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Improvement in selective catalytic reduction of nitrogen oxides by using dielectric barrier discharge

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Abstract

The behavior of the selective catalytic reduction of nitrogen oxides (NO_x) assisted by a dielectric barrier discharge was investigated. The principal function of the dielectric barrier discharge in the present system is to generate ozone, which is continuously fed to a chamber where the ozone and NO-rich exhaust gas (NO forms the large majority of NO_x) are mixed. In the ozonization chamber, a part of NO contained in the exhaust gas is oxidized to NO_2, and then the mixture of NO and NO_2 enters the catalytic reactor. The ozonization method proposed in this study was found to be more energy-efficient for the oxidation of NO to NO_2 than the typical nonthermal plasma process. The degree of NO oxidation was approximately equal to the amount of ozone added to the exhaust gas, implying that the decomposition of ozone into molecular oxygen was relatively slow, compared to its reaction with NO. When the exhaust gas was first treated by ozone to produce a mixture of NO and NO_2, a remarkable enhancement in the catalytic reduction of nitrogen oxides was observed. Neither NO_3 nor N_2O_5 was formed in the present system, but small amounts of ozone and N_2O (less than 5 ppm) were detected in the outlet gas.

Keywords: Catalytic reduction; Dielectric barrier discharge; Ozonization; Nitrogen oxides

1. Introduction

Nitrogen oxides, NO and NO_2 (called NO_x) have been implicated as precursors to acid rain and photochemical smog. A commercially proven technology available for NO_x control is the selective catalytic reduction (SCR). A tremendous amount of research has been carried out on the SCR processes that use ammonia and hydrocarbon reductants [1–5]. In general, SCR catalysts are highly efficient in reducing NO_x to N_2 at temperatures in the range of 250–450 °C. However, NO_x conversion efficiency largely decreases as the reaction temperature goes down, which has been pointed out as an important drawback of the SCR technology.

When the reaction temperature is not sufficiently high for efficient SCR, it may be possible to increase the efficiency of NO_x removal if a part of NO contained in exhaust gas were first converted into NO_2. As shown by many researchers [2,6], the selective catalytic reduction of NO_x in the exhaust gas containing a balanced mixture of NO and NO_2 is faster than in the exhaust gas with the large majority of NO (so-called NO-rich exhaust gas). This type of the SCR is called a “fast” SCR [2,6]. A new technology, in which NO is partially converted into NO_2 prior to the SCR processing, is based on the nonthermal plasma produced by dc or pulsed corona discharge and dielectric barrier discharge [6–10].

In our previous study [10], we found that the rate of NO oxidation to NO_2 by the nonthermal plasma significantly decreases with the increase in reaction temperature. To overcome this problem, we used a hydrocarbon additive (ethylene), which enhanced the oxidation of NO at high temperatures. This method, however, has a drawback producing such byproducts as carbon monoxide and formaldehyde. The alternative method capable of oxidizing NO to NO_2 without

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any harmful byproducts is to use ozone as an oxidizing additive. Ozone can be efficiently produced by the dielectric barrier discharge [11]. The NO oxidation by ozone is more efficient than that by the nonthermal plasma process since the reduction of NO_2 back to NO does not occur [12].

This paper deals with the reduction of NO_x in a simulated exhaust gas by using a two-stage hybrid process consisting of an ozonization chamber and a SCR reactor. For the present hybrid system, a dielectric-packed bed reactor, which is a kind of dielectric barrier discharge reactor, was employed as the ozone generator. In the ozonization chamber, ozone injected into the exhaust gas oxidized a part of NO to NO_2, forming a mixture of NO and NO_2. The modified exhaust gas with a mixture of NO and NO_2 was then directed to the SCR reactor. In the SCR reactor, a commercially available monolithic V_2O_5-WO_3/TiO_2 catalyst was used in the presence of ammonia as the reductant to remove NO_x from the exhaust gas. The experimental data on the reduction of NO_x and the formation of byproducts in the present hybrid system show that the ozonization method can significantly improve the SCR process.

