

## Reduction of Nitrogen Oxides by Ozonization-Catalysis Hybrid Process

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**Abstract**—Treatment of nitrogen oxides (NO<sub>x</sub>) by using a hybrid process consisting of ozonization and catalysis was investigated. The ozonization method may be an alternative for the oxidation of NO to NO<sub>2</sub>. It was found that nitric oxide (NO) was easily oxidized to nitrogen dioxide (NO<sub>2</sub>) in the ozonization chamber without using any hydrocarbon additive. In a temperature range of 443 to 503 K, the decomposition of ozone into molecular oxygen was not significant, and one mole of ozone approximately reacted with one mole of NO. A kinetic study revealed that the oxidation of NO to NO<sub>2</sub> by ozone was very fast, almost completed in a few tens of milliseconds. When the amount of ozone added was less than stoichiometric ratio with respect to the initial concentration of NO, negligible NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> were formed. The oxidation of a part of NO to NO<sub>2</sub> in the ozonization chamber enhanced the selective reduction of NO<sub>x</sub> to N<sub>2</sub> by a catalyst (V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>), indicating that the mixture of NO and NO<sub>2</sub> reacts faster than NO.

Key words: Nitrogen Oxides, Ozonization, Catalysis, Hybrid Process

### INTRODUCTION

Many recent studies have reported that nonthermal plasma including pulsed corona discharge and dielectric barrier discharge improves the performance of selective catalytic reduction (SCR) of nitrogen oxides [Penetrante et al., 1999; Bröer and Hammer, 2000; Hoard, 2001; Miessner et al., 2002]. In this regard, the catalytic reduction of a mixture of NO and NO<sub>2</sub> has been recognized to be faster than that of NO [Bröer and Hammer, 2000; Koebel et al., 2000]. Therefore, the essential function of the nonthermal plasma in this kind of hybrid process is to increase the fraction of NO<sub>2</sub> by oxidizing NO [Penetrante et al., 1999; Hoard, 2001; Yoon et al., 2002; Mok et al., 2003]. In the previous work, it was found that the oxidation of NO to NO<sub>2</sub> by nonthermal plasma largely decreases with the increase in reaction temperature, and a hydrocarbon additive is necessary to convert NO into NO<sub>2</sub> effectively at relatively high temperatures from 373 to 473 K [Mok et al., 2003]. This can be a drawback of the nonthermal plasma-catalysis hybrid process.

The other feasible method capable of oxidizing NO to NO<sub>2</sub> is to use ozone generator. Generally, ozone is produced by a dielectric barrier discharge [Kogelschatz, 2003]. When ozone is used for the oxidation of NO to NO<sub>2</sub>, a hydrocarbon additive such as ethylene and propylene is not needed, and accordingly the formation of possible byproducts such as carbon monoxide and formaldehyde can be avoided. At room temperature, the oxidation capability of ozone is well understood [Mok et al., 1998], but a question arises: is the oxidation capability still maintained at high temperatures or not? Furthermore, it is not clear whether the performance of SCR combined with ozonization is similar to that with nonthermal plasma.

The present investigation deals with the ozonization-SCR hybrid process for the reduction of nitrogen oxides (NO<sub>x</sub>). For this hybrid system, a dielectric-packed bed reactor was employed for the pro-

duction of ozone, and a commercially available monolithic V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was used. This catalyst shows its ability to reduce NO<sub>x</sub> in the presence of ammonia (NH<sub>3</sub>). The NH<sub>3</sub>-SCR is a well-established method, and it is presently considered as the best available technology to remove NO<sub>x</sub> from various pollution sources [Choo et al., 2003; Pârvulescu et al., 1998; Koebel and Elsener, 1998; Lee et al., 2002].

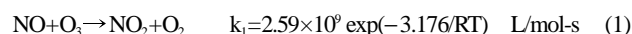
The objectives of this study are to examine the effect of the reaction temperature on the oxidation of NO in the ozonization chamber, and evaluate the NO<sub>x</sub> reduction performance of the hybrid process. The oxidation of NO to NO<sub>2</sub> in the ozonization chamber was studied both experimentally and theoretically at temperatures up to 503 K. The performance of the present ozonization-SCR hybrid process was compared with that of nonthermal plasma-SCR hybrid process. The details for the present investigation are described below.

