Influence of Ratio of NO/NO_2 on NO_x Removal using DBD with Urea Solution

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Abstract: Air pollution due to the exhaust gas from motorcars causes serious environmental problems, so it is necessary to remove NO_x from the exhaust gas. In this study, NO_x removal by dielectric barrier discharge (DBD) with an urea solution without any catalyst at room temperature has been investigated. The NO_x removal rate and NO_x removal efficiency has been measured with and without adding an urea solution. Furthermore, the influence of the ratio of NO and NO_2 on the amount of removed NO_x by DBD with the urea solution in actual apparatus has been measured experimentally. The ratio of NO and NO_2 of an initial mimic exhaust gas was adjusted by DBD treatment. From the results of measurement, it has been found that NO_x removal by DBD with an urea solution is effective and the optimum concentration of the urea solution is 23% in the present study. And it was estimated that the optimum ratio of NO and NO_2 is about 6 to 1 for NO_x removal with an urea solution.

Keywords: NO_x removal, dielectric barrier discharge, urea solution, the ratio of NO and NO_2

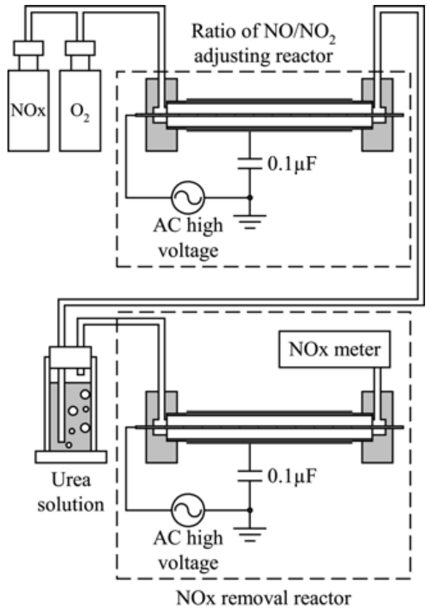
1 INTRODUCTION

The harmful effects of NO_x (NO and NO_2) such as the formations of photochemical smog and acid rain as well as unfavorable effects on a human respiratory system are well known. NO_x is formed in all combustion processes from the high temperature reaction between N_2 and O_2. The selective catalytic reduction (SCR) of NO_x with a reduction agent, i.e. NH_3 is one of the most successful techniques for the removal on NO_x in power generation plants [1]. The NH_3 selectively reacts with NO_x component of an exhaust gas without reacting O_2. However, it would not be possible to use NH_3 on a diesel powered car because it is corrosive, toxic and difficult to store, transport and handle. It has been proposed that NH_3 would be replaced by aqueous solutions of urea ($(NH_2)_2CO$) and much interest has been focused on using as a safer source of ammonia in automotive applications with some catalysts at high temperature [2, 3]. We think that NO_x would be reduced by dielectric barrier discharge with aqueous solution of urea without any catalysts at room temperature. The NO_x removal rate and NO_x removal efficiency has been measured with and without adding urea solution at room temperature in this study. Furthermore, the influence of the ratio of NO and NO_2 on the amount of removed NO_x by DBD with an urea solution in actual apparatus have been measured experimentally.

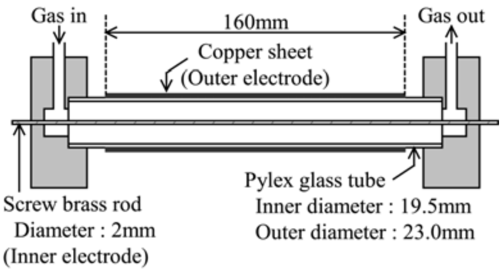
1.1 Measuremental Setup

NO_x removal by DBD with an urea solution

The schematic diagram of NO_x removal by DBD with an urea solution system is shown in Fig. 1. As shown in Fig. 1 (a), the system is composed of gas cylinders, a bubbling pot, a discharge reactor (a ratio of NO/NO_2 adjusting reactor, NO_x removal reactor), and a NO_x meter. NO_x and O_2 were mixed and introduced into the discharge reactor. The bubbling pot was used to add an urea solution to the mix gas. As shown in Fig. 1(b), the discharge reactor is a coaxial cylinder which is consists of a brass screw rod as an inner electrode and a pylex glass tube wrapped with a copper sheet as an outer electrode. The brass screw rod had length of 300 mm and diameter of 2 mm. The pylex glass tube had length of 200 mm, inner diameter of 19.5 mm, and outer diameter of 23.0 mm. DBD was occurred between the inner electrode and the outer electrode by applying AC high voltage with a frequency of 50



