

Effective combination of non-thermal plasma and catalyst for removal of volatile organic compounds and NOx

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(Received 30 August 2006 • accepted 1 November 2006)

Abstract—A plasma/catalyst hybrid reactor was designed to overcome the limits of plasma and catalyst technologies. A two-plasma/catalyst hybrid system was used to decompose VOCs (toluene) and NOx at temperature lower than 150 °C. The single-stage type (Plasma-driven catalyst process) is the system in which catalysts are installed in a non-thermal plasma reactor. And the two-stage type (Plasma-enhanced process) is the system in which a plasma and a catalyst reactor are connected in series. The catalysts prepared in this experiment were Pt/TiO₂ and Pt/Al₂O₃ of powder type and Pd/ZrO₂, Pt/ZrO₂ and Pt/Al₂O₃ which were catalysts of honeycomb type. When a plasma-driven catalyst reactor with Pt/Al₂O₃ decomposed only toluene, it removed just more 20% than the only plasma reactor but the selectivity of CO₂ was remarkably elevated as compared with only the plasma reactor. In case of decomposing VOCs (toluene) and NOx using plasma-enhanced catalyst reactor with Pt/ZrO₂ or Pt/Al₂O₃, the conversion of toluene to CO₂ was nearly 100% and about 80% of NOx was removed.

Key words: Non-thermal Plasma, Catalyst, Volatile Organic Compounds, NOx

INTRODUCTION

Heterogeneous catalysts have been used to treat combustion exhaust gases and the emissions from numerous other air pollution sources for many years [1]. More recently, non-thermal plasma processes have been under intensive investigation for the removal of nitrogen oxides, sulfur dioxide, and many organic compounds (e.g., toluene, trichloroethylene, vinyl chloride) and other inorganic species (e.g., mercury) from industrial and commercial gas phase sources. These processes include pulsed corona discharge [2], dielectric barrier discharge (DBD) [3], and electron beam processes [4]. Although the electrode surfaces in such systems may have very high temperatures, and, in some selected applications, products may form and react on the surface of the electrode, typically the key chemical transformations in conventional plasma processes for waste control occur in the bulk gas.

There are two important issues in the research of non-thermal plasma processing for industrial applications. One is the cost factor consisting of energy efficiency, degree of maintenance, life-time and the use of additives, etc. The other one is the reaction products or byproducts formed from substrates and background gases. Many approaches have been made to overcome these obstacles during the last decade, and some promising results have been achieved. One of the effective approaches is the combination of non-thermal plasma with other methods such as chemical scrubber or catalyst [5-7]. The combination of non-thermal plasma with catalyst is divided into single-stage and two-stage processes. In the two-stage system, the main role of plasma is partial conversion of pollutants or production of ozone to facilitate catalytic reactions over subse-

quent proper catalysts [8,9]. Therefore, this two-stage configuration is also referred to as a plasma-enhanced or plasma-assisted catalyst process [10]. In the case of single stage configuration, catalysts are placed in the plasma reactor and are activated by high energy particles (electron, excited molecules) and photons produced by non-thermal plasma [11,12]. The typical temperature window of this process is below 200 °C, where the normal thermal catalytic reactions do not take place. In this sense, a single stage plasma-catalyst hybrid system is also referred to as a plasma-driven catalyst process [13].

This paper describes the effectiveness of a combined system of non-thermal plasma and catalysts for volatile organic compound and NOx removal at temperatures lower than 150 °C. The screening tests to select optimum condition in a combined system of non-thermal plasma and catalyst were also carried to enhance the volatile organic compounds and the NOx removal rate.

EXPERIMENTAL

1. Preparation of Catalysts

The commercial TiO₂ catalysts (P-25: TiO₂(P), Hombikat: TiO₂ (H)) and Pt/Al₂O₃ of powder type were coated on the surface of plasma electrodes. Pt/Al₂O₃ was prepared by incipient wetness impregnation of γ -Al₂O₃ support with an aqueous solution of hexachloroplatinic acid (H₂PtCl₆). Subsequently, the catalyst was dried at 100 °C over night and then calcined at 500 °C for 5 hr. The catalysts of powder type were coated on the electrodes of plasma by silkscreen method.