### BACKGROUND

#### 1. Oxidation of NO to NO<sub>2</sub> by Ozone

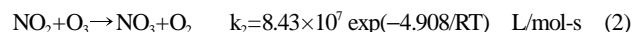
In most cases, the majority of nitrogen oxides contained in practical exhaust gases is NO (more than 90% of NO<sub>x</sub>), and NO<sub>2</sub> content is very small [Koebel et al., 2000]. Some important reactions related to the ozonization of exhaust gas are summarized below. The rate constants for the relevant reactions were obtained from National Institute for Standards and Technology (NIST) Chemical Reactions Database (Version 2Q98).

In the present hybrid system consisting of an ozonization chamber and a catalytic reactor, the crucial role of ozonization is to oxidize NO to NO<sub>2</sub> as follows:



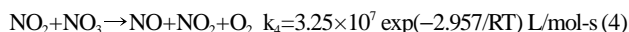
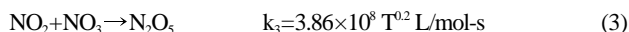
where R is 1.987 kcal/mol-K, and T is in K.

The NO<sub>2</sub> formed can be further oxidized to NO<sub>3</sub> by ozone, and NO<sub>2</sub> and NO<sub>3</sub> can recombine to form N<sub>2</sub>O<sub>5</sub>, or can decompose into NO and NO<sub>2</sub>:

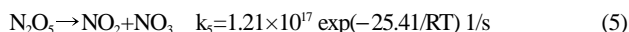


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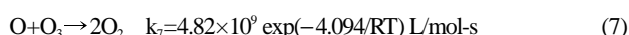
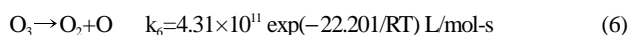


Here, it should be noted that reaction (2) is much slower than reaction (1), and the N<sub>2</sub>O<sub>5</sub> produced by reaction (3) decomposes fast into NO<sub>2</sub> and NO<sub>3</sub> by reverse reaction as below:



Thus, the concentrations of either NO<sub>3</sub> or N<sub>2</sub>O<sub>5</sub> are very low.

The ozone added may decompose by the following reactions, which makes a part of ozone lose its oxidizing ability:



The rates of these reactions are proportional to the temperature; the temperature dependence of reaction (6) is especially great. Thus, the ozone wasted by these reactions increases with the reaction temperature.

If the axial dispersion and the concentration difference in the radical direction are neglected, the material balance of any component in the ozonization chamber can be expressed as follows, in a manner analogous to a batch reactor:

$$\frac{dC_i}{d\tau} = R_i \quad (8)$$

where C<sub>i</sub> is the concentration of any component, τ is the residence time of the feed gas, and R<sub>i</sub> is the net reaction rate with respect to generation given by

$$R_i = \sum \text{generation reaction} - \sum \text{disappearance reaction} \quad (9)$$

As an example, for NO<sub>3</sub>, Eq. (8) can be written as

$$\frac{d[\text{NO}_3]}{d\tau} = k_2[\text{NO}_2][\text{O}_3] + k_5[\text{N}_2\text{O}_5] - k_3[\text{NO}_2][\text{NO}_3] - k_4[\text{NO}_2][\text{NO}_3] \quad (10)$$

Similar equations can be derived for the other components including NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, O, and O<sub>3</sub>. Note that the change in O<sub>2</sub> content due to reactions (1), (2), (4), (6) and (7) is negligible. The concentrations of NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, O and O<sub>3</sub> at the inlet of the ozonization chamber are

$$[\text{NO}] = [\text{NO}]_0, [\text{NO}_2] = [\text{NO}_2]_0, [\text{NO}_3] = 0, [\text{N}_2\text{O}_5] = 0, [\text{O}] = 0, [\text{O}_3] = [\text{O}_3]_0 \quad (11)$$

To obtain the concentrations of the relevant components at the outlet of the ozonization chamber, six differential equations for NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, O and O<sub>3</sub> including Eq. (10) should be solved simultaneously. In this study, they were numerically solved by a software (Chemical Kinetics Simulator Version 1.01, International Business Machines Corporation).

