# Decomposition of benzene using $Ag/TiO_2$ packed plasma-driven catalyst reactor: influence of electrode configuration and Ag-loading amount

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This paper describes the effects of electrode configuration and the loading amount of Ag catalyst on the decomposition of gas-phase benzene using plasma-driven catalyst (PDC) reactors. Modification of ground electrode brought out a great enhancement in the energy efficiency for benzene decomposition by reducing abnormal discharges outside the reactor tube. The data of carbon balance and the selectivity of $CO_2$ indicated that the Ag catalyst played an important role in the decomposition of benzene, especially for the intermediates. The larger the Ag-loading amounts on the $TiO_2$, the better the performance of benzene decomposition in terms of the carbon balance and the selectivity of $CO_2$. Formation of $NO_2$ and $N_2O$ indicated that the maximum specific input energy applicable to the PDC reactor should be determined not only by the decomposition efficiency but also by the formation of nitrogen oxides.

**KEY WORDS:** nonthermal plasma; corona discharge; $Ag/TiO_2$; benzene.

## 1. Introduction

Nonthermal plasma (NTP) technology, which can induce various chemical reactions under atmospheric pressure and room temperature, has been investigated for the removal and decomposition of many air pollutants such as $SO_2$, $NO_x$, odors, volatile organic compounds (VOCs) from industrial processes, as well as the generation of ozone [1–5]. Many of recent works has been oriented toward optimization in energy consumption and byproducts and the development of scaling model of the NTP process [6–8]. In recent years, some promising results have been reported to reduce energy consumption and byproducts using the hybrid processes combining NTP with adsorbents [9,10] or catalysts [11–15]. The type of combination can be divided into single-stage and two-stage. In the hybrid processes, the role of NTP is quite different depending on the type of combination. In the two-stage process, where the catalysts place downstream of the plasma reactor, the main roles of NTP are the partial oxidation of reactant and the formation of ozone. The partial oxidation (NO to $NO_2$) is a key step in $NO_x$ removal using the two-stage plasma hybrid process. $O_3$ is known to enhance the decomposition of VOCs over the catalyst bed [15–18]. In the single-stage process, also referred to as plasma-driven catalyst (PDC) reactor, catalysts are directly activated by NTP at relatively lower temperature compared to those in the conventional thermal catalysis. The packing materials tested for the combined system include molecular sieve (MS) [10,14], (Pt)/$\gamma$-alumina [12–15], $MnO_2$ [17], $ZrO_2$ [19], $V_2O_5/TiO_2$ and Cu-ZSM-5 [20], (Ag)/$TiO_2$ [12,21,22].

In the previous work, we have already reported that the Ag is more effective than Pt in the PDC reactor packed with $TiO_2$ catalyst [21]. The primary advantages of PDC system over the conventional thermal catalysis include rapid start-up and shut-down, simple construction requiring no heat insulation, low-operating temperature, etc. However, the PDC system is still far from the optimization and needs further study for the better understanding of the PDC system.

In the current study, benzene decomposition using the PDC reactors packed with $Ag/TiO_2$ catalysts was investigated. The operating temperature of the PDC system was 100 °C, where the normal thermal catalytic decomposition of benzene did not occur. The main objective of the current study is to determine how Ag catalyst affects the decomposition of gas-phase benzene in the PDC reactors. Experimental results were discussed in terms of benzene removal, carbon balance and the $CO_2$ yield. The effect of reactor geometry of ground electrode, which is very important in optimizing the NTP reactors, will be also presented.

## 2. Experimental

### *2.1. Setup and PDC Reactors*

Flow-type experimental system was used in the benzene decomposition. The PDC reactors packed with $Ag/TiO_2$ catalyst were set in an oven to maintain the temperature at 100 °C. Thermal catalysis of benzene (without plasma application) in the typical conditions of PDC runs indicated that the $Ag/TiO_2$ catalyst had no

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catalytic activity at temperature below 200 °C, and thus thermal catalysis of benzene can be ignored in the conditions of this study. Synthetic air (20% $O_2$/ 80% $N_2$) was used in this work. The initial concentration of benzene was in the range of 203–210 ppmv. Gas-flow rate was fixed at 4 L/min at the standard conditions (0 °C, 0.1 MPa). The corresponding residence time and gas hourly space velocity (GHSV) in the PDC reactor were 0.16 sec and 22,500 $h^{-1}$, respectively.