Pd and Pt catalysts were supported on ceramic cordierite honeycomb with a cell size of 200 cells/in². The honeycombs were wash-coated with ZrO₂ and γ -Al₂O₃. Catalysts were then added to the wash-coated honeycomb by impregnation with aqueous palladium nitrate (Pd(NO₃)₂) for the Pd catalyst and hexachloroplatinic acid (H₂PtCl₆) for the Pt catalysts. The catalysts were dried at 100 °C for 12 h and

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[‡]This work was presented at the 6th Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006.

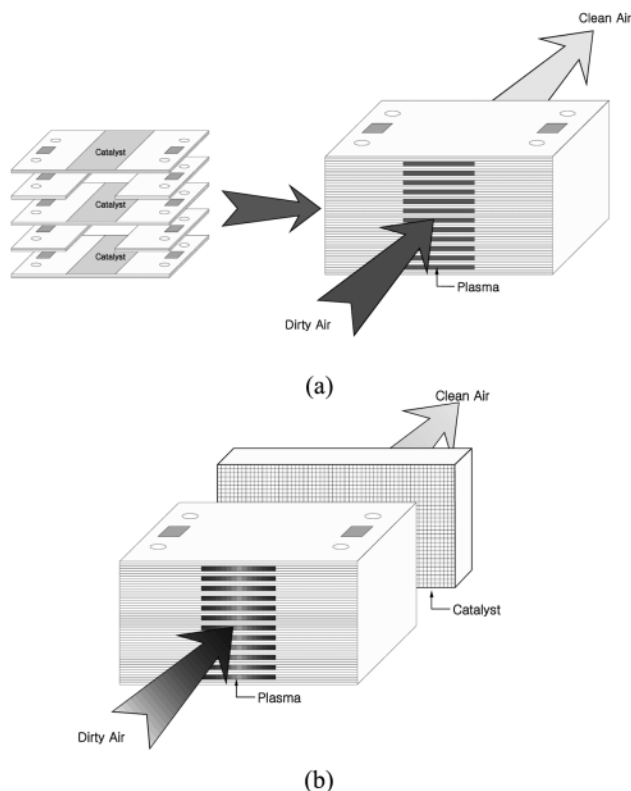


Fig. 1. Schematic diagram of non-thermal plasma system with catalyst: (a) Plasma-driven catalyst process, (b) Plasma-enhanced catalyst process.

calcined at 550 °C for 6 hr.

The powder type catalyst is installed in the single-stage which is referred to as a plasma-driven catalyst process. Also, the two-stage process, which is referred as a plasma-enhanced catalyst process, uses the catalyst of honeycomb type. The honeycomb catalyst was fixed in the reactor with dimension of 80 mm×60 mm×20 mm.

2. Plasma/Catalyst Hybrid System

Two different types of non-thermal plasma system with catalyst reaction systems were used in order to distinguish separate effects of plasma and catalysts from the combined effects (Fig. 1). In the single-stage system (plasma-driven catalyst process, shown in Fig. 1a), catalysts are installed in non-thermal plasma reactor to discharge a corona near the catalyst bed. The two-stage system (plasma-enhanced catalyst, shown in Fig. 1b) consists of a plasma reactor and a catalyst reactor which are connected in series. The reactor was energized with 60 Hz ac with a voltage up to 7.5 kV rms. No breakdowns occurred during operations at lower voltages than its maximum value. The applied voltage and current waveforms were measured by using a digital oscilloscope (Tektronix TDS3034) with a 1,000 : 1 high voltage probe (Tektronix P6015) and current measurement system (Tektronix AM503S).

