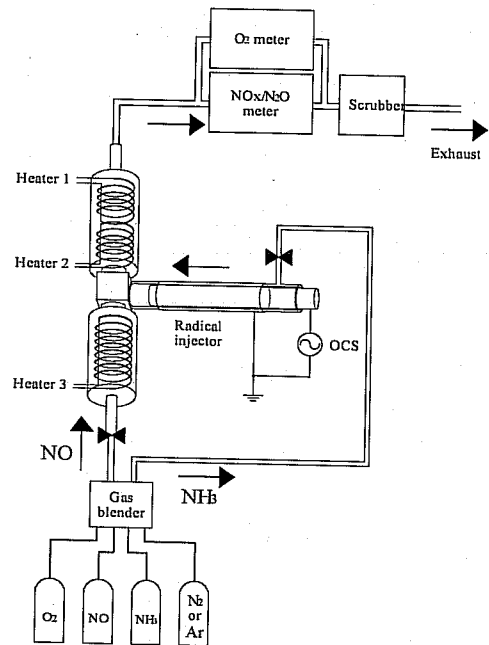


Fig.1 Schematic diagram of experimental apparatus.

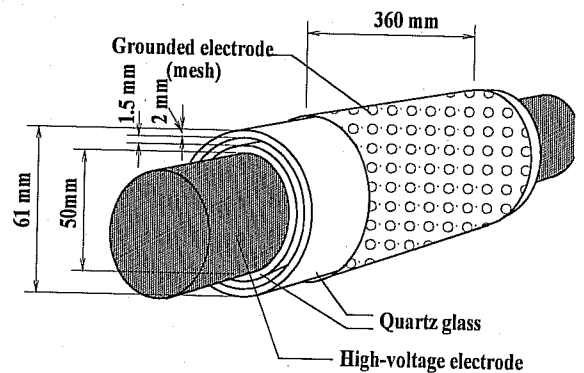


Fig.2 Structure of radical injector.

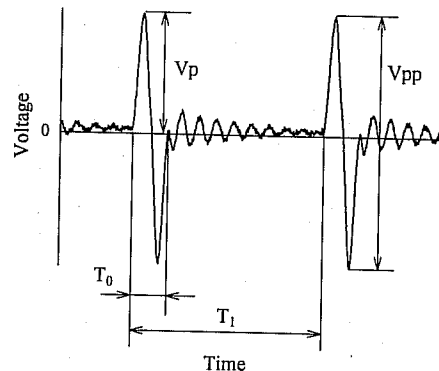


Fig.3 Waveform of voltage supplied from a one-cycle sinusoidal power source.

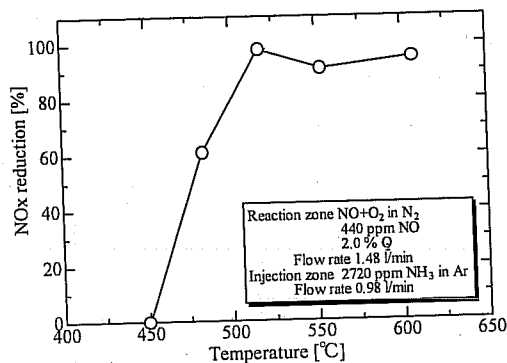


Fig.4 Thermal NO reduction as a function of the reaction temperature.

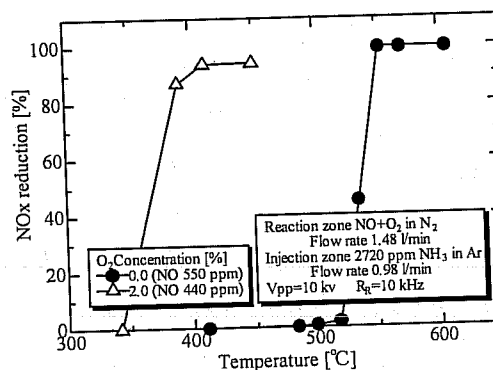


Fig.5 NO reduction with and without O₂ in DBD ammonia radical injection as a function of the reaction temperature.

4.1 Effect of O₂ on thermal deNO_x

The effect of O₂ on thermal de-NO_x was discussed. The reaction temperature was varied from 450 to 620 °C at a NH₃ concentration of 2720 ppm and at a flow rate of 0.98 l/min. The concentration of NO gas was 440 ppm, and the flow rate was 1.48 l/min. **Figure 4** shows NO reduction with and without O₂ as a function of the reaction temperature. Without O₂, NO was not reduced at a temperature below 607 °C. With 2 % O₂, it is partly reduced at a temperature above 450 °C and is completely reduced at about 525 °C. Thus a small quantity of O₂ markedly decreases the reaction temperature in the thermal process. This fact suggests that the production of ammonia radicals through the interacting reactions among NH₃, O₂ and OH group occurs at a temperature far lower than that of the thermal reactions without O₂.

4.2 Effect of O₂ in radical process

Figure 5 shows NO reduction with and without O₂ in DBD ammonia radical injection as a function of reaction temperature. Under the O₂ concentration of 2%, the reaction temperature is lowered by 200°C. This fact suggests that the O₂ promotes elementary thermal reactions of de-NO_x triggered by ammonia radicals at a low temperature. A comparison with the result in Fig 4 shows that the reaction temperature is lower than that of the thermal de-NO_x with O₂. Thus, the inclusion of 2% O₂ is more effective in plasma process than in thermal process. In de-NO_x process using O₂, a white powder of NH₃NO₄ was observed inside the exhaust tube behind the reaction chamber. The following results were obtained at a reaction temperature of 411 °C.

5. CONCLUSION

The inclusion of 2% O₂ lowers the reaction temperatures for both thermal and plasma de-NO_x processes compared to those without O₂. The reaction temperature for plasma process is lower than that for thermal process. An optimum concentration of O₂ in promotion of de-NO_x, might be caused by the production of OH radicals.

REFERENCES

- [1] I. Nagao, K. Yukimura, S. Kambara, and T. Maruyama, "Optimum values for De-Nox by Dielectric Barrier Discharge" The papers of Technical Meeting on Pulsed Power Technology, IEE Japan, PPT-02-1 (2002.3) .
- [2] M. Nishida, K. Yukimura, S. Kambara, and T. Maruyama, Reduction of Nitrogen Oxide in NH₃ Using Intermittent Dielectric Barrier Discharge, J. Appl. Phys., 2001, 90, pp.2672-2677.