Figure 1 shows the details of the three PDC reactors used in this study. The PDC reactors were essentially similar to that used in the previous work [21], except for the materials of dielectric and the ground electrodes. Quartz tubes were used as dielectric in this study. The inner diameter and the effective length of the quartz tubes were 13 and 200 mm, respectively. To investigate the effect of configuration of ground electrode on the reactor performance, three types of ground electrodes were prepared: silver-paste (a) aluminum tape (b) and copper mesh (c). The high voltage electrodes were made of stainless steel wire (0.45 mm in diameter) in a shape of coil, which were placed inside wall of the tubes. These electrode configurations are similar to that of surface discharge.

### 2.2. Preparation of $Ag/TiO_2$ catalyst

The $TiO_2$ pellets were anatase type, which is well known as a photocatalyst. The BET surface area of the $TiO_2$ pellet was 62 $m^2/g$. The average diameter of the $TiO_2$ pellets was 1.8 mm. To investigate the effect of Ag catalyst, $Ag/TiO_2$ catalysts with Ag-loading amount of 0–2 wt% were prepared. Silver (Ag) catalyst was loaded on the $TiO_2$ pellets by impregnation method using silver nitrate ($AgNO_3$, Wako Ltd.) precursor. The $AgNO_3$ of 99.8% purity was dissolved into deionized water with vigorous stirring. The $AgNO_3$ solution was added to a $TiO_2$-filled round bottom flask and then held for 24 h under room temperature. Water was removed using a rotary evaporator. The Ag-loaded $TiO_2$ catalysts were calcined in air at 500 °C, where the structure transition of $TiO_2$ does not occur. As a way to reduce the effect of other parameters, the $TiO_2$ pellets without Ag catalyst were also calcined at the same temperature.

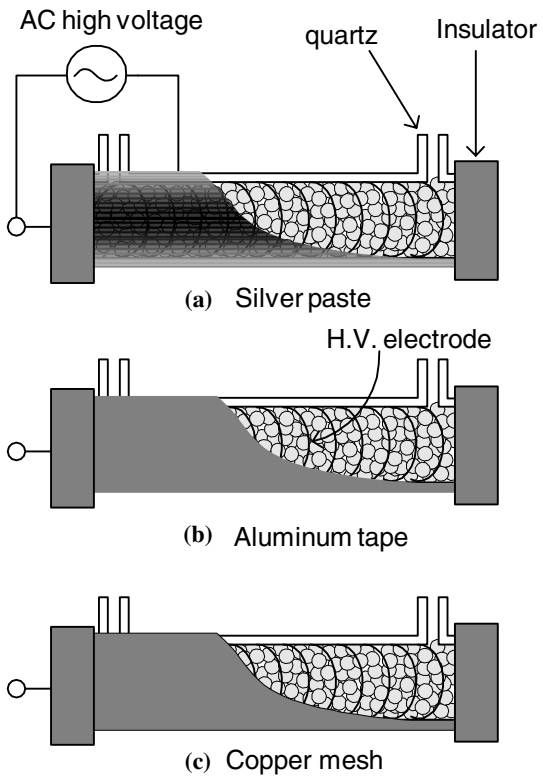


Figure 1. Schematic diagram of plasma reactors with different ground electrodes.

### 2.3. Electrical and chemical measurements

Because of the presence of dielectric barrier (quartz tube), DC voltage can not be used for plasma generation. The PDC reactors were energized with an AC high-voltage power supply equipped with an amplifier (Trek, 20/20B) and a function generator (Tektronix, AFG 310). Applied high voltage ($V$) was measured with a 1000:1 high voltage probe (Tektronix, P6015A). $V$–$Q$ Lissajous method was used to determine the discharge power in the plasma reactors. The charge $Q$ was determined by measuring the voltage across the capacitor of 100 nF connected in series to the ground line of the plasma reactors. The voltage across this capacitor is proportional to the charge (i.e. time-integrated current). The signals of applied voltage and charge were recorded with a digitizing oscilloscope (Tektronix, TDS3032) by averaging 64 scans. The discharge power ($P_{dis}$) was calculated from the area of $V$–$Q$ parallelogram by multiplying the frequency. Specific input energy (SIE), which is defined as the energy input per unit gas-flow rate, can be obtained as follows

$$\text{SIE (J/L)} = \frac{P_{dis}(\text{watt})}{\text{gas flow rate(L/min)}} \times 60 \qquad (1)$$