(a) Schematic diagram



(b) Discharge reactor

Fig. 1 Experimental setup

Hz to inner electrode. NO_x concentration of the treated gas was measured by NO_x meter (TESTO, testo350III). From the measured NO_x concentration, NO_x removal rate R_x and NO_x removal efficiency η_x were calculated using equation (1) and equation (2).

$$R_x = \frac{C_1 - C_0}{C_0} \times 100\,[\%] \quad (1)$$

$$\eta_x = \frac{Q \times (C_1 - C_0) \times 30 \times 10^3}{P_d \times 22.4}\,[\text{g/kWh}] \quad (2)$$

where C_0 is the NO_x concentration before DBD treatment [ppm], C_1 is the NO_x-concentration after DBD treatment [ppm], Q is the gas flow rate [m^3/h], and P_d is discharge power [kW]. NO_x removal efficiency indicates how many gram of NOx the system can treated per 1 kWh, therefore the system which has high NO_x removal efficiency has high performance.

To simulate an atmosphere including NO_x, a mimic gas with 75% N_2 and 25% O_2 was used. The gas flow rates of N_2 and O_2 were 1 l/min and 0.25 l/min respectively. N_2 contained NO of 780 ppm. The concentration of an urea solution was varied from 9 to 33%.

Measurement of residual NH_3 when using urea solution

Although it has been reported that using NH_3 for NO_x removal is effective, if there is the residual NH_3 in a gas which is treated by DBD, it would be problematical, because NH_3 is poisonous to human. The amount of residual NH_3 in the DBD treated gas was measured by FTIR (IR Prestige 21, Shimazu).

Influence of ratio of NO/NO_2 on NO_x removal

To change ratio of NO and NO_2 of the mimic exhaust gas, a DBD treatment reactor was set before the bubbling pot as shown in Fig. 2. The size of the added reactor was the same with the DBD reactor of the NO_x removal system shown in Fig. 1 (a). AC high voltage applied to the added reactor was varied from 9.5 kV to 12 kV.

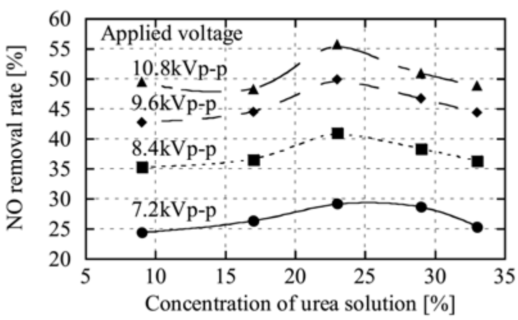


Fig. 2 Dependence of NO removal rate on concentration of a urea solution

Chemical reaction equation during NO_x removal

One of remarkable points of NO_x removal by DBD is that only electrons are accelerated because of very small mass. Gas molecules which have large mass are not accelerated and the temperature of these molecules is not changed. Electrons which get high energy cause chemical reactions by collision with gas molecules. Typical chemical reactions in DBD of NO_x removal are as follows.

$$N_2 + e = 2N + e$$

$$O_2 + e = 2O + e$$

$$NO + N = N_2 + O$$

$$NO + O + M = NO_2 + M$$

$$NO_2 + N = N_2O + O$$

$$NO_2 + O = NO + O_2$$

where e denotes an electron. In the presence of water, the next chemical reactions may also occur.

$$H_2O + e = H + OH + e$$

$$NO_2 + OH + M = HNO_2 + M$$

where M denotes other molecules (i.e. N_2 or O_2). In the presence of an urea solution, additional chemical reactions may also occur.

$$(NH_2)_2CO + H_2O = NH_3 + CO_2$$

$$NO + NO_2 + 2NH_3 = 2N_2 + 3H_2O$$

From these equations, it is expected that NO_x removal would be proceeded effectively for that the stoichiometry ratio of NO and NO_2 is 1 to 1.

