acta physica slovaca vol. 55 No. 5, 467 – 478 October 2005

OPTIMUM NO_2/NO_x RATIO FOR EFFICIENT SELECTIVE CATALYTIC REDUCTION[1]

Y.S. Mok[2]*, E.Y. Yoon*, M. Dors†, J. Mizeraczyk[3]†
**Department of Chemical Engineering, Cheju National University, Jeju 690-756, South Korea*
†*Institute of Fluid-Flow Machinery, Polish Academy of Sciences, 80-952 Gdańsk, Poland*

Received 18 April 2005, in final form 31 May 2005, accepted 1 June 2005

A new method of using ozone generator to improve selective catalytic reduction of nitrogen oxides (NO_x) was investigated. In most practical exhaust gases, NO_x (NO plus NO_2) consists mainly of NO. Injecting ozone into the exhaust gas as a means for the oxidation of NO to NO_2, it was experimentally shown that the catalytic reduction of NO_x was remarkably enhanced. For the present study, a dielectric barrier discharge device using ac high voltage was employed to produce ozone, which was continuously fed to the exhaust gas. The experiments were primarily concerned with the influence of the NO_2/NO_x ratio on the catalytic reduction of NO_x. The effect of reaction temperature, water vapor content, oxygen content, initial NO_x concentration, and ammonia concentration on the catalytic reduction of NO_x under various NO_2/NO_x ratios were examined. The changes in the NO_2/NO_x ratio as a result of the ozone injection into the exhaust gas were found to largely improve the catalytic reduction of NO_x, especially at low temperatures.

PACS: 52.80.-s, 52.80.Pi

1 Introduction

Removal of nitrogen oxides such as NO and NO_2, called NO_x, from a variety of exhaust gases is a significant industrial concern. Selective catalytic reduction (SCR) process is a well-known technology to remove NO_x efficiently [1-5]. In the SCR process, ammonia (NH_3) is generally used as the reducing agent, and NO_x contained in the exhaust gas is converted into nitrogen (N_2) and water (H_2O) by reacting selectively with NH_3. This process usually works well in a certain temperature range from 250 to 400°C, but at lower temperatures the NO_x removal performance largely decreases [6, 7].

In most exhaust gases, the majority of NO_x is NO and the content of NO_2 is less than 5% . A notable attempt to improve the NO_x removal performance at lower temperatures was to combine

---

[1] Presented at Joint 15th Symposium on Applications of Plasma Processes (SAPP) and 3rd EU-Japan Symposium on Plasma Processing, Podbanské (Slovakia), 15 – 20 January 2005.

[2] E-mail address: smokie@cheju.ac.kr

[3] E-mail address: jmiz@imp.gda.pl

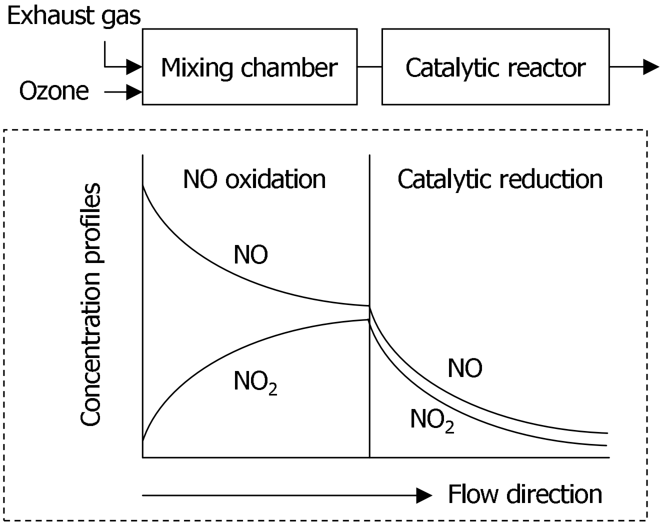

Fig. 1. Description of the catalytic NO_x reduction process enhanced by the ozone injection.

a nonthermal plasma process with the SCR [6, 8-10]. In this kind of combined process, the main role of the nonthermal plasma is to convert NO into NO_2. As reported in many papers [6, 7, 9, 11], the catalytic reduction of NO_x in the exhaust gas containing a mixture of NO and NO_2 is faster than in the exhaust gas with the large majority of NO.