SIE was varied by changing either applied voltage or frequency from 100 to 600 Hz. A on-line Fourier transform infrared (FTIR) spectrometer (Perkin Elmer, Spectrum one) was used for the quantitative analysis of benzene and reaction products (CO, $CO_2$, HCOOH, $O_3$, $N_2O$, $NO_2$). Other products such as $HNO_2$, $HNO_3$, $N_2O_5$ were measured qualitatively due to the problems in calibration. One set of experiments was run for around 10 h varying the SIE. Plasma was turned on after the 1–1.5 h from the feeding of benzene containing gas mixtures to allow adsorption equilibrium in the PDC reactor. At each SIE conditions, data were taken after a steady state was reached. A gas-cell had an optical pathlength of 6.4 m. The concentrations of benzene and products were monitored at 2 min intervals

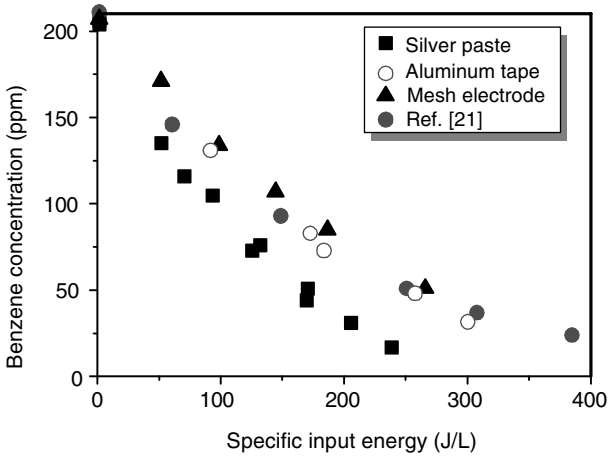


Figure 2. Effects of ground electrode geometry on the decomposition of benzene.

using average spectra of 5 scans, which were taken with a resolution of 1 $cm^{-1}$.

## 3. Results and discussion

### 3.1. Effect of ground electrode geometry

Figure 2 shows the influence of ground electrode geometry on the decomposition of benzene using the three PDC reactors with 1.0 wt% Ag-loaded $TiO_2$ catalyst. Although the other conditions were the same, the PDC reactors with different ground electrodes showed different performances in benzene decomposition. The highest benzene removal was obtained with the reactor of (a) silver-paste electrode, and followed by (b) aluminum tape and (c) copper-mesh electrodes. The result with aluminum tape electrode agrees well with the previous result, which was also obtained with aluminum tape electrode [21]. The main reason for this discrepancy in the removal efficiencies can be explained by the abnormal corona outside the reactor. During a half cycle of applied voltage, ions of the same sign with the applied voltage are accumulated on the surface of dielectric barrier, and these surface charges increase the electric field in the air gaps between the electrodes in a subsequent opposite half-cycle. If there is air gap (void) between the dielectric barrier and the ground electrode, corona can also take place in the void, as in the case of aluminum tape or copper mesh electrode. However, there was no void between the electrode and the dielectric barrier in the PDC reactor with Ag electrode. The energy consumed in the coronas outside the tube does not contribute to the benzene decomposition and directly leads to the high energy consumption. Assuming that the difference in SIE to achieve the same removal efficiency was equal to the wasted energy in the outside of the PDC reactors, the amount of wasted energy in the PDC reactors with aluminum tape or copper mesh electrodes was estimated to be 20–40%.