2. Experimental

2.1. Experimental apparatus

Fig. 1 shows the schematic diagram of the present hybrid process consisting of an ozonization chamber and a catalytic reactor. A cylindrical glass tube with a volume of 245 cm^3 was used as the ozonization chamber. The exhaust gas treated in the ozonization chamber was directed to the catalytic reactor where a commercial monolithic V_2O_5-WO_3/TiO_2 catalyst (20 channels per square inch; apparent catalyst volume: 40 cm^3) was placed. The vanadium and tungsten contents in the catalyst were 1.6 and 7.3 wt.%, respectively. The surface area determined by Brunauer–Emmett–Teller (BET) adsorption isotherm was 60 m^2/g. In order to adjust the reaction temperature to a desired value, the ozonization chamber and the catalytic reactor were installed in an oven.

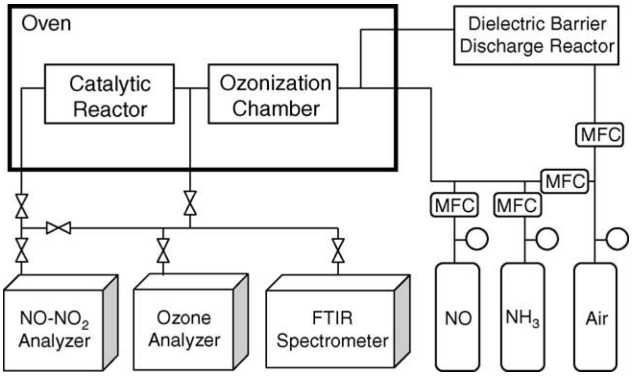

Fig. 1. Schematic of the experimental apparatus for ozonization–catalysis hybrid process.

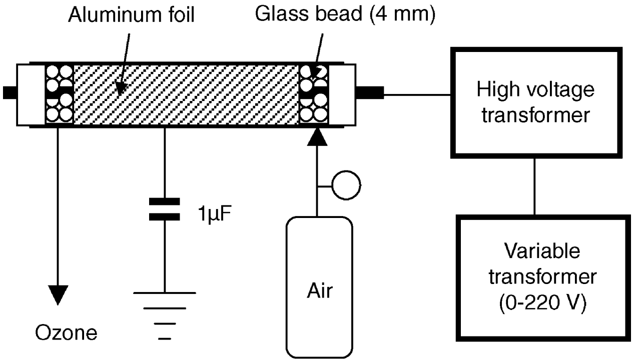

Fig. 2. Schematic diagram of the ozone generator using dielectric barrier discharge.

A dielectric-packed bed reactor as shown in Fig. 2 was employed as the ozone generator. It consisted of a glass tube (i.d.: 16 mm; o.d.: 20 mm), and a stainless steel rod with a diameter of 6.35 mm. The 4 mm glass beads (Sigmund Lindner, Germany) filled the space between the glass tube and the stainless steel rod. ac high voltage was applied to the stainless steel rod (discharging electrode). Both the glass tube and glass beads acted as the dielectric material. The outer surface of the glass tube was wrapped with aluminum foil, which was grounded. The discharge region, defined by the aluminum foil cover of the glass tube, was 190 mm long. A 1.0 μF-capacitor connected to the ozone generator was used for measuring the discharge power. The ac voltage (60 Hz) applied to the ozone generator was varied from 12 to 17 kV (peak value) to change the concentration of ozone generated. The ozone generator was operated at room temperature.

2.2. Experimental methods

The main component of the simulated exhaust gas was air whose flow rate was controlled by mass flow controller (MFC) (Model 1179A, MKS Instruments Inc.). Air was also used as the oxygen source for the production of ozone in the dielectric-packed bed reactor. The flow rates of NO (5.0%, v/v, balanced with N_2) and NH_3 (5.0%, v/v, balanced with 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 NO_2 due to the oxygen in the simulated exhaust gas.

The concentration of NO_x ($NO + NO_2$) at the inlet of the ozonization chamber was 300 ppm (parts per million, 1 ppm corresponds to 4.1×10^{-5} mol/m^3 at 298 K and 1.0 atm). For the catalytic reduction of nitrogen oxides, ammonia was used as the reducing agent, and the injection ratio of ammonia to initial NO_x was 1.0 throughout the present work. The total flow rate of the feed gas stream, prepared as mentioned above, was 5 L/min on the basis of room temperature. The residence time in the ozonization chamber was calculated to be about 3 s. The experiments for the oxidation of NO in the ozonization chamber and the catalytic reduction of NO_x were conducted at reaction temperatures in the range of 170–200 °C.