1.2 Results and Discussion

Improvement of NO_x removal by adding urea solution

The variation of the NO removal rate when a concentration of an urea solution varied from 9 to 33% is shown in Fig. 2. AC high voltage applied to the inner electrode of the discharge reactor was varied from 7.2 kVpp to 10.8 kVpp. In spite of an applied voltage, the NO_x removal rate was highest when the concentration of an urea solution was 23%.

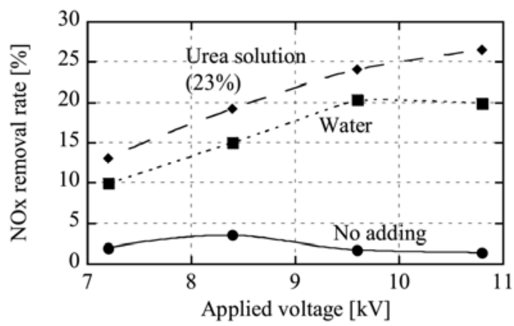


Fig. 3 NO removal rate by DBD treatment with or without a urea solution.

The change in the NO_x removal rate when the applied voltage varied from 7.2 to 10.8 kVpp is shown in Fig. 3. For comparison, the NO_x removal rates with adding pure water and no adding are also shown in Fig. 3. The NO_x removal rate became large in order of no adding, pure water, and the urea solution of 23%. The NO_x removal rates of the urea solution of 23% were larger than that of pure water by 8%. The NO_x

removal rate with an urea solution increased with the applied voltage, however, the NO$_x$ removal rate with pure water was saturated above 9.6 kVpp. In adding the pure water, the NO$_2$ concentration increased by DBD. On the other hand, in adding urea solution, the NO$_x$ concentration was not saturated because NH$_3$ generated from an urea solution removed NO$_2$.

The NO$_x$ removal rate increased with the applied voltage, but the discharge power also increased. The NO$_x$ removal efficiency for each experiment is shown in Fig. 4. The NO$_x$ removal efficiency decreased with the removal rate. It is found that the removal efficiency for an urea solution is highest in the present experiments.

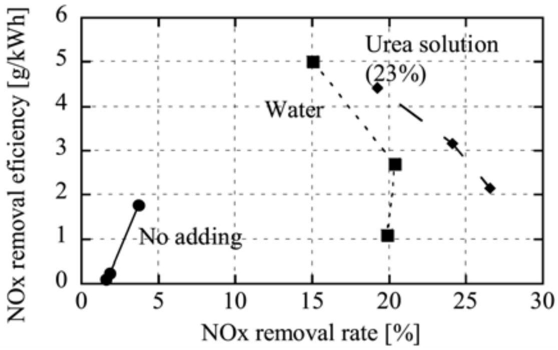


Fig. 4 NO$_x$ removal efficiency by DBD treatment with or without a urea solution.

Residual NH3 in exhaust gas after treatment of DBD with urea solution

FTIR measurements of the exhaust gas after DBD treatment with the 23% urea solution is shown in Fig. 5. AC high voltage applied to the discharge reactor was 7.2 kVpp. NH$_3$ has a local peak at about 1000 cm^{-1}. When an urea solution was used, the peak of 1000 cm^{-1} was not detected as shown Fig. 5. From these results, it seems that NH$_3$ generated from an urea solution has been consumed to remove NO$_x$. It is clear that there is no residual NH$_3$ or less than the detectable level for DBD treatment with an urea solution.

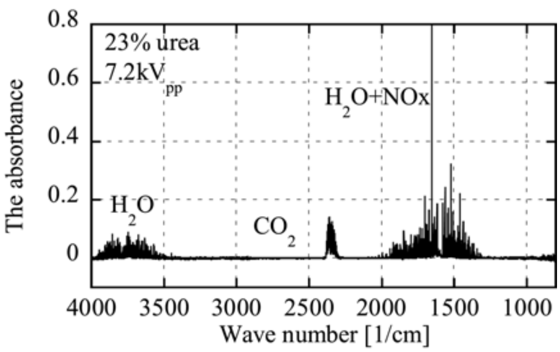


Fig. 5 FTIR spectrum of exhaust gas after DBD treatment with urea solution.