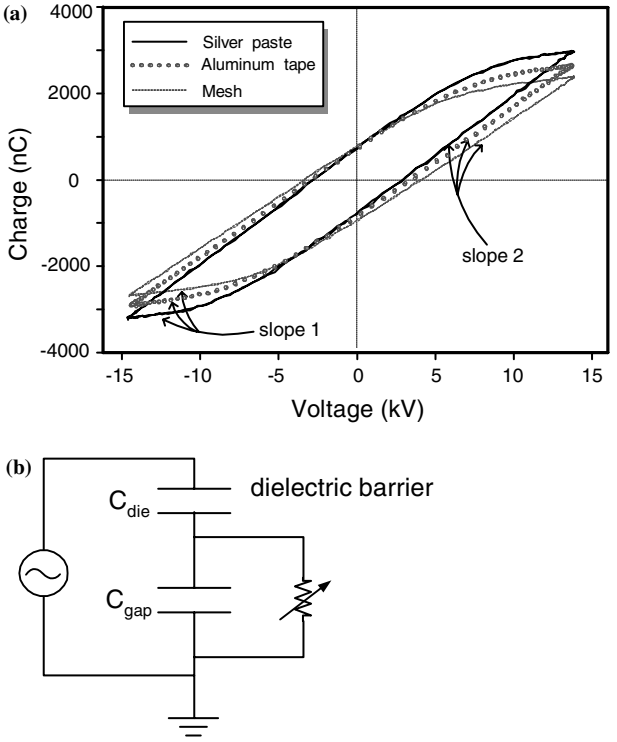


Figure 3. Lissajous figures (a) of the PDC reactors with different ground electrode and the equivalent electrical circuit (b) of the PDC reactor.

Figure 3 shows Lissajous $V$–$Q$ plots (a) with the PDC reactors of three different types of ground electrode and the equivalent circuit (b). The $V$–$Q$ plots showed slightly different patterns depending of the type of ground electrode. The shape of $V$–$Q$ plots were not an ideal parallelogram, that is found in a dielectric-barrier discharge, but was rather close to an ellipse. These $V$–$Q$ patterns indicate the presence of ions over the full cycle of applied voltage. Slope 1 and slope 2 indicate the capacitances in the period of non-discharge and the capacitances ($dQ/dV$) of dielectrics ($C_{die}$), respectively. Since the air gap has a certain capacitance in the nondischarge period, the total capacitance $C_T$ equals to the serial connection of $C_{die}$ and $C_{gap}$; ($C_T = (C_{die} \cdot C_{gap})/(C_{die} + C_{gap})$).

In the discharge period, the air gap can be regarded as resistor, and then the slope 2 equals to $C_{die}$. There were no differences in slopes 1 of each $V$–$Q$ plots. However, the slopes 2 ($C_{die}$) had different values with the types of ground electrode; silver-paste (a) > aluminum tape (b) > copper mesh (c). It is worth to note that the dielectrics are made of the same material with same dimensions, therefore the values of $C_{die}$ should be also the same. The smaller values of $C_{die}$ with aluminum tape (b) and copper mesh (c) electrodes can be attributed to the insufficient contact between the ground electrodes and the dielectrics. The voltages to sustain the discharge were the highest for the mesh electrode (4.0 kV) and followed by the aluminum tape (3.6 kV) and the silver-paste electrode (3.1 kV).

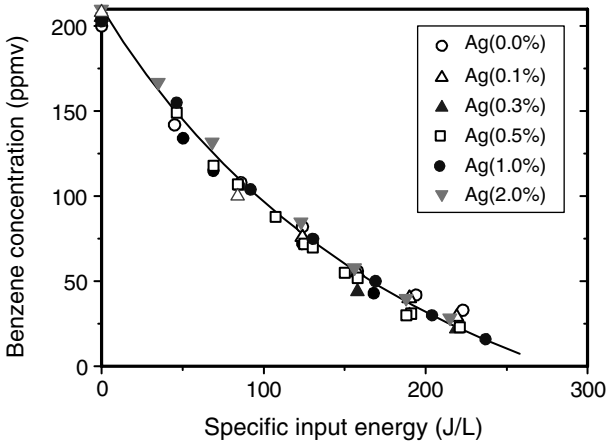


Figure 4. Influence of Ag-loading amount on the decomposition of benzene.