According to the previous study [10], the threshold temperature above which ammonium nitrate formation in the SCR does not occur is 170 °C.

2.3. Analyses and measurements

The concentrations of NO and NO_2 were analyzed by a chemiluminescence NO–NO_2–NO_x analyzer (Model 42C, Thermo Environmental Instruments Inc.). This kind of NO–NO_2–NO_x analyzer has a problem in measuring NO_2 concentration when ammonia is present, and thus, a Fourier transform infrared (FTIR) spectrophotometer (Model 1600, Perkin-Elmer) equipped with a 2.4 m permanently aligned long path gas cell (Pike Technologies Inc.) was utilized for the analysis of NO_2 concentration. The concentration of ozone was measured by 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 1000:1 high voltage probe (PVM-4, North Star Research Corporation) and a digital oscilloscope (TDS 3032, Tektronix). For the measurement of the voltage across the 1.0 μF-capacitor connected to the ozone generator, a 10:1 voltage probe (P6139A, Tektronix) was used. The voltage across the 1.0 μF-capacitor corresponds to the charge stored in the ozone generator, and the power dissipated in the ozone generator (discharge power) can be estimated by the so-called Lissajous figure (charge–voltage plot). The discharge power measurement method is described in detail in the literature [11].

3. Results and discussion

3.1. Ozonization chamber

Fig. 3 presents the concentrations of NO and NO_2 as a function of ozone concentration added to the exhaust gas in the ozonization chamber over a temperature range of 170–230 °C. The concentration of ozone was changed by varying the voltage applied to the ozone generator, i.e., higher the voltage was, more ozone was produced. The simulated exhaust gas consisted mainly of NO. When the exhaust gas was mixed with ozone, NO was oxidized to NO_2 as follows:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

Since the degree of NO oxidation is determined by the amount of ozone added to the feed gas, the concentration of NO decreased with increasing the concentration of ozone. As can be seen, the NO oxidation also depended on the reaction temperature. Although it was not significant, higher temperature resulted in lower NO oxidation. The ozone added to the exhaust gas reacts with NO according to reaction (1), but at the same time, ozone thermally decomposes into molecular oxygen. It is well known that the rate of ozone decomposition increases with temperature. That is why the oxidation of NO to NO_2 at higher temperature was lower. Without ozone decomposition, the decreased NO would have been equal to the added ozone, as understood in reaction (1). According to Fig. 3, however, the amount of NO decreased was smaller than the amount of ozone added, which may be an evidence for the decomposition of ozone. In addition, incomplete mixing of the exhaust gas and the added ozone in the ozonization chamber may partly explain this result, i.e., if the exhaust gas and the added ozone was not mixed well, some unreacted ozone would come out of the ozonization chamber. Fig. 4 shows the concentration of unreacted ozone (ozone slip) emitted from

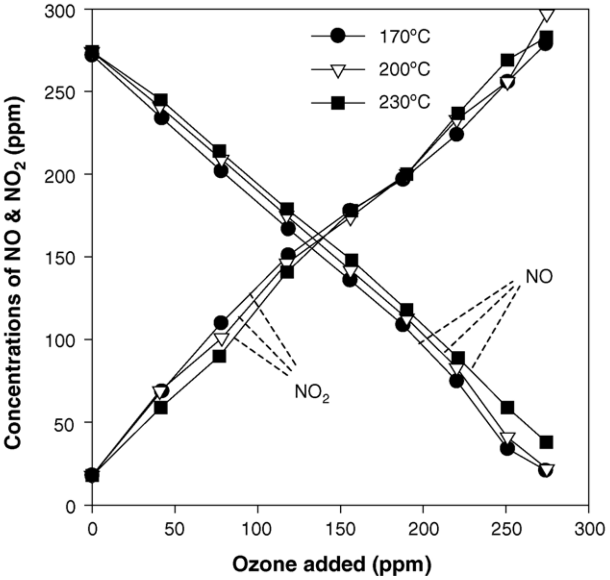

Fig. 3. Effect of the ozone concentration added to the exhaust gas on the oxidation of NO (initial NO_x: 300 ppm; flow rate: 5 L/min).