The simulated flue gas consists of mixtures of toluene (1,000 ppm), NO (500 ppm) and air (balance). Water was not added to the simulated gas to clarify the effects of catalysts. Toluene and their reaction product were analyzed by two gas chromatographs (GC 5890 Series II, HP) equipped with a hydrogen flame ionization detector and a thermal conductivity detector. CO and CO₂ were separated with a

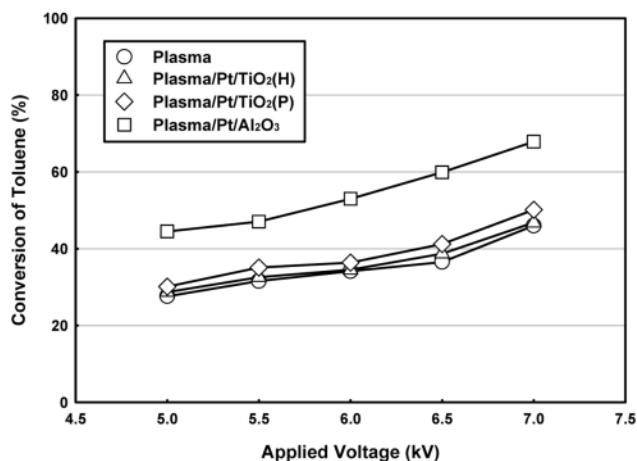


Fig. 2. Toluene decomposition of plasma-driven catalyst reactors as a function of applied voltage (Flow: 3 L/min, Temp.: 150 °C, Toluene: 1,000 ppm).

15 ft×1/8 inch Carboxen 1,000 column and Toluene with 60 m×0.56 mm HP-1 column. Concentrations of NO and NO₂ at the inlet and the outlet of the reactor were measured by a chemiluminescence NO_x analyzer (Thermo Environmental Co., 42C). NO_x concentration is the sum of the individual concentrations of NO and NO₂. Experiments were conducted at temperatures below 150 °C.

RESULTS AND DISCUSSIONS

1. Decomposition of Only Toluene in the Plasma-driven Catalyst Process

When the plasma was turned off, decomposition of toluene did not occur under 150 °C for all the catalysts tested in the present study. Decomposition of toluene was initiated only after the plasma was turned on. Therefore, it would be reasonable to present the result on the basis of plasma energy. Fig. 2 shows the performance of the plasma-driven catalyst reactor on the decomposition of toluene together with that of the plasma DBD reactor as a function of applied voltage. With an increase of the applied voltage, the conversion of toluene using Pt/Al₂O₃ was enhanced compared to the plasma DBD reactor under the same applied voltage. The conversion was up to about 70% at 7 kV, whereas, other catalysts did not show any synergy effect on decomposition efficiency of toluene.

Decomposed toluene was mostly converted to CO₂ and CO, and byproducts such as organic compound were detected from gas analysis. Fig. 3 shows the selectivity of CO and CO₂ selectivity in the tested plasma-driven catalyst reactors as a function of applied voltage. Here, the selectivity of CO and CO₂ was calculated as follows:

$$\text{CO Selectivity (\%)} = \frac{[\text{CO}]}{7([\text{Toluene}]_0 - [\text{Toluene}])} \times 100,$$

$$\text{CO}_2 \text{ Selectivity (\%)} = \frac{[\text{CO}_2]}{7([\text{Toluene}]_0 - [\text{Toluene}])} \times 100$$

where the [Toluene]₀ and [Toluene] indicate inlet and outlet concentration of toluene, respectively. As in the case of toluene decomposition, the plasma-driven catalyst reactor using Pt/Al₂O₃ showed higher selectivity for CO₂ without forming CO in all the test runs despite the improvement in toluene decomposition. Selectivity of