These findings clearly indicate that the reactor geometry of ground electrode is a highly important factor in optimizing the NTP reactors. Proper modification of ground electrode may optimize the electrical characteristics of the PDC reactor and resulting in better performance in the decomposition of benzene. This situation can be also applied to the dielectric-barrier discharges with narrow gaps. The rest of experiments were carried out using the PDC reactor with (a) silver-paste electrode.

### 3.2. *Effects of Ag-loading amount on the benzene decomposition and the carbon balance*

Figure 4 shows the effect of Ag-loading amount on the decomposition of benzene as a function of SIE. As one can see from the figure, the degree of benzene removal was principally controlled by the SIE regardless of Ag-loading amount over $TiO_2$. All the data points converged on a single line. Because all the tests were conducted after the adsorption equilibrium was reached, contribution of adsorption in the superficial benzene removal can be ignored. Figure 5 shows the carbon balance versus SIE in the benzene decomposition tests shown in Figure 4. Decomposition of benzene produced CO and $CO_2$ as major products and formic acid (HCOOH) as minor one. Carbon balance was obtained from the sum of these three products:

$$\text{Carbon balance } (\%) = \frac{[\text{CO}] + [\text{CO}_2] + [\text{HCOOH}]}{6([\text{Benzene}]_0 - [\text{Benzene}])} \times 100 \quad (2)$$

Formation of HCOOH increased with SIE up to 80 J/L, and then it decreased with further increase of SIE. Maximum yield of HCOOH was not higher than 2% in all tested conditions.

Although there was no remarkable effect of Ag catalyst on benzene removal, Ag catalyst preferably influenced on the carbon balance. The behavior of carbon balance showed different pattern with Ag-loading amount higher or lower than 0.5 wt%. In the cases of Ag-loading amount below 0.5 wt%, carbon balances increased with SIE and became higher than 100% at SIE higher than 130 J/L. Because the contribution of adsorption to the benzene removal is negligible, a plausible explanation on the behavior of carbon balance at smaller Ag-loading amount will be the deposition of intermediates of partially decomposed benzene on the surface of catalysts at lower SIE. As the SIE increased larger than 130 J/L, decomposition of deposited intermediates took place as well as the benzene decomposition, resulting in carbon balance larger than 100%. When the Ag-loading amounts were larger than 0.5 wt%, however, relatively constant carbon balances of around 100% were obtained even at SIE higher than 150J/L. The carbon balance data indicated that the Ag catalyst played an important role in the decomposition of benzene, especially for the oxidative decomposition of intermediates.

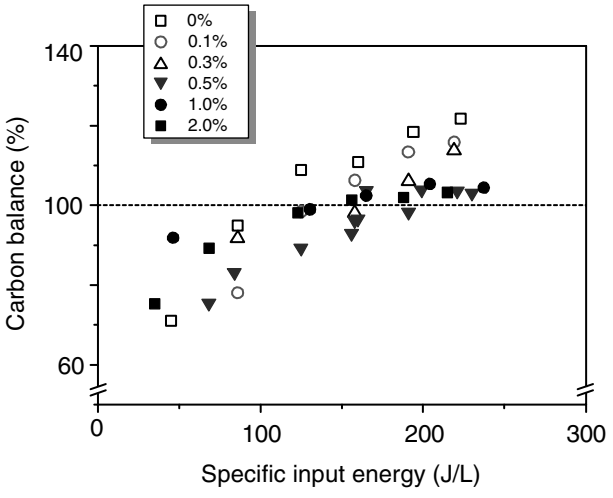


Figure 5. Effect of Ag-loading amount on the carbon balance.

### 3.3. *Effect of Ag-loading amount on the $CO_2$ yield and the $CO_2$ selectivity*

Figure 6 shows the yield of $CO_2$ (a) and the selectivity of $CO_2$ (b), which is one of most preferable products in the benzene decomposition. The $CO_2$ yield ($Y_{CO_2}$) and the $CO_2$ selectivity ($S_{CO_2}$) were calculated as follows:

$$Y_{CO_2}(\%) = \frac{CO_2}{6([\text{Benzene}]_0 - [\text{Benzene}])} \times 100, \quad (3)$$

$$S_{CO_2}(\%) = \frac{[CO_2]}{[CO_2] + [CO]} \times 100. \quad (4)$$

The yields of $CO_2$ were increased with SIE in all tested conditions. The yields of $CO_2$ depended also on the loading amounts of Ag catalyst, indicating the important role of Ag catalyst in the oxidative decomposition. The highest $Y_{CO_2}$ of 76% was obtained with the Ag-loading