The other favorable method capable of oxidizing NO to NO_2 is to inject ozone into the exhaust gas. In this work, the injection of ozone into the exhaust gas, instead of using nonthermal plasma directly, was suggested as a NO oxidation method for improving the SCR process at low temperatures. A dielectric barrier discharge (DBD) device was employed to produce ozone. Since the rate of the reaction between NO and ozone ($NO+O_3 \rightarrow NO_2+O_2$) is extremely fast, the ozone injection can be a preferable method to readily change the content of NO_2, i.e., the ratio of NO_2 to NO_x. The present system was formed with a chamber to mix the exhaust gas and ozone, followed by a catalytic reactor, as shown in Fig. 1. In this chamber, a part of NO was oxidized to NO_2 by ozone injected, prior to the exhaust gas entering the catalytic reactor. The exhaust gas treated by this way, containing the mixture of NO and NO_2, was then directed to the catalytic reactor where NH_3 reacted with NO and NO_2 to convert them into nitrogen and water. The details for the present investigation are described below.

2 Experimental methods

In Fig. 2, the schematic diagram of the experimental apparatus consisting of a DBD device to generate ozone, a chamber to mix the exhaust gas and ozone, and a catalytic reactor is shown. The volume of the mixing chamber was 245 cm^3. The DBD device using ac high voltage has been discussed in detail previously [14]. The exhaust gas first treated by ozone in the mixing chamber

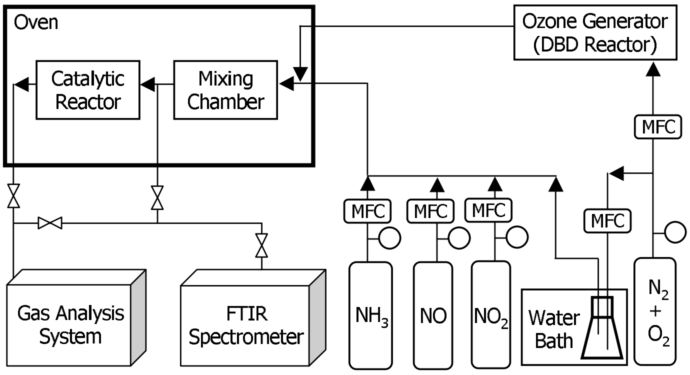

Fig. 2. Schematic diagram of the experimental apparatus.

entered the catalytic reactor in which a commercially available monolithic V_2O_5-WO_3/TiO_2 catalyst (20 channels per square inch; apparent volume: 30 cm^3) was placed. The vanadium and tungsten contents in the catalyst were 1.6 and 7.3 wt.%, respectively, and the surface area determined by BET (Brunauer-Emmett-Teller) adsorption isotherm was 60 m^2/g. In order to adjust the reaction temperature to a desired value, the mixing chamber and the catalytic reactor were installed in an oven.

The simulated exhaust gas was prepared by mixing air-like gas (nitrogen plus oxygen) and a small amount of concentrated NO gas (5.0%(v/v) balanced with N_2). The unit %(v/v) is the percent concentration of a substance on the basis of volume, i.e., 100 times the volume of the substance of interest divided by total volume. The flow rate of the concentrated NO gas was controlled by a mass flow controller (MFC, Model 1179A, MKS Instruments, Inc., USA). In the air/NO mixture prepared as mentioned above, a small portion of NO (about 4%) was naturally oxidized to NO_2 due to the presence of oxygen. The oxygen source for the ozone generator was also air. Typical inlet concentration of NO_x (NO+NO_2) was 300 ppm (parts per million, volumetric; 1 ppm corresponds to 4.1×10^{-5} mol/m^3 at 298 K and 1.0 atm), and it was varied from 200 to 500 ppm. For the catalytic reduction, ammonia (NH_3) was used as the reducing agent. The ratio of NH_3 to NO_x concentration was typically 1.0, and it was varied from 0.5 to 1.0. The flow rate of the simulated exhaust gas was typically 8.33×10^{-5} m^3/s (5 L/min) on the basis of room temperature. The experiments were conducted at temperatures in the range of 90 to 230°C. The NO_2/NO_x ratio at the inlet of the catalytic reactor was adjusted by changing the amount of ozone produced in the DBD device, i.e., the higher ac voltage applied to the DBD device was, the more ozone was produced, thereby converting more NO into NO_2 in the mixing chamber placed in front of the catalytic reactor. In an experiment performed without oxygen, the simulated exhaust gas was prepared by mixing nitrogen, concentrated NO gas (5.0%(v/v) balanced with N_2) and concentrated NO_2 gas (5.0%(v/v) balanced with N_2).