## 2. Catalytic Reduction

Selective catalytic reduction is a highly developed and widespread technology for the removal of NO<sub>x</sub>. Usually this process employs ammonia or hydrocarbon as reducing agent [Pârăulescu et al., 1998; Koebel and Elsener, 1998; Kim et al., 2001; Lee et al., 2002; Praserthdam et al., 2003]. It is generally accepted that the catalytic reduction of nitrogen oxides in the presence of ammonia proceeds as follows [Pârăulescu et al., 1998; Koebel and Elsener, 1998]:



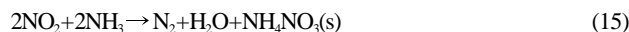
Since most practical exhaust gases consist mainly of NO (more than 90% of total NO<sub>x</sub>), reaction (12) is the major one when a catalytic reactor alone is used. Unfortunately, the rate of this reaction largely decreases with the reaction temperature due to its high activation energy [Bröer and Hammer, 2000]. If the gas contains NO<sub>2</sub>, the reaction as below rapidly occurs [Bröer and Hammer, 2000; Koebel et al., 2000]



Reaction (13) is faster than reaction (12) at low temperatures. Besides, the following reaction can also reduce NO<sub>x</sub> at low temperatures:



Another reaction that may occur in the combination process is the formation of ammonium nitrate from NO<sub>2</sub> and NH<sub>3</sub> added as the reducing agent:



This reaction converts NO<sub>2</sub> into N<sub>2</sub> and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) equally. Ammonium nitrate deposits can lead to deactivation of catalyst. According to the previous study [Mok et al., 2004], for a monolithic V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst, the lower threshold temperature at which ammonium nitrate formation is not observed is around 443 K, which indicates that the hybrid process should be operated above this temperature.

## EXPERIMENTAL

### 1. Experimental Setup

Fig. 1 shows the schematic diagram of the present hybrid process consisting of an ozonization chamber and a catalytic reactor. A cylindrical glass tube whose inner diameter and length are 2.5 cm and 50 cm was used as the ozonization chamber. The effective volume of the ozonization chamber is calculated to be about 245 cm<sup>3</sup>. The gas treated by the ozonization chamber is directed to the catalytic reactor. For the catalytic reactor, a commercial monolithic V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst (20 channels per square inch) was used. The vanadium content of the catalyst is 5.0 wt%, and its dimensions are 1.8 cm × 1.8 cm × 9.7 cm. For the purpose of adjusting the reaction temperature to a desired value, an ozonization chamber and a catalytic reactor

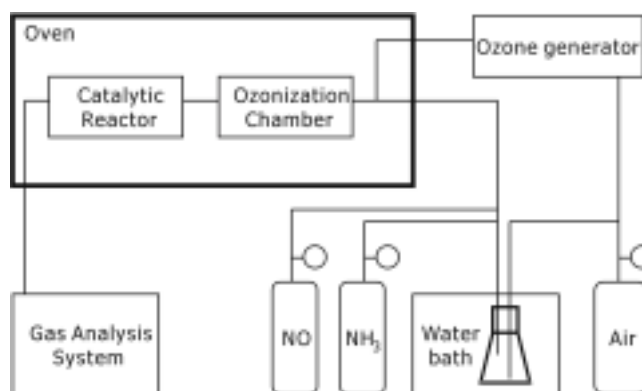


Fig. 1. Schematic diagram of the experimental apparatus.

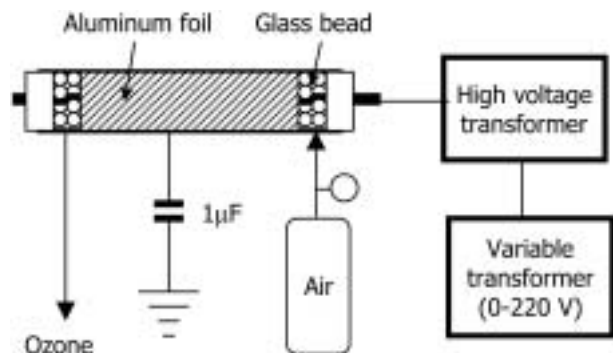


Fig. 2. Schematic diagram of the ozone generator using dielectric barrier discharge.

tor were installed in an oven.

A dielectric-packed bed reactor as shown in Fig. 2 was employed as the ozone generator. It consists of a glass tube (inner diameter: 25.8 mm; outer diameter: 30.2 mm), a 3/8 inch (9.5 mm) stainless steel rod, and 5 mm glass beads (Sigmund Lindner, Germany) that are filled between the glass tube and the stainless steel rod. AC high voltage is applied to the stainless steel rod (discharging electrode), and the glass tube and glass beads act as the dielectric material. The outer surface of the glass tube was wrapped with aluminum foil, and it was grounded. The discharge region that aluminum foil covers the glass tube is 260 mm. A 1.0  $\mu\text{F}$ -capacitor connected to the ozone generator is for measuring the discharge power. The ozone generator was operated at room temperature. The AC voltage applied to the ozone generator was varied from 10 to 25 kV (peak value) to change the concentration of ozone generated. At a given voltage, the fluctuation in the concentration of ozone generated was not significant because the temperature variation of the ozone generator was not large during the operation.