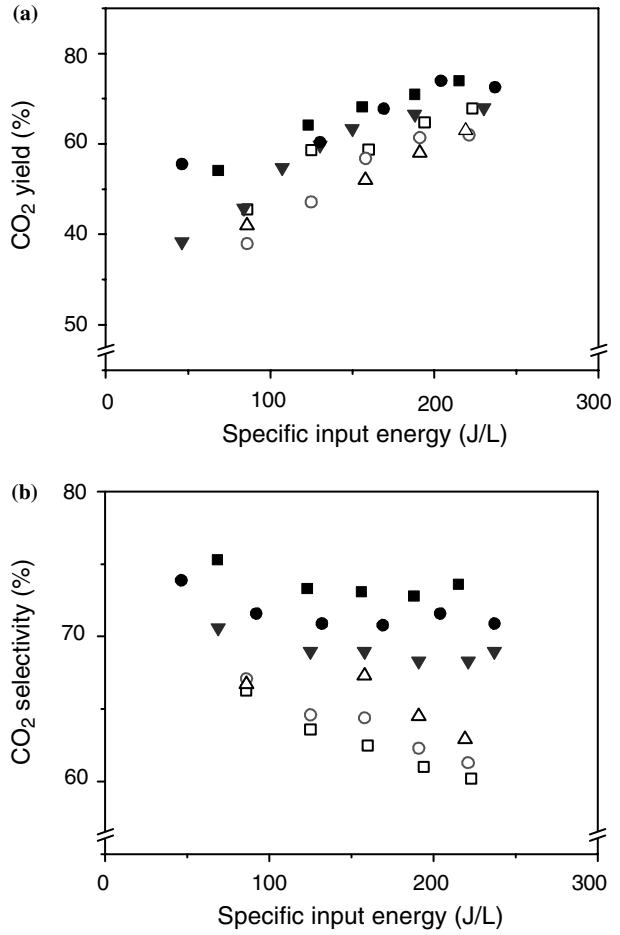


Figure 6. Effect of Ag-loading amount on (a) the yields of $CO_2$ and (b) the selectivities of $CO_2$. The symbols are the same as Fig. 4.

amount of 2.0 wt%. Since the $Y_{CO_2}$ data with the Ag amount lower than 0.3 wt% contain the portion of intermediates deposited on the $TiO_2$ surface as well as benzene, it is difficult to compare the effect of Ag-loading amount using the $Y_{CO_2}$ data alone. To compensate this, the $S_{CO_2}$ under different amount of Ag-loading was also compared. The selectivities of $CO_2$ depended strongly on the Ag-loading amount. The larger the Ag-loading amounts the higher the $S_{CO_2}$. It is worth to note that there are two patterns in $S_{CO_2}$ data. At the Ag-loading amounts higher than 0.5 wt% the $S_{CO_2}$ showed relatively constant values regardless of SIE. These observations suggested that the reaction pathway to produce $CO_2$ were determined mainly by the surface condition of catalyst rather than the energy of NTP. In the cases with the amounts of Ag-loading lower than 0.3 wt%, however, the $S_{CO_2}$ decreased with the increase of SIE. The reason for the different trends of the $S_{CO_2}$ at Ag amount lower than 0.3 wt% may due mostly to the deposition of intermediates on the catalyst surface. The larger the Ag-loading amounts the better the performance of benzene decomposition in terms of carbon balance and the selectivity of $CO_2$. Incorporation of Ag catalyst on the