The concentrations of NO and NO_2 were analyzed by a chemiluminescence NO-NO_2-NO_x analyzer (Model 42C, Thermo Environmental Instruments, Inc., USA). 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, Inc., USA) equipped with a 2.4 m permanently aligned long path gas cell (Pike Technologies, Inc., USA) 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., USA).

3 Results and discussion

3.1 Influence of the inlet NO_2/NO_x ratio on the catalytic reduction

As described in the preceding paper [14], the injection of ozone into the exhaust gas does not lower the NO_x level ($NO+NO_2$), simply converting NO into NO_2. But, the change in the NO_2/NO_x ratio can significantly affect the performance of the catalytic reactor. This section deals with the effect of the NO_2/NO_x ratio on the catalytic reduction of NO_x.

In the typical SCR process using NH_3 as the reducing agent, the NO contained in the exhaust gas is reduced to N_2 as follows:

$$4NO+ 4NH_3+O_2 \rightarrow 4N_2+6H_2O \tag{1}$$

Since most practical exhaust gases are made up mainly of NO, reaction (1) is the major one when ozone is not injected.

If the exhaust gas contains a considerable amount of NO_2 by the ozone injection, the reaction as below rapidly occurs:

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

Besides, the following reactions can also reduce NO_x at low temperatures:

$$6NO_2+8NH_3 \rightarrow 7N_2+12H_2O \tag{3}$$

$$2NO_2+2NH_3 \rightarrow N_2+H_2O+NH_4NO_3(s) \tag{4}$$

In a certain range of NH_3 concentration, it does not affect the reaction rate, i.e., the reaction order of NH_3 is zero, while the reaction orders of NO and NO_2 are reported to be one [1, 6, 12, 13].

As an example to elucidate the behavior of the catalytic reduction according to the change in the NO_2/NO_x ratio at the inlet of the catalytic reactor, Fig. 3 shows the variations of NO, NO_2 and NO_x concentrations at the outlet of the catalytic reactor when the temperature was 150°C. As the NO_2/NO_x ratio at the inlet of the catalytic reactor increased by the ozone injection, the concentration of NO at the outlet decreased while the concentration of NO_2 increased. The concentration of NO_x (NO plus NO_2) showed a minimum when the NO_2/NO_x ratio was about 0.5. From the results in Fig. 3, it is obvious that the NO_2/NO_x ratio at the inlet of the catalytic reactor can influence the NO_x removal and there exists an optimum inlet NO_2/NO_x ratio for efficient catalytic NO_x removal.

3.2 Effect of the temperature of gaseous mixture on the NO_x removal efficiency

The temperature dependence of the catalytic reduction of NO_x is shown in Fig. 4. In this figure, the NO_x removal efficiency (Re%) was calculated as follows:

$$\mathrm{Re}\% = 100 \times \frac{[NO_x]_0 - [NO_x]_f}{[NO_x]_0} \tag{5}$$

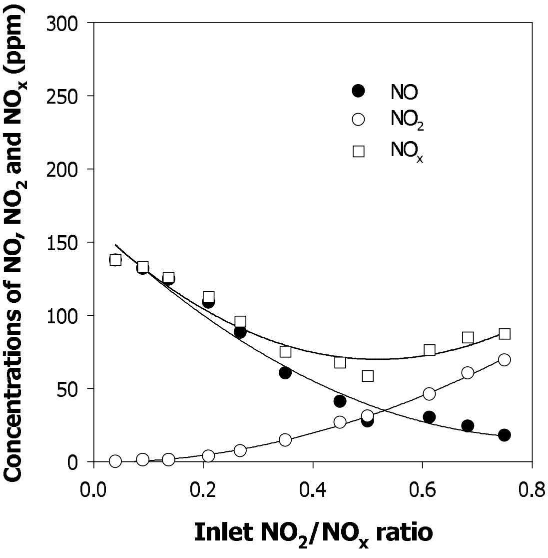

Fig. 3. Concentration variations of NO, NO_2 and NO_x at the outlet of the catalytic reactor as a function of the inlet NO_2/NO_x ratio (reaction temperature: 150°C; initial NO_x: 300 ppm; ammonia: 300 ppm; oxygen: 20%(v/v); water vapor: 0%(v/v)).

In Eq. (5), the subscripts 0 and f stand for the inlet and outlet of the reactor system, respectively. From 150 to 230°C, there was an optimal inlet NO_2/NO_x ratio at each temperature, leading to a maximum NO_x removal efficiency. Without the ozone injection, the NO_x removal efficiencies obtained at 150, 170, 200 and 230°C were 51, 67, 76 and 93%, respectively. When the NO_2/NO_x ratio at the inlet of the catalytic reactor was increased to 0.5 by the ozone injection, the respective NO_x removal efficiencies at the corresponding temperatures increased to 80, 86, 90 and 97%. As mentioned above, the catalytic reduction of NO_x via reaction (2) is faster than that via reaction (1). As well, reaction (2) implies that the content of NO_2 should be equal to that of NO. That is why maximum NO_x removal efficiency occurred when the NO_2/NO_x ratio was around 0.5. On the other hand, at temperatures lower than 120°C, the NO_x removal efficiency was kept increasing with the inlet NO_2 content. This result means that reactions (3) and (4) as well as reaction (2) played an important role in the NO_x removal in the low temperature range.

Meanwhile, the dependence of the NO_x removal efficiency on the reaction temperature was very large when ozone was not injected into the exhaust gas (inlet NO_2/NO_x ratio: 0.04). However, when the inlet NO_2/NO_x ratio was increased to 0.5 by the ozone injection, NO_x removal efficiency was largely enhanced, and also the temperature dependence of the NO_x removal efficiency became smaller. This small temperature dependence of the NO_x removal efficiency in the presence of the ozone injection is because the activation energy of reaction (2) is much less than that of reaction (1) [6].

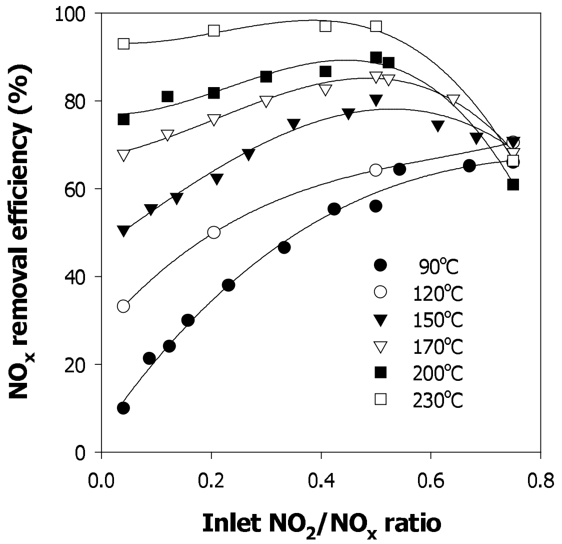

Fig. 4. Temperature dependence of the catalytic reduction of NO_x at various inlet NO_2/NO_x ratios (initial NO_x: 300 ppm; ammonia: 300 ppm; oxygen: 20%(v/v); water vapor: 0%(v/v)).