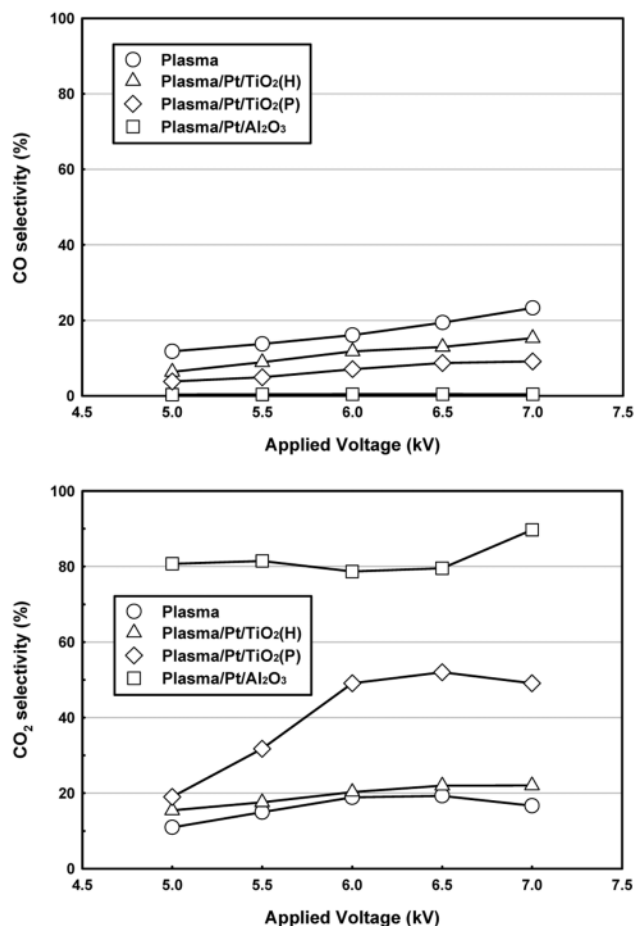


Fig. 3. CO and CO₂ selectivity of plasma-driven catalyst reactors as a function of applied voltage (Flow: 3 L/min, Temp.: 150 °C, Toluene: 1,000 ppm).

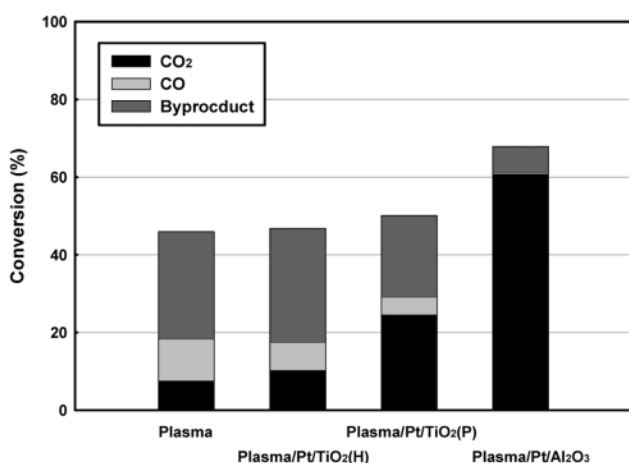


Fig. 4. Composition of product in removal of toluene using various plasma-driven catalyst processes (Applied voltage: 7 kV, Flow: 3 L/min, Temp.: 150 °C, Toluene: 1,000 ppm).

CO₂ for the plasma combined with Pt/Al₂O₃ ranged from 80% to 90%, which was four times higher than that of the plasma DBD reactor. The plasma-driven catalyst reactor with Pt/TiO₂(P) was also effective in increasing the selectivity of CO₂, although Pt/Al₂O₃ had

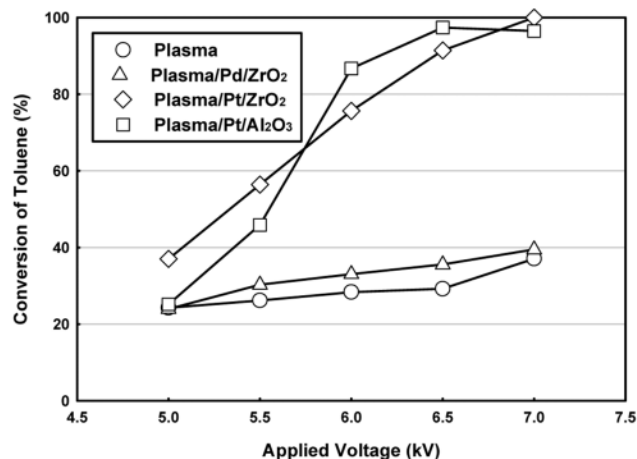


Fig. 5. Toluene decomposition of plasma-enhanced catalyst reactors as a function of applied voltage (Flow: 3 L/min, Temp.: 150 °C, Toluene: 1,000 ppm, NO: 500 ppm).