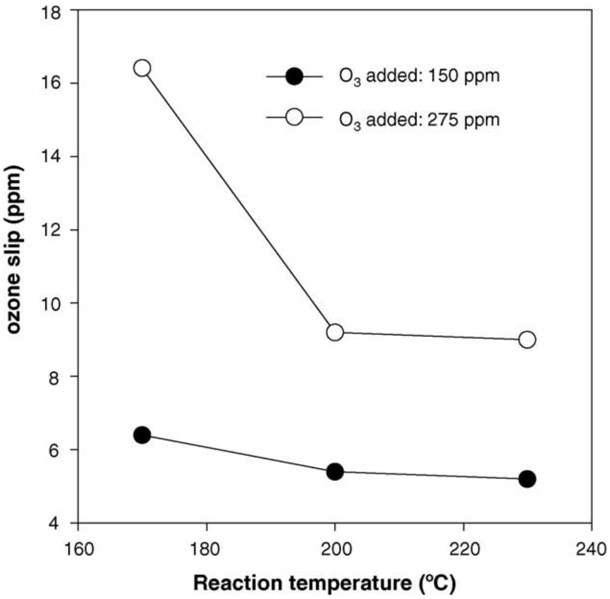

Fig. 4. Ozone slip from the ozonization chamber as a function of reaction temperature (initial NO_x: 300 ppm; flow rate: 5 L/min).

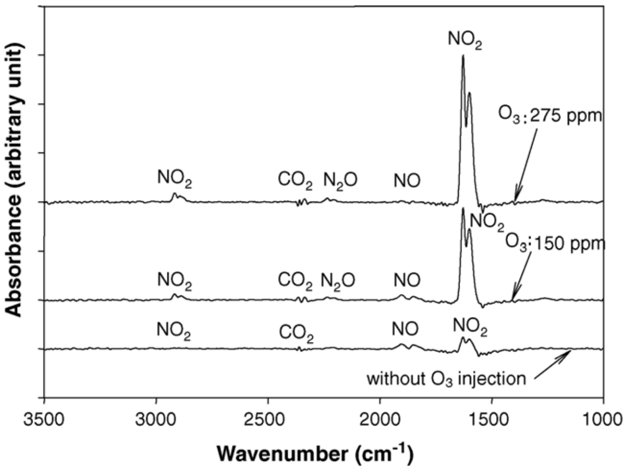

Fig. 5. Fourier transform infrared spectra obtained at the outlet of the ozonization chamber (initial NO_x: 300 ppm; flow rate: 5 L/min; temperature: 170 °C).

the ozonination chamber at different temperatures. The emission of ozone at all temperatures implies that there was an incomplete mixing between the exhaust gas and the added ozone, which leads to lower NO oxidation. The black and white circles in this figure indicate the emission of ozone when the amount of ozone added was 150 and 275 ppm, respectively. In both cases, the ozone slip tended to decrease with the increase in temperature because the rate of ozone decomposition into molecular oxygen is proportional to the temperature.

The NO_2 generated in reaction (1) can be further oxidized to NO_3 by ozone, and NO_2 and NO_3 can combine to form N_2O_5 as below:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (2)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \quad (3)$$

Here, it should be noted that reaction (2) is much slower than reaction (1), and the N_2O_5 produced by reaction (3) decomposes fast into NO_2 and NO_3 by the reverse reaction as:

$$N_2O_5 \rightarrow NO_2 + NO_3 \quad (4)$$

In this context, the concentrations of either NO_3 or N_2O_5 are necessarily very low. This was confirmed by the FTIR spectra at the outlet of the ozonization chamber presented in Fig. 5. Neither NO_3 nor N_2O_5 was observed in the spectra when ozone was added to the exhaust gas, but small amount of nitrous oxide (N_2O) (wavenumber 2236 cm^{-1}) was identified. Note that the N_2O was produced from air (N_2 and O_2) fed to the dielectric-packed bed reactor for the generation of ozone. This means that if oxygen instead of air is used as the oxygen source for the generation of ozone, the N_2O production can be avoided.