3.3 Effect of the initial NO_x concentration on the NO_x removal efficiency

The effect of the initial NO_x concentration on the NO_x removal efficiency is given in Fig. 5. The initial NO_x concentration was changed from 200 to 500 ppm, fixing the ratio of NH_3 to the initial NO_x to 1.0. As can be seen, the NO_x removal efficiency showed little dependence on its initial concentration over the range of 200 to 500 ppm. The fact that the NO_x removal efficiency is not affected by the initial concentration can be a merit from the practical application point of view. Compared to the case of NO-rich exhaust gas (without the ozone injection), the NO_x removal efficiency was improved by 20% when the inlet NO_2/NO_x ratio was increased to 0.5 by the ozone injection.

The main NO_x removal pathway in the absence of the ozone injection is reaction (1), which is a first order reaction in terms of NO concentration, as mentioned above. The first order reaction means that the NO_x removal efficiency does not depend on the concentration. That is why the NO_x removal efficiency without the ozone injection was nearly independent on the initial concentration. On the other hand, when NO and NO_2 coexists by the ozone injection, NO_x is removed by reactions (1)-(4). Among them, reaction (2) playing important role in the removal of NO_x is a second order reaction in terms of both NO and NO_2. When the reaction order is two, the removal efficiency should depend on the concentration. But, the NO_x removal efficiency in the presence of the ozone injection was also not relevant to the initial concentration. To explain this result, more detailed reaction mechanism should be considered. According to the literature [15], the first step of reaction (2) is the adsorption of NO_2 on the catalyst surface, and

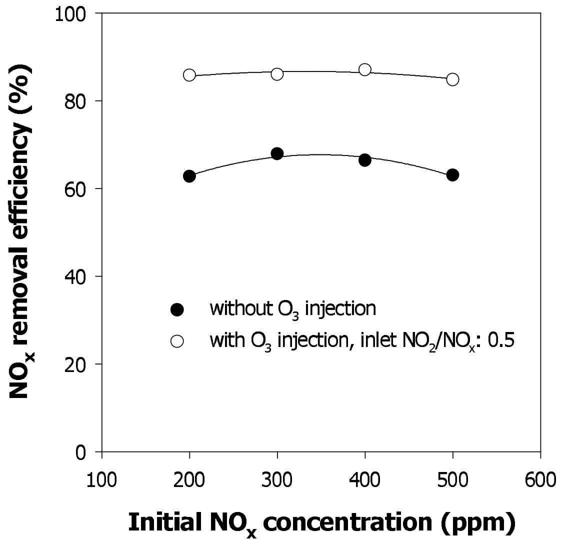

Fig. 5. Effect of the initial NO_x concentration on the NO_x removal efficiency (reaction temperature: 170°C; NH_3/initial NO_x: 1.0; oxygen: 20%(v/v); water vapor: 0%(v/v)).

then the adsorbed NO_2 reacts with NO in the gas phase to form N_2O_3. The N_2O_3 fixed on the catalyst surface is reduced to N_2 and H_2O through the reaction with the adsorbed NH_3. The formation of N_2O_3 and the reaction of N_2O_3 with NH_3 are fast whereas the adsorption of NO_2 on the catalyst surface is very slow. Since the adsorption of NO_2 that is the rate-determining step is a first order reaction in terms of NO_2 concentration, the NO_x removal efficiency in the presence of the ozone injection was almost independent on the initial concentration.

3.4 Effect of the oxygen content on the NO_x removal efficiency

The effect of the oxygen content in the exhaust gas on the NO_x removal efficiency is presented in Fig. 6. In the range from 4 to 20%(v/v), the oxygen content did not largely affect the NO_x removal efficiency. Particularly, the NO_x removal efficiency at the inlet NO_2/NO_x ratio of 0.5 was similar in this range of the oxygen content. Since the oxygen content from 4 to 20%(v/v) is excessive, compared to the initial NO_x concentration of 300 ppm, the weak influence on the NO_x removal is reasonable. Meanwhile, when oxygen was not present, lower NO_x removal efficiencies were observed. For reaction (1), oxygen is necessary. Without oxygen, this reaction occurs slowly, resulting in low NO_x removal efficiency. When NO and NO_2 coexists by the ozone injection, reaction (2) that does not require oxygen can significantly contribute to the removal of NO_x. Thus, high NO_x removal efficiency can be achieved even in the absence of oxygen.