better performance. Fig. 4 shows the change of product composition with respect to treatment methods of toluene at applied voltage of 7 kV. As shown in the figure, all the reactors produced a large amount of the byproduct except the plasma-driven catalyst reactor using Pt/Al₂O₃. The yield of byproduct for the plasma DBD reactor and plasma reactor combined with Pt/TiO₂(H) was beyond 50%. The plasma-driven catalyst reactor with Pt/TiO₂(P) also had high yield of byproduct, although it had lower yield than plasma DBD and plasma reactor combined with Pt/TiO₂(H). From these results, it was confirmed that the plasma-driven catalyst process using Pt/Al₂O₃ was very useful for decomposition of only toluene.

2. Simultaneous Removal of Toluene and NO_x in the Plasma-enhanced Catalyst Process

In order to remove toluene and NO_x simultaneously, an experiment using plasma-enhanced catalyst process was carried out. Fig. 5 shows decomposition of toluene using plasma DBD reactor and plasma-enhanced catalyst reactor with three different types of catalyst: Pd/ZrO₂, Pt/ZrO₂ and Pt/Al₂O₃. While the plasma DBD reactor and plasma combined with Pd/ZrO₂ indicated low activity, the decomposition efficiency of toluene was remarkably elevated by applying Pt/ZrO₂ or Pt/Al₂O₃ to plasma. In case of plasma-enhanced catalyst process with Pt/ZrO₂, the conversion of toluene was increased up to almost 100% with increasing applied voltage. The plasma combined with Pt/Al₂O₃ showed similar performance, too.

CO and CO₂ selectivity of plasma-enhanced catalyst reactors is illustrated in Fig. 6. As in the case of toluene decomposition, the conversion of CO to CO₂ in the plasma combined with Pt/ZrO₂ or Pt/Al₂O₃ was also enhanced with the increase of applied voltage resulting in low CO selectivity at higher applied voltage. These showed higher selectivity for CO₂ and lower selectivity for CO in all range of applied voltage in spite of the improvement in toluene decomposition.

The combined effect of plasma and the catalyst for the NO_x reduction as a function of applied voltage is shown in Fig. 8. When only the electrical discharge was applied, the NO removal rate was around 50% but the NO_x removal rate was almost constant at about 20%. This indicates that inlet NO is converted to NO₂. In case of the plasma-enhanced catalyst reactor with Pd/ZrO₂, the removal