## 2. Experimental Methods

The main component of the simulated exhaust gas and the oxygen source for the ozone generator was air whose flow rate was controlled by mass flow controllers (MFC) (Model 1179A, MKS Instruments, Inc.). The flow rates of NO (5.0% (v/v) balanced with  $\text{N}_2$ ) and  $\text{NH}_3$  (5.0% (v/v) balanced with  $\text{N}_2$ ) were also controlled by mass flow controllers, and they were mixed with air and ozone. A small amount of NO was spontaneously oxidized to  $\text{NO}_2$  due to the oxygen in the air. The concentration of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) at the inlet of the ozonization chamber was 300 ppm (parts per million, volumetric). Ammonia was used as the reducing agent, and the concentration ratio of ammonia to initial  $\text{NO}_x$  was 1.0 throughout the present work. The content of water vapor was adjusted to 2% (v/v) by using its vapor pressure. The total flow rate of the feed gas stream prepared as mentioned above was 5 L/min on the basis of room temperature. This flow rate corresponds to 10,000/h of space velocity in the catalytic reactor on the basis of room temperature. The residence time in the ozonization chamber is calculated to be about 3 sec. The experiments for the oxidation of NO in the ozonization chamber and the catalytic reduction of  $\text{NO}_x$  were conducted at reaction temperatures in the range of 443 to 503 K. As mentioned above, the threshold temperature above which ammonium nitrate formation is not observed is 443 K for the present  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst.

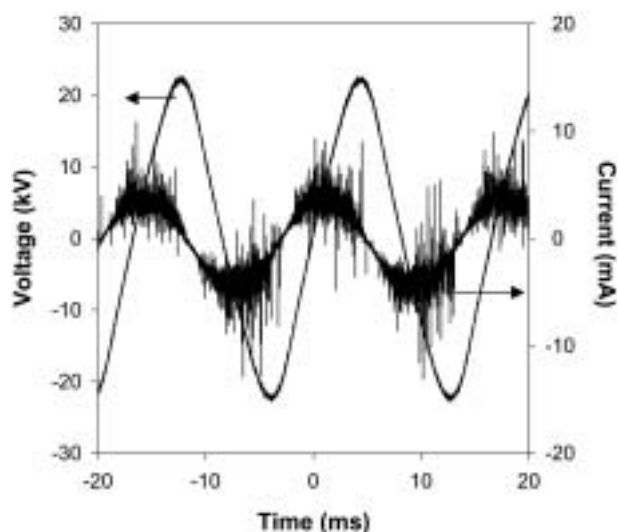


Fig. 3. Voltage and current waveforms.

The concentrations of NO and  $\text{NO}_2$  were analyzed by means of a chemiluminescence  $\text{NO}-\text{NO}_2-\text{NO}_x$  analyzer (Model 42C, Thermo Environmental Instruments, Inc.). This kind of  $\text{NO}-\text{NO}_2-\text{NO}_x$  analyzer has a problem in measuring  $\text{NO}_2$  concentration when ammonia is present, and thus, a Fourier Transform Infrared (FTIR) spectrometer (Model 1600, Perkin-Elmer) equipped with a 2.4 m permanently aligned long path gas cell (Pike Technologies) was utilized to analyze  $\text{NO}_2$  concentration. The concentration of ozone was measured at the inlet of the ozonization chamber by using a portable gas analyzer (Porta Sens II, Analytical Technology, Inc.). The high voltage applied to the discharging electrode of the ozone generator was measured by a 1,000 : 1 high voltage probe (PVM-4, North Star Research, Corporation) and a digital oscilloscope (TDS 3032, Tektronix). For the measurement of the voltage between both ends of the 1.0  $\mu\text{F}$  capacitor connected to the ozone generator, a 10 : 1 voltage probe (P6139A, Tektronix) was used.