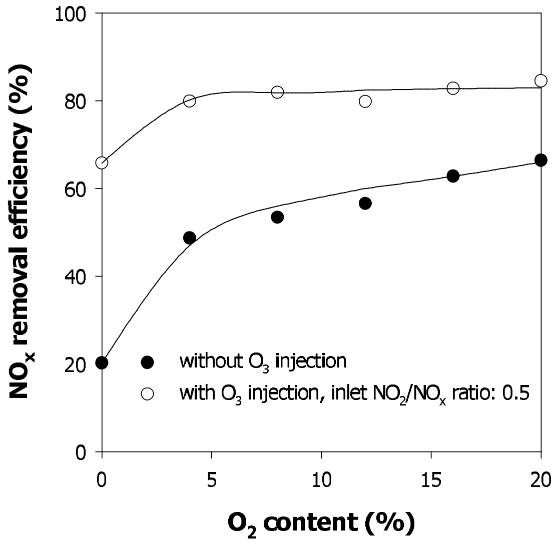

Fig. 6. Effect of the oxygen content on the NO_x removal efficiency (reaction temperature: 170°C; initial NO_x: 300 ppm; ammonia: 300 ppm; water vapor: 0%(v/v)).

3.5 Effect of the water vapor content on the NO_x removal efficiency

Real exhaust gases from hydrocarbon combustions contain considerable amounts of water vapor. So as to examine the effect of the water vapor content on the catalytic reduction of NO_x, it was varied between 0 and 5%(v/v) with the other conditions kept constant. Since water molecules can occupy some of the active sites of the catalyst, they may inhibit the catalytic reduction of NO_x. From Fig. 7, it is apparent that the increase in the inlet NO_2/NO_x ratio by the ozone injection resulted in a remarkable improvement in the catalytic reduction of NO_x regardless of the presence of the water vapor. When the water vapor content increased from 0 to 1.5%(v/v), slight decreases in the NO_x removal efficiency were observed both with and without the ozone injection. On the contrary, further increases in the water vapor content up to 5%(v/v) did not nearly affect the catalytic reduction. It is also reported in the literature that water vapor above 1.0%(v/v) exhibits similar inhibiting action on the catalytic reduction of NO_x [16]. This phenomenon may be explained by the high adsorption energy of ammonia. The catalytic reduction of NO_x gets started by the adsorption of ammonia, which reacts with nitrogen oxides molecule in the next step. Thus, the adsorption of ammonia plays an important role in the catalytic reduction process. Generally, the adsorption energy of ammonia is higher than that of water vapor, i.e., the water molecule adsorbed on the catalyst surface can be easily replaced by ammonia.

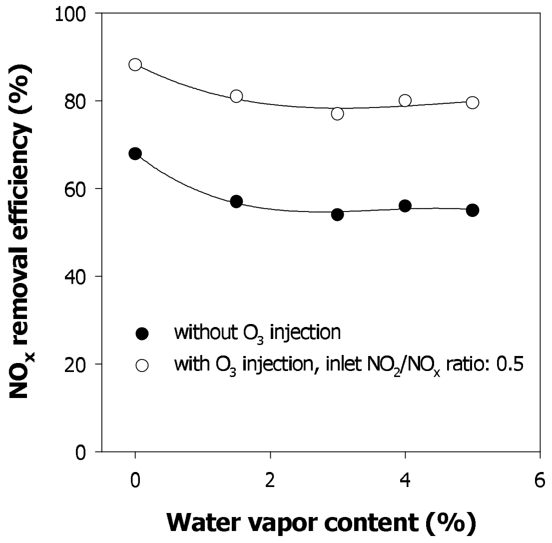

Fig. 7. Effect of the water vapor content on the NO_x removal efficiency (reaction temperature: 170°C; initial NO_x: 300 ppm; ammonia: 300 ppm; oxygen: 20%(v/v)).