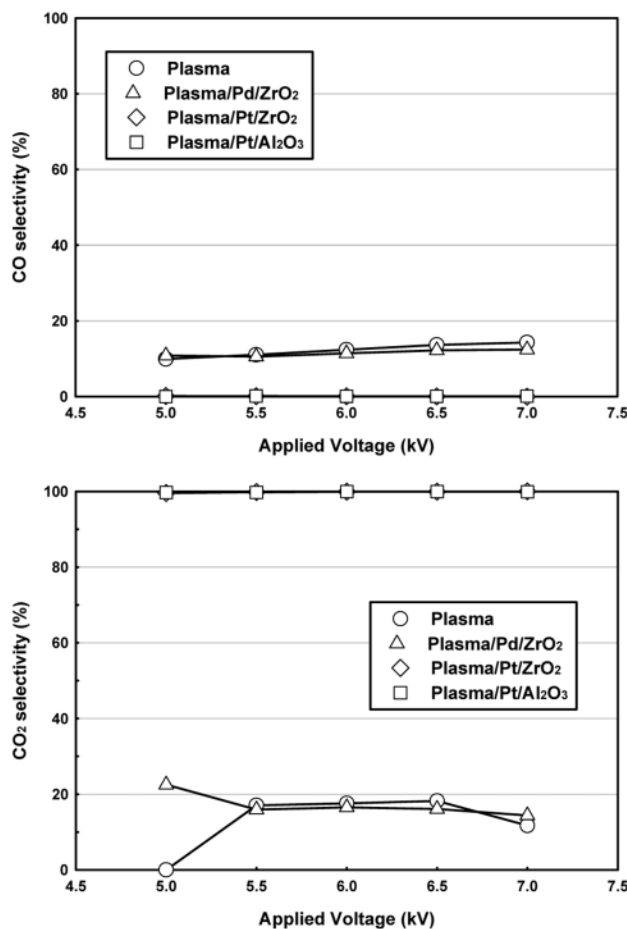


Fig. 6. CO and CO₂ selectivity of plasma-enhanced catalyst reactors as a function of applied voltage (Flow: 3 L/min, Temp.: 150 °C, Toluene: 1,000 ppm, NO: 500 ppm).

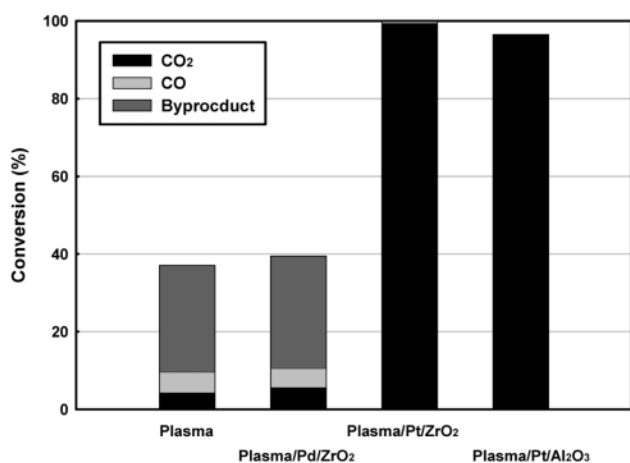


Fig. 7. Composition of product in removal of toluene using various plasma-enhanced catalyst processes (Applied voltage: 7 kV, Flow: 3 L/min, Temp.: 150 °C, Toluene: 1,000 ppm, NO: 500 ppm).

rate was rather lower than one of the plasma DBD reactor. However, when plasma was combined with Pt/ZrO₂ or Pt/Al₂O₃, NOx removal rate increased from around 50% to around 70% as a func-

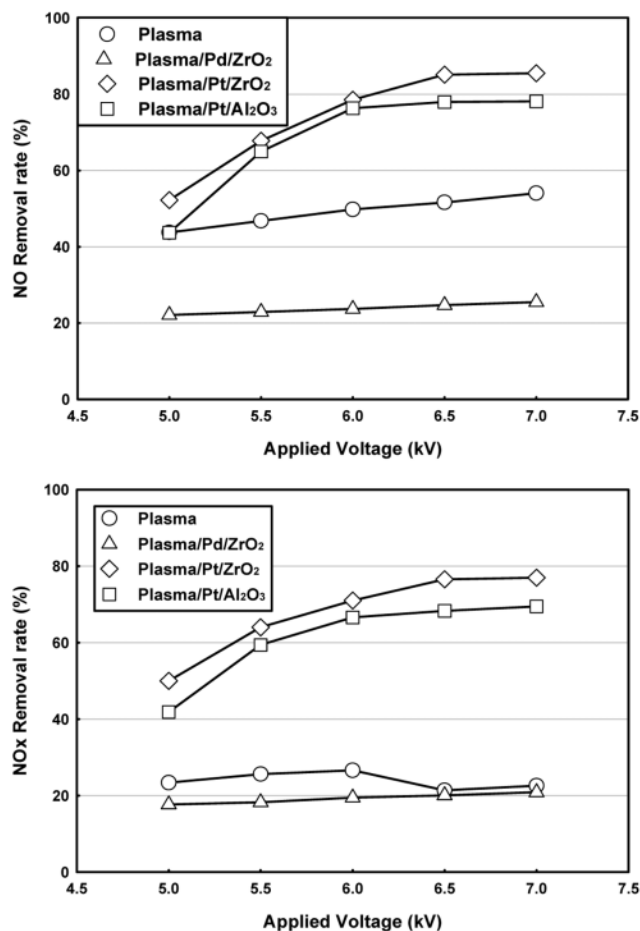


Fig. 8. Removal efficiency of NO and NOx in plasma-enhanced catalyst reactors as a function of applied voltage (Flow: 3 L/min, Temp.: 150 °C, Toluene: 1,000 ppm, NO: 500 ppm).