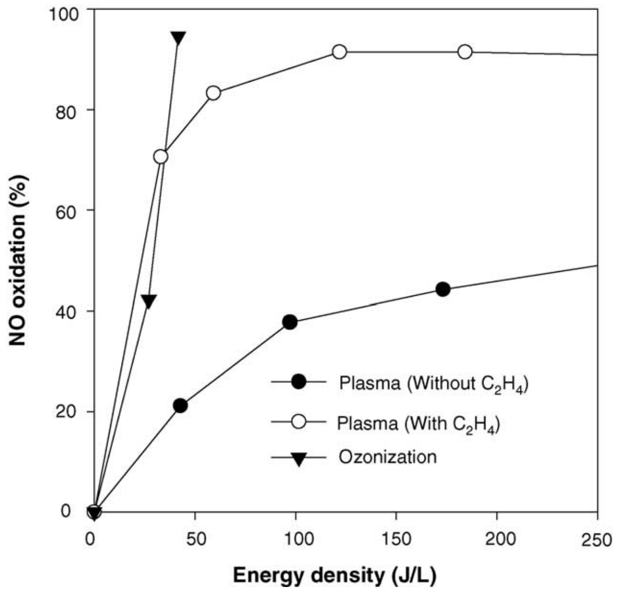

Fig. 6. Comparison of the present ozonization method with typical nonthermal plasma process in terms of NO oxidation performance (initial NO_x: 300 ppm; flow rate: 5 L/min; temperature: 200 °C).

Fig. 6 compares the NO oxidation results obtained by the present ozonization method with those by a typical nonthermal plasma process induced with dielectric barrier discharge [13]. 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 the discharge power to the 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 200 °C, the rate of NO oxidation in the plasma reactor was very slow in the absence of hydrocarbon additive. When ethylene (750 ppm) was added to the exhaust gas, the rate of NO oxidation by the nonthermal plasma was greatly enhanced. But, the formation of unwanted byproducts (CO, formaldehyde) from ethylene was observed, and this should be considered as a disadvantage of the nonthermal plasma method with hydrocarbon additive [13]. The detailed chemistry related to the enhancement in the oxidation of NO and the formation of byproducts in the presence of ethylene was discussed in [13]. On the other hand, the ozonization method was able to efficiently oxidize NO without the help of ethylene, as shown in Fig. 6. This is an advantage of the ozonization method over the typical nonthermal plasma process. But, the energy efficiency can be similar in both cases if sufficient amount of hydrocarbon is present in the exhaust gas, as occurs in the diesel exhaust gases in which unburned hydrocarbon exists.

3.2. *Catalytic reduction of nitrogen oxides*

This section deals with the catalytic removal of NO_x when a part of NO was converted into NO_2 by means of the ozonization. As an example, Fig. 7 shows the behavior of NO and NO_2 concentrations at the outlet of the ozonization–catalysis hybrid process at a reaction temperature of 200 °C. When the simulated exhaust gas was introduced into the process without ammonia and ozone, the concentrations of NO and NO_2

at the outlet of the hybrid process gradually increased with the time elapsed, and after a while reached the steady values. Then, ammonia was added to the simulated exhaust gas. As time went by after the addition of ammonia, the concentration of NO at the outlet of the hybrid process was gradually lowered while the concentration of NO_2 decreased rapidly to zero. After about 30 min, the steady-state concentrations of NO and NO_2 were established at 83 and 0 ppm, respectively, which corresponds to a NO_x removal efficiency of 72%. When 150 ppm of ozone was added to the exhaust gas to produce approximately equimolar NO/NO_2 mixture, the concentration of NO decreased further, and NO_2 slightly increased. At this condition, the steady-state NO_x removal efficiency increased to 88%. On the other hand, when the concentration of NO_2 at the outlet of the ozonization chamber was much higher than that of NO (275 ppm of ozone was added), poorer NO_x removal efficiency (59%) was obtained due to the large increase in the NO_2 concentration. The results in Fig. 7 emphasize that an excessive oxidation of NO in the ozonization chamber should be avoided if the effective catalytic reduction of NO_x is considered. Thus, further experiments were conducted with equimolar mixture of NO and NO_2, which gives the highest NO_x removal efficiency.