3.6 Effect of the ammonia concentration on the NO_x removal efficiency

Fig. 8 presents the effect of the ammonia concentration used as the reducing agent on the NO_x removal efficiency. In order to examine the effect of the ammonia concentration, the ratio of NH_3 to the initial NO_x concentration was changed from 0.5 to 1.0 with the other variables fixed. One general trend is that the NO_x removal efficiency increased with the amount of NH_3 added, which indicates that the reducing agent is necessary in the catalytic NO_x removal process. In the same manner with the above results, best NO_x removal efficiency was observed at the NO_2/NO_x ratio of 0.5, i.e., when the concentration of NO was equal to that of NO_2. This result emphasizes again that the amount of ozone injected into the exhaust gas should be adjusted to give equimolar NO and NO_2 mixture.

3.7 Comparison between the present process and the plasma-catalysis hybrid process

A comparison between the nonthermal plasma-catalysis hybrid process and the present process was made as in Fig. 9. So as to compare the results on an identical basis, the data for the NO_x removal efficiencies were presented with respect to the energy density applied to the nonthermal plasma reactor or the ozone generator. In case of the nonthermal plasma-catalysis process using dielectric barrier discharge [9], both ethylene and ammonia were used because the rate of NO oxidation was very slow without hydrocarbon additive. As can be seen, the NO_x removal efficiency obtained in the present process was similar to that obtained in the nonthermal plasma-catalysis

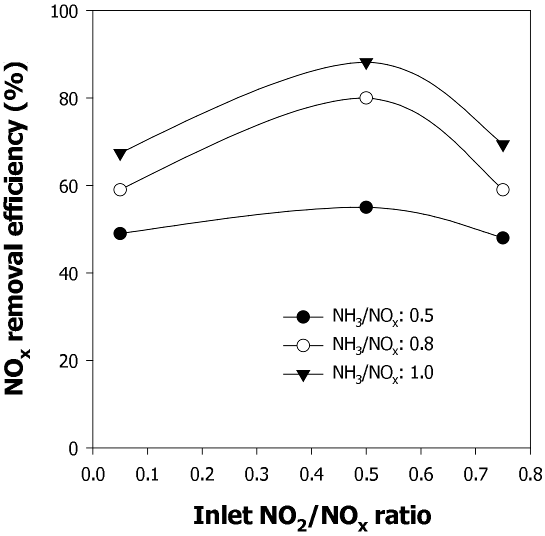

Fig. 8. Effect of the ammonia concentration on the NO_x removal efficiency (reaction temperature: 170°C; initial NO_x: 300 ppm; oxygen: 20%(v/v); water vapor: 0%(v/v)).

hybrid process when the energy density was below 25 J/L. However, at higher energy densities the nonthermal plasma-catalysis hybrid process showed better NO_x removal performance than the present process. As reported in the previous study [6, 9], the nonthermal plasma can remove some NO_x although the main role of the nonthermal plasma is to oxidize NO to NO_2. In Fig. 9, the better NO_x removal performance of the plasma-catalysis hybrid process may be attributed to the removal of NO_x by the action of the nonthermal plasma. But, the formation of unwanted byproducts from hydrocarbon additive when using the nonthermal plasma should be resolved. In this context, the present ozone injection method producing no byproducts may be more promising for practical uses.

4 Concluding remarks

The application of ozone injection method to the catalytic reduction of nitrogen oxides (NO_x) was investigated. The addition of ozone to the exhaust gas increased the NO_2/NO_x ratio as a result of the oxidation of NO to NO_2, leading to the enhancement in the catalytic reduction of NO_x. Main conclusions drawn in this study can be summarized as follows. Above 150°C, there was an optimum inlet NO_2/NO_x ratio for the efficient catalytic reduction of NO_x, which was found to be around 0.5. On the other hand, at lower temperatures less than 120°C, the NO_x removal efficiency in the catalytic reactor tended to keep increasing with the inlet NO_2/NO_x ratio. The NO_x removal efficiency showed large dependence on the reaction temperature, but