Influence of ratio of NO/NO$_2$ on NO$_x$ removal

The change in the ratio of NO/NO$_2$ when AC high voltage is varied from 9.5 kVrms to 12 kVrms is shown in Fig. 6. It was found that the ratio of NO/NO$_2$ was changed from 6.76 to 3.84 by adjusting AC applied voltage. When the applied voltage was less than 9.5 kVrms, the ratio of NO/NO$_2$ did not change because DBD did not occur in the discharge reactor. And, the AC high voltage source which was used in this study could not generate a high voltage greater than 12 kVrms.

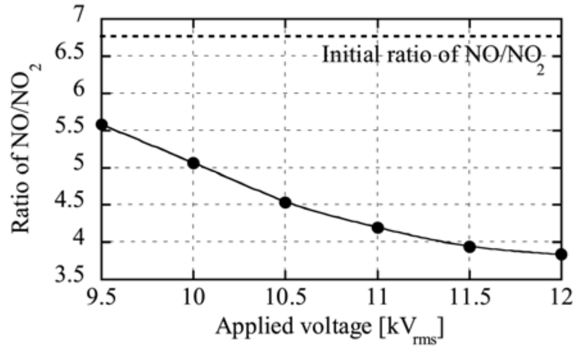


Fig. 6 Change in a ratio of NO/NO$_2$ with AC applied voltage

The variation of the removed amount of NO$_x$ when the ratio of NO/NO$_2$ was changed is shown in Fig. 7. The linear relation between the removed amount of NO$_x$ and the ratio of NO/NO$_2$ was observed when the ratio of NO/NO$_2$ was less than 5.58 and the removal amount of NO$_x$ showed the highest value when the ratio of NO/NO$_2$ was 5.58. The removal amount of NO$_x$ was decreased when the ratio of NO/NO$_2$ was increased from about 5.5. From the graph shown in Fig. 7, it was estimated that the optimum ratio of NO/NO$_2$ was about 6:1.

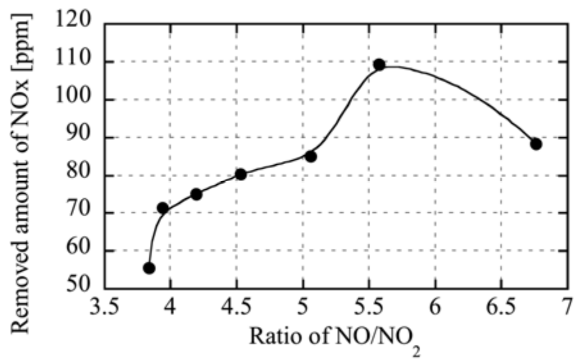


Fig. 7 Change in a removed amount of NO$_x$ with the ratio of NO/NO$_2$.

During DBD process, various chemical reactions occur in the discharge reactor as in section 3. The reason why the optimum ratio of NO/NO$_2$ was not 1:1 but about 6:1 would be as follows:

(1) NO was changed into NO$_2$ by oxidation in the NO$_x$ removal reactor, that is, the ratio of NO/NO$_2$ inside the NO$_x$ removal reactor was different from the ratio of NO/NO$_2$ at the inlet of the NO$_x$ removal reactor.

(2) NO$_x$ removal reaction was hard to occur because the amount of NH$_3$ was not enough even if the ratio of NO/NO$_2$ was 1:1.

2 CONCLUSIONS

In this study, NO_x removal by DBD with an urea solution was investigated in detail. Results obtained from the experimental are as follow.

(1) It is found that NO removal by DBD using an urea solution is very effective. The NO and NO_x removal rate by DBD was improved by 8% when using an urea solution comparing to using pure water, and the optimum concentration of an urea solution was 23%. For using an urea solution, any residual NH_3 was not detected.

(2) It is found that the optimum ratio of NO/NO_2 for NO_x removal by DBD with an urea solution is about 6:1 is the present study.

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