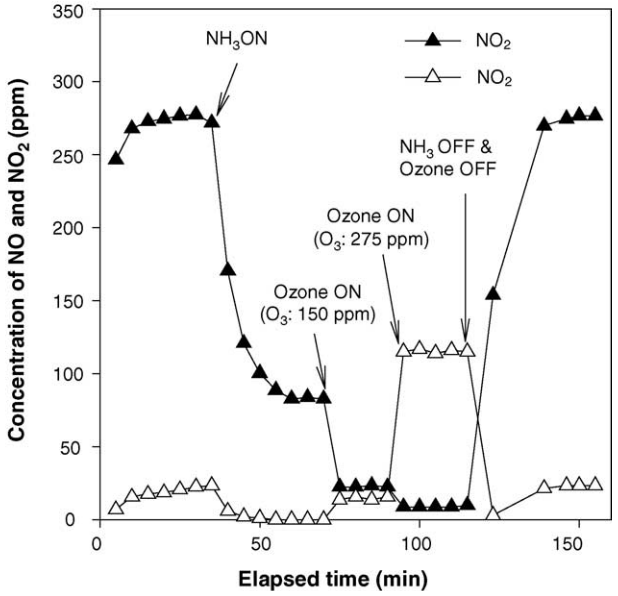

Fig. 7. Concentration variations of NO and NO_2 in the ozonization–catalysis hybrid process (initial NO_x: 300 ppm; flow rate: 5 L/min; temperature: 200 °C).

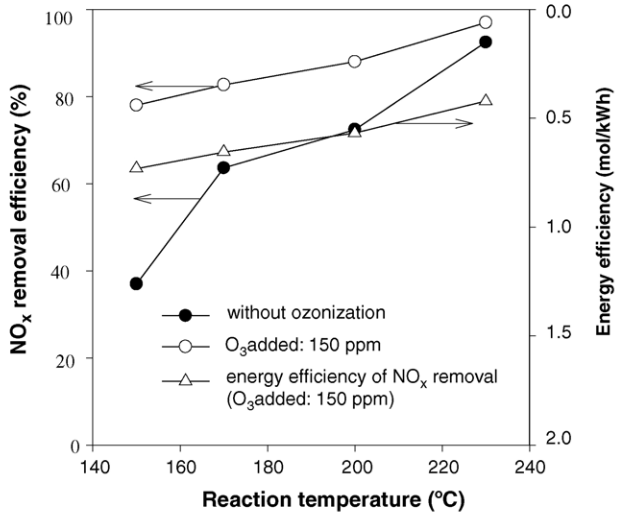

Fig. 8. Effect of reaction temperature on the catalytic reduction of NO_x in the presence and in the absence of the ozonization (initial NO_x: 300 ppm; flow rate: 5 L/min).

The effect of the reaction temperature on the NO_x removal efficiency is shown in Fig. 8, where the NO_x removal efficiencies either in the presence or in the absence of ozonization were compared. In this figure, the energy efficiency of the NO_x removal in the presence of ozonization is also given. When the catalytic reactor was independently used without the ozonization of the exhaust gas, i.e., when the major constituent of NO_x was NO, the reaction temperature significantly affected the removal of NO_x. It is generally accepted that the catalytic reduction of NO_x with the majority of NO in the presence of ammonia proceeds as follows [1]:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{5}$$

When ozone was not added to the exhaust gas, reaction (5) is the major NO_x removal pathway because of very small amount of NO_2 in the exhaust gas. Unfortunately, the temperature dependence of this reaction is very large due to its high activation energy [6]. As a result, the decrease in the reaction temperature significantly decreases the NO_x removal. On the other hand, when 150 ppm of ozone was added to the exhaust gas to produce approximately equimolar NO/NO_2 mixture, the temperature dependence of NO_x removal became much smaller. If the gas contains NO_2, the following reaction as well as reaction (5) occurs [2,6]:

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \tag{6}$$

In Fig. 8, the smaller temperature dependence of NO_x removal in the presence of the ozonization indicates that the activation energy of reaction (6) is smaller than that of reaction (5). According to the literature [6], the estimated activation energies of reactions (5) and (6) are 73.5 and 25.2 kJ/mol, respectively. Therefore, the contribution of reaction (6) to the catalytic reduction becomes increasingly important as the temperature decreases. As can be seen in Fig. 8, when the reaction temperature was low, the ozonization of the exhaust gas largely improved the catalytic reduction of NO_x, but at a temperature as high as 230 °C, such an improvement was almost disappeared.