## 3. Power Measurement Method

Fig. 3 shows an example of the voltage and current waveforms. As observed, the current waveform is very spiky and untidy since a number of microdischarges are created and extinguished in the ozone generator. Thus, the general power measurement method, i.e., multiplying voltage by current, is not applicable to this kind of system. In this study, the electric power dissipated in the ozone generator (discharge power) was measured as follows [Manley, 1943; Kogelschatz, 1988]. A 1.0  $\mu\text{F}$  capacitor was connected in series with the ozone generator as shown in Fig. 2. Since the ozone generator using dielectric barrier discharge can electrically be treated as a capacitor, the charge stored in the capacitor (1.0  $\mu\text{F}$ ) is equal to that in the ozone generator. The charge stored in the 1.0  $\mu\text{F}$  capacitor is the product of capacitance and voltage, which can directly be read by the voltage across the capacitor. In other words, the charge stored in the capacitor is equal to  $10^{-6}$  times the voltage. The voltage-charge plot corresponding to Fig. 3, so-called, Lissajous figure is presented in Fig. 4, where the area of the parallelogram conforms to the discharge energy per one cycle. The average discharge power can be obtained by multiplying the discharge energy per one cycle by AC frequency (i.e. 60 Hz). A mathematical formula is available for cal-

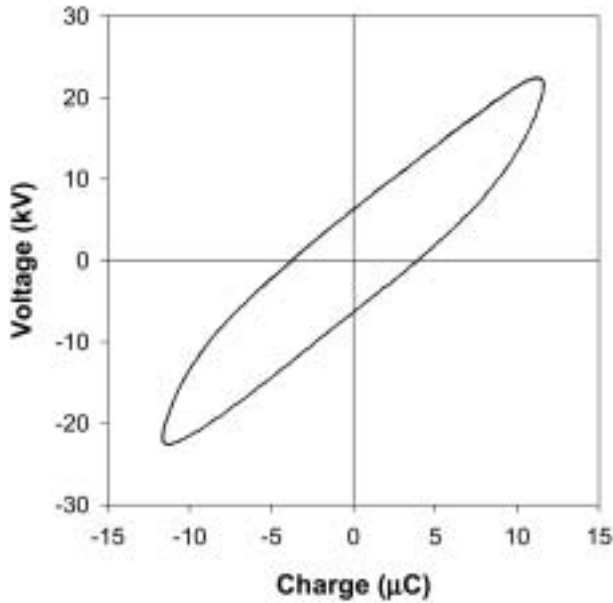


Fig. 4. Charge-voltage plot (Lissajous figure).

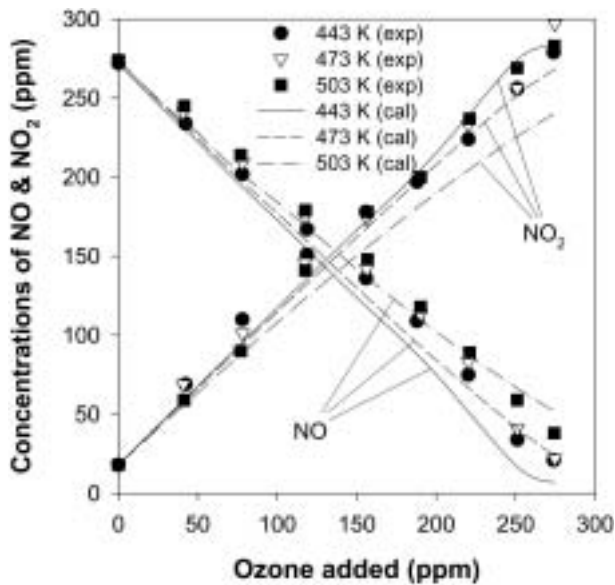


Fig. 5. Concentration profiles of NO and NO<sub>2</sub> as a function of ozone concentration at different reaction temperatures.

culating the area of the parallelogram [Manley, 1943; Kogelschatz, 1988]. For the Lissajous figure in Fig. 4, the discharge energy per cycle was found to be 0.24 J/cycle. Hence the average discharge power is 0.24 J/cycle $\times$ 60 Hz=14.4 W.

## RESULTS AND DISCUSSION

### 1. Ozonization Chamber

The concentration profiles of NO and NO<sub>2</sub> as a function of ozone concentration at different temperatures are shown in Fig. 5. The oxidation of NO to NO<sub>2</sub> is determined by the amount of ozone added to the simulated exhaust gas. As can be seen in Fig. 5, the concentration of NO decreased in proportion to the increase in the con-

centration of ozone. For this experiment, the concentration of ozone was changed up to 275 ppm, corresponding to the initial concentration of NO. Nevertheless, a small amount of NO was left unoxidized. As reaction (1), NO reacts with ozone in one to one stoichiometry, but at the same time, ozone decomposes into oxygen according to reactions (6) and (7). Since the rates of these ozone decomposition reactions increase with temperature, more NO was left unoxidized when the temperature was higher. In Fig. 5, the concentrations of NO and NO<sub>2</sub> calculated by Eqs. (8) to (11) are also presented. Although the calculated results slightly underestimated the experimental data, the general trends of the calculated results agreed well. According to the kinetic study, the oxidation of NO to NO<sub>2</sub> by ozone was very fast, almost completed in a few tens of milliseconds, which means that an ozonization chamber with very small volume can be used.