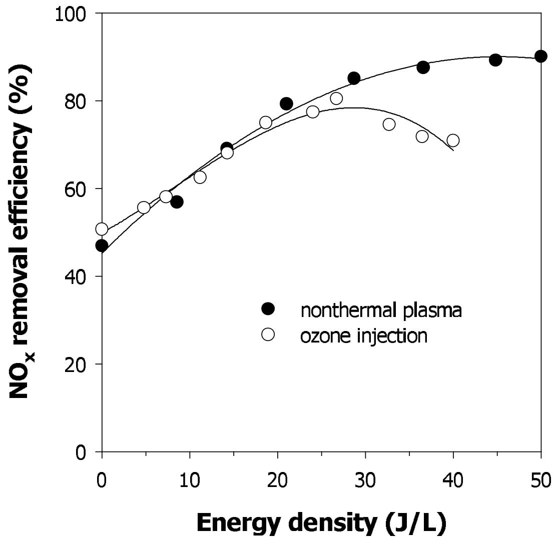

Fig. 9. Comparison of the NO_x removal efficiency between the present hybrid process and the nonthermal plasma-catalysis hybrid process (reaction temperature: 150°C; initial NO_x: 300 ppm; ammonia: 300 ppm; oxygen: 20%(v/v); water vapor: 0%(v/v)).

the relationship between the NO_x removal efficiency and its initial concentration in the range of 200 to 500 ppm was hardly observed. Besides, the oxygen content from 4 to 20%(v/v) and the water vapor content from 1.5 to 5.0%(v/v) did not largely affect the NO_x removal efficiency. The ozone injection method was very efficient to improve the catalytic reduction of NO_x in a wide range of temperatures, and the NO_x removal efficiency was comparable to the nonthermal plasma-catalysis hybrid process.

Acknowledgement: This work was supported by the International Cooperative Research Program of the Korea Science and Engineering Foundation (KOSEF) under Grant number F01-2004-000-10043-0.

References

[1] H. Bosch, F. Janssen: *Catal. Today* **2** (1998) 369
[2] M. Farber, S. P. Harris: *J. Phys. Chem.* **88** (1984) 680
[3] H. H. Kim, K. Takashima, S. Katsura, A. Mizuno: *J. Phys. D: Appl. Phys.* **34** (2001) 604
[4] H. S. Roh, Y. K. Park, S. E. Park: *J. Ind. Eng. Chem.* **9** (2003) 341
[5] E. Tronconi, P. Forzatti, J. P. Gomez Martin, S. Malloggi: *Chem. Eng. Sci.* **47** (1992) 2401
[6] S. Bröer, T. Hammer: *Appl. Catal. B: Environ.* **28** (2000) 101

[7] M. Koebel, M. Elsener, G. Madia: *Ind. Eng. Chem. Res.* **40** (2001) 52
[8] H. Miessner, K.-P. Francke, R. Rudolph, T. Hammer: *Catal. Today* **75** (2002) 325
[9] Y. S. Mok, V. Ravi, H. C. Kang, B. S. Rajanikanth: *IEEE Trans. Plasma Sci.* **31** (2003) 157
[10] T. Oda, T. Kato, T. Takahashi, K. Shimizu: *J. Electrostatics* **42** (1997) 151
[11] R. G. Tonkyn, S. E. Barlow, J. Hoard: *Appl. Catal. B: Environ.* **40** (2003) 207
[12] M. Inomata, A. Miyamoto, Y. Murakami: *J. Catal.* **62** (1980) 140
[13] S. T. Choo: *A Kinetic Study for Selective Catalytic Reduction of NO_x by NH_3 over V_2O_5-WO_3/TiO_2 Catalyst*, Ph.D. Thesis, Pohang University of Science and Technology, Korea 1996
[14] Y. S. Mok: *J. Chem. Eng. Japan* **37** (2004) 1337
[15] F. Luck, J. Roiron: *Catal. Today* **4** (1989) 205
[16] M. Koebel, M. Elsener: *Chem. Eng. Sci.* **53** (1998) 657