Fig. 9 shows the FTIR spectra which inform the formation of byproducts when 150 ppm of ozone was added to the exhaust gas. Both NO_3 and N_2O_5 were not detected at the outlets of the ozonization chamber (before catalyst) and the catalytic reactor (after catalyst). This result signifies that there is no chemistry for the formation of NO_3 and N_2O_5 in the

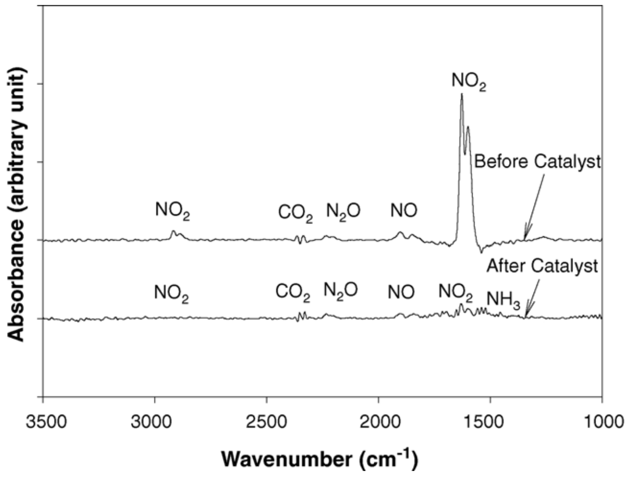

Fig. 9. Fourier transform infrared spectra before and after catalytic reactor (initial NO_x: 300 ppm; ozone added: 150 ppm; flow rate: 5 L/min; temperature: 170 °C).

catalytic reactor. Meanwhile, the commercially available catalyst based on V_2O_5-WO_3/TiO_2 tends to form nitrous oxide (N_2O) [2]. The small peak at the wave number $2236\,cm^{-1}$ reveals the presence of nitrous oxide. The possible reaction leading to nitrous oxide is as follows [2]:

$$4NO + 4NH_3 + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad (7)$$

As mentioned above, the ozone generator using air as the ozone source can produce nitrous oxide, thus the nitrous oxide measured at the outlet of the catalytic reactor also includes that produced in the ozone generator. More data on the formation of nitrous oxide will be presented and discussed below.

Fig. 10 presents the ozone slip downstream the ozonization chamber (before catalyst) and downstream the catalytic reactor (after catalyst) at temperatures from 170 to 230 °C when 150 ppm of ozone was added to the exhaust gas. The ozone concentration measured at the outlet of the ozonization chamber was around 6 ppm, slightly depending on the reaction temperature. As the exhaust gas treated in the ozonization chamber passed through the catalytic reactor, the unreacted ozone decreased to below 4 ppm. This decrease in the concentration of ozone is due to the thermal decomposition of ozone in the catalytic reactor.

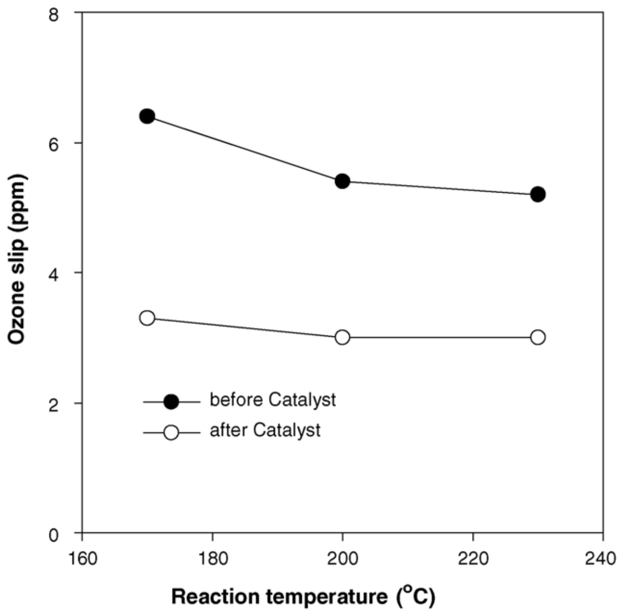

Fig. 10. Emission of unreacted ozone as a function of reaction temperature (initial NO_x: 300 ppm; ozone added: 150 ppm; flow rate: 5 L/min).