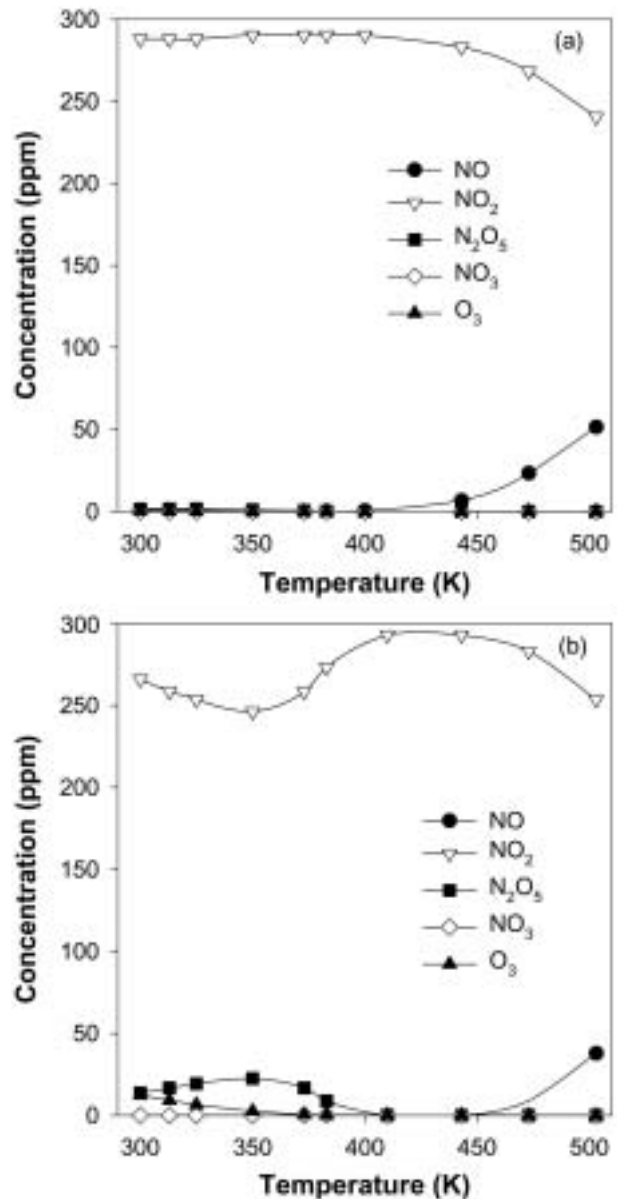


Fig. 6. Calculated concentrations of NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and O<sub>3</sub> as a function of reaction temperature (initial ozone concentration: 275 ppm (a), and 300 ppm (b)).

As can be understood by reactions (2) to (5),  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  are the ultimate fate of some of the initial NO in the ozonization chamber. Fig. 6(a) shows the calculated results for the concentrations of NO,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ , and  $\text{O}_3$  as a function of reaction temperature when the initial concentrations of both NO and ozone were 275 ppm, and the residence time was 3 sec. As can be seen,  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  were almost zero in the entire temperature range. Below 400 K, all of the initial NO was depleted, but at higher temperatures a small amount of NO was left unoxidized. Fig. 6(b) presents the calculated concentrations of NO,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ , and  $\text{O}_3$  when excess ozone (300 ppm) was used. In case of  $\text{N}_2\text{O}_5$ , the concentration increased with the reaction temperature, showing a maximum around 350 K. When the reaction temperature was further elevated, the concentration of  $\text{N}_2\text{O}_5$  decreased, and vanished at about 400 K. On the other hand, the concentration of  $\text{NO}_3$  was almost zero regardless of the reaction temperature. The decrease in the concentration of  $\text{NO}_2$  in the range of 300 to 350 K is related to the formation of  $\text{N}_2\text{O}_5$  by reactions (2) and (3) whereas that in the range of 440 to 500 K is due to low NO oxidation resulting from the decomposition of ozone.