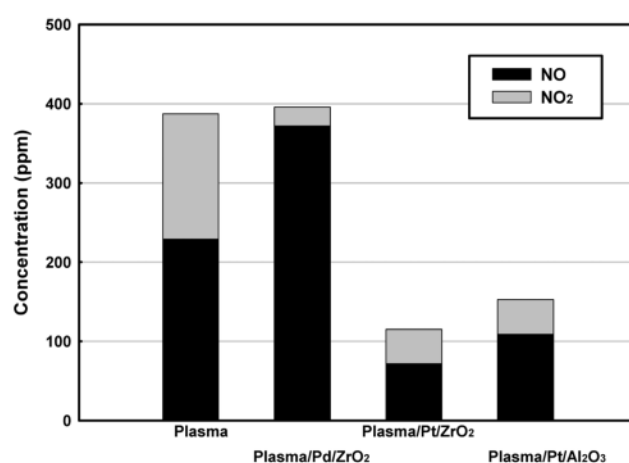


Fig. 9. Outlet concentration of NO and NO₂ in NOx removal using the various plasma-enhanced catalyst processes (Applied voltage: 7 kV, Flow: 3 L/min, Temp.: 150 °C, Toluene: 1,000 ppm, NO: 500 ppm).

tion of applied voltage.

To analyze the influence of plasma and catalyst in more detail, the outlet concentration of NO and NO₂ was detected. Fig. 9 shows

the outlet concentration of NO and NO₂ in NO_x removal using the various plasma-enhanced catalyst processes. With discharge alone, a significant portion of the NO is oxidized to NO₂. Also, Plasma-enhanced catalyst process with Pd/ZrO₂ has the lower removal efficiency than the plasma DBD reactor. When plasma is combined with Pt/Al₂O₃, about 70% of NO is reduced to N₂ with slight oxidation of NO to NO₂. In the case that plasma was combined with Pt/ZrO₂, more than 75% of NO is converted to N₂.

This synergistic effect can be explained by the partial conversion of toluene or the production of ozone which is generated by plasma discharge. A low-temperature electrical discharge in gas mixture containing the oxygen and hydrocarbon produces mainly oxygen and hydrocarbon radical as active species. These radicals oxidize NO to NO₂. With plasma-enhanced catalyst process using Pd/ZrO₂, this oxidation is limited by the reverse reaction of NO₂ being reduced to NO and oxygen radicals and equilibrium will be reached at that reaction condition. In the presence of Pt/ZrO₂ or Pt/Al₂O₃, however, NO₂ is removed from the gas stream by the fast catalytic reaction, thus preventing the undesirable reduction of NO₂ to NO.

CONCLUSIONS

In this study, we presented a comparative assessment of toluene decomposition and NO_x removal using the two types of plasma/catalyst hybrid system. When a plasma-driven catalyst reactor with Pt/Al₂O₃ decomposed the only toluene, it removed just more 20% than only the plasma reactor, but the selectivity of CO₂ was remarkably elevated as compared with only the plasma reactor. In the case of decomposing VOCs (toluene) and NO_x using plasma-enhanced catalyst reactor with Pt/ZrO₂ or Pt/Al₂O₃, the conversion of toluene to CO₂ was nearly 100% and about 80% of NO_x was removed. From

these results, it could be concluded that the plasma-driven catalyst system with Pt/Al₂O₃ and the plasma-enhanced catalyst system with Pt/ZrO₂ or Pt/Al₂O₃ were useful for decomposition of only VOCs and for simultaneous removal of VOCs and NO_x, respectively.

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