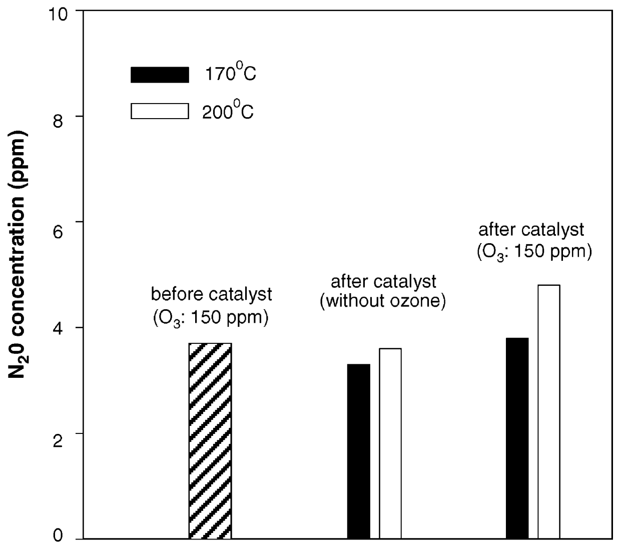

Fig. 11. Formation of nitrous oxide in the ozonization chamber and in the catalytic reactor (initial NO_x: 300 ppm; flow rate: 5 L/min).

The formation of N_2O on the catalyst in the presence and in the absence of the ozonization was reported in Fig. 11, where the concentration of N_2O at the outlet of the ozonization chamber was also presented for comparison. Without the ozonization, 3.3 and 3.6 ppm of N_2O were formed in the catalytic reactor at 170 and 200 °C, respectively. On the other hand, the concentration of N_2O at the outlet of the catalytic reactor slightly increased when the exhaust gas was first treated in the ozonization chamber. But, it should be noted that the net amount of N_2O produced in the catalytic reactor in the presence of the ozonization is smaller than that in the absence of it. That is, the concentration of N_2O measured at the outlet of the catalytic reactor in the presence of the ozonization includes not only that produced in the ozone generator, but also that produced in the catalytic reactor. Except for the N_2O produced in the ozone generator, the selectivity to the formation of N_2O on the catalyst was much lower when the mixture of NO and NO_2 resulting from the ozonization was used. Similar results were obtained by Madia et al. [3] who investigated the formation of N_2O on V_2O_5-WO3/TiO_2 catalyst for feed gases containing pure NO, equimolar mixture of NO and NO_2, and pure NO_2. This lower selectivity to N_2O with the mixture of NO and NO_2 is believed to arise from fast depletion of NO by reaction (6), thereby suppressing reaction (7).

4. Conclusions

In the present ozonization–catalysis hybrid process, NO in the simulated exhaust gas is converted into NO_2 by means of ozonization, prior to catalytic reduction, and then the exhaust gas containing both NO and NO_2 enters the catalytic reactor. When the exhaust gas was first treated by the ozonization to produce equimolar mixture of NO and NO_2, the catalytic NO_x reduction efficiency was improved by 5–40%, depending on the reaction temperature. We found that excessive oxidation of NO to NO_2 should be avoided because NO_2-rich exhaust results in poorer NO_x reduction efficiency. The ozonization method was more energy-efficient for the oxidation of NO to NO_2 than the typical nonthermal plasma process in the absence of a hydrocarbon additive. The decomposition of ozone into molecular oxygen was not significant in the present ozonization–catalysis hybrid process. The degree of NO oxidation was approximately equal to the amount of ozone added to the exhaust gas. Neither NO_3 nor N_2O_5 was detected after the ozonization chamber as well as after the catalytic reactor. A small amount of unreacted ozone was detected at the outlet of the ozonization chamber, but it was further reduced to below 4 ppm in the catalytic reactor. The formation of N_2O in the catalytic reactor in the presence of the ozonization was smaller than that in the absence of it, probably due to faster depletion of NO leading to lower selectivity to N_2O.

Acknowledgement

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