Fig. 7 compares the NO oxidation results obtained by the present ozonization chamber with those by a nonthermal plasma process (dielectric-packed bed reactor) [Mok et al., 2003]. To compare the results on an identical basis, the concentrations of NO were plotted against energy density. The energy density was defined as the ratio of discharge power to gas flow rate. The discharge power is the electric power dissipated in the plasma reactor or in the ozone generator. At a temperature as high as 443 K, the rate of NO oxidation in the plasma reactor was very slow in the absence of ethylene additive. When 750 ppm of ethylene was added to the feed gas, the rate of NO oxidation was greatly enhanced. But, it is important to consider the formation of byproducts from ethylene [Mok et al., 2003]. On the other hand, the ozonization method was able to oxidize most of the initial NO without using ethylene. The results in Fig. 7

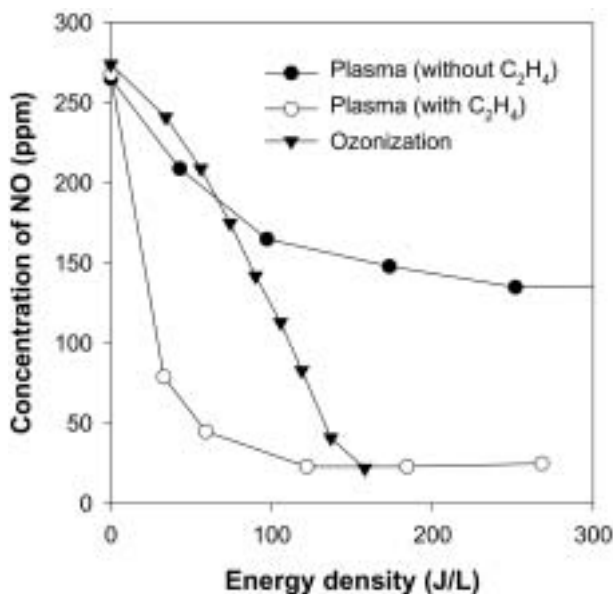


Fig. 7. Comparison of the present ozonization chamber with the dielectric barrier discharge reactor in terms of NO oxidation performance (reaction temperature: 473 K).

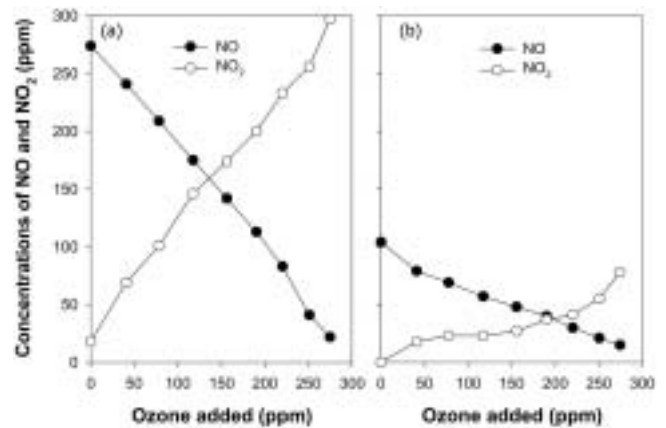


Fig. 8. Concentration variations of NO and  $\text{NO}_2$  at the outlet of the ozonization chamber (a), and at the outlet of the hybrid process (b) (reaction temperature: 473 K).

strongly suggest that ozonization method can successfully be used for the oxidation of NO.

## 2. Ozonization-Catalysis Hybrid Process

Fig. 8(a) and (b) shows the typical concentration variations of NO and  $\text{NO}_2$  at the outlet of the ozonization chamber, and at the outlet of the hybrid process when the reaction temperature was 473 K. As the ozone concentration increased, the concentration of NO at the outlet of the ozonization chamber decreased while the concentration of  $\text{NO}_2$  increased. This result indicates that the ozonization method should be combined with another process in order to reduce  $\text{NO}_x$  level. In Fig. 8(b), the concentration profiles of NO and  $\text{NO}_2$  at the outlet of the hybrid process are also presented by contrast. The foremost distinction is that the concentrations of both NO and  $\text{NO}_2$  were maintained very low when the feed gas was first treated by ozone before being directed to the catalytic reactor.

Fig. 9 presents the effect of ozone concentration on the reduc-

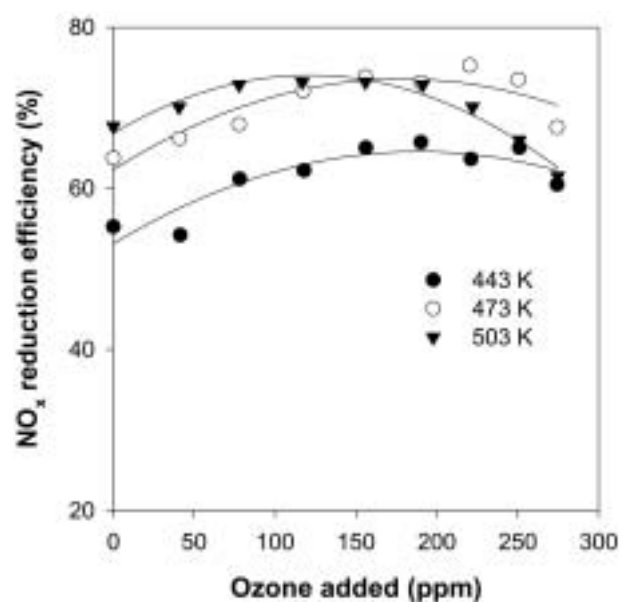


Fig. 9. Effect of ozone concentration on the catalytic reduction of  $\text{NO}_x$  at different reaction temperatures.

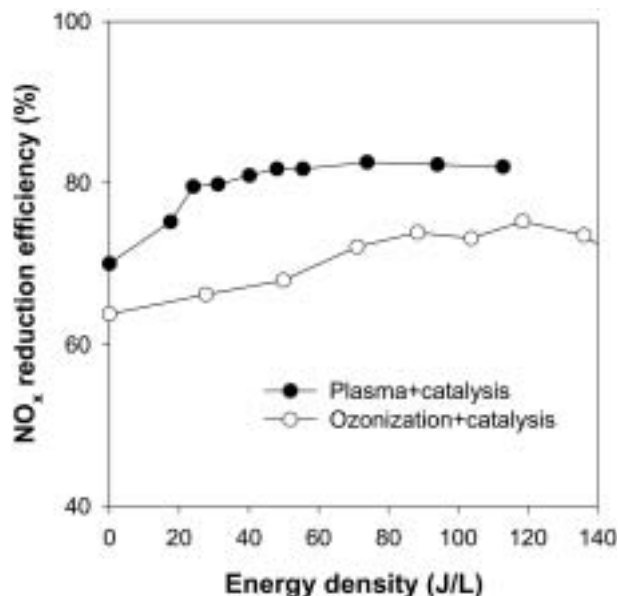


Fig. 10. Comparison of the NO<sub>x</sub> reduction efficiency between the present hybrid process and the nonthermal plasma-catalysis hybrid process (reaction temperature: 473 K).

tion of NO<sub>x</sub> at different reaction temperatures in the range of 443 to 503 K. When ozone was not added, the NO<sub>x</sub> reduction efficiencies at 443, 473 and 503 K were 55, 64 and 68%, respectively. However, the catalytic reduction of NO<sub>x</sub> was considerably improved with the increase in the concentration of ozone up to about 150 ppm, and then decreased, implying that reaction (13) significantly contributed to the reduction of NO<sub>x</sub>. From this result, it can be said that the oxidation of a part of NO with the help of the ozonization method may be useful to improve the performance of the catalytic reduction system.

A comparison between the nonthermal plasma-catalyst process and the present hybrid process was made as in Fig. 10. So as to compare the results on an identical basis, the data for the NO<sub>x</sub> reduction efficiencies were presented with respect to the energy density applied to the nonthermal plasma reactor and ozone generator. In case of the nonthermal plasma-catalyst process [Mok et al., 2003], both ethylene and ammonia were used because the rate of NO oxidation was very slow without ethylene. As can be seen, the nonthermal plasma-catalyst process showed better NO<sub>x</sub> reduction performance than the present hybrid process. In terms of gas composition, the only difference between these two processes is the presence of ethylene. The better NO<sub>x</sub> reduction performance of the plasma-catalytic process may be attributed to the presence of ethylene.

## CONCLUSIONS

Reduction of nitrogen oxides using an ozonization-catalysis hybrid process was investigated. Nitric oxide (NO) was found to be easily oxidized to nitrogen dioxide (NO<sub>2</sub>) in the ozonization chamber. In a temperature range of 443 to 503 K, ozone reacted with NO in approximately one to one stoichiometry, and the decomposition of ozone into molecular oxygen was not significant. The kinetic study revealed that the oxidation of NO to NO<sub>2</sub> by ozone was very fast,

and negligible NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> were formed when the amount of ozone added was less than stoichiometric ratio. As a result of the oxidation of NO to NO<sub>2</sub> in the ozonization chamber, the reduction of NO<sub>x</sub> on a monolithic V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was improved without giving rise to a problem regarding byproducts formation. The observed increase in the NO<sub>x</sub> reduction efficiency by the use of ozonization method was about 10% in the range of 443 to 503 K.

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