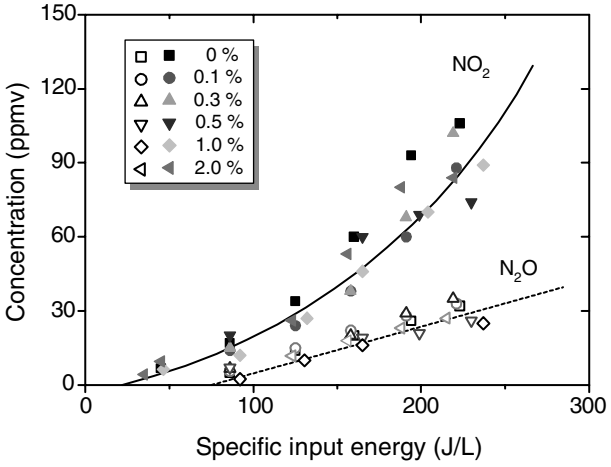


Figure 7. The effect of the Ag-loading amount on the formation of nitrogen oxides.

$TiO_2$ surface facilitated the surface reaction for benzene decomposition resulting in higher selectivity and better carbon balance. The detailed mechanism in the PDC reactors packed with $Ag/TiO_2$ catalyst is still unknown as to whether Ag catalyst directly facilitates the decomposition process or Ag catalyst modify the surface condition of $TiO_2$ by trapping the electrons in the conduction bands [23–25]. Further studies are necessary to elucidate the mechanism for catalyst activation in the PDC system as well as that for the decomposition of benzene over the PDC system.

### 3.4. Formation of $N_2O$ and $NO_2$ in the PDC reactor

The NTP can produce nitrogen oxides (such as NO, $NO_2$, $N_2O_5$, $N_2O$, and its acids) in air-like mixtures [26]. As mentioned in the experimental section, only $N_2O$ and $NO_2$ were measured quantitatively in this work. Figure 7 shows the formation of nitrous oxide ($N_2O$) and nitric dioxide ($NO_2$) as a function of SIE under different loading amount of Ag catalyst. The formation of $N_2O$ started at SIE larger than around 60 J/L and linearly increased with the increase of SIE. The behavior of $N_2O$ formation was the same in humid conditions (not shown in the figure). On the other hand, the $NO_2$ formation showed a quadratic increase with SIE. Maximum production rate of $NO_2$ was about $5.3 \times 10^{12}$ $NO_2$ mol/J. From the linear fit of $N_2O$ formation, the $N_2O$ production rate in the PDC reactor was estimated to approximately $1.4 \times 10^{11}$ $N_2O$ mol/J. This value is about 28 times lower than that of spark discharge ($4 \times 10^{12}$ $N_2O$ mol/J) [27]. The amount of produced $N_2O$ was slightly suppressed with the increase of Ag-loading amount. These data also show one of the beneficial effects caused by Ag-loading on $TiO_2$ catalyst in the PDC system. Considering the stability of $N_2O$, the Ag catalyst play an important role in the formation steps of $N_2O$ rather than the decomposition the $N_2O$.

Energy consumption is one of important parameters in assessing the capability of NTP processing for industrial applications. Formation of nitrogen oxides in the PDC reactor, however, indicates that maximum energy applicable to the reactor should be determined not only by the decomposition efficiency but also by the formation of these byproducts.

## 4. Conclusions

In this paper, we presented the effects of electrode configuration and the Ag-loading amount on the decomposition of gas-phase benzene using PDC system. The main findings can be summarized as follows.

(1) Modification of the geometry of ground electrode greatly enhanced the energy efficiency of benzene decomposition using the PDC system. Reducing void between the ground electrode and the dielectrics greatly enhanced the energy efficiency by reducing abnormal coronas outside the reactor tube. The highest efficiency was obtained with the PDC reactor of silver-paste electrode, and followed by aluminum tape and copper-mesh electrodes. In the cases of aluminum tape and copper-mesh electrodes, electrical energies of 20–40% were consumed outside the PDC reactors, which did not contribute to the chemical reaction.

(2) When the Ag-loading amount was less than 0.5 wt%, reaction intermediates were deposited on the surface at lower SIE and they started to decompose as the SIE increased resulting in carbon balance higher than 100%. Comparison of the yields of $CO_2$ and the selectivities of $CO_2$ under different loading amount of Ag indicated the important role of Ag catalyst in the decomposition process. The larger the Ag-loading amounts on the $TiO_2$ the better the performance of benzene decomposition in terms of carbon balance and the selectivity of $CO_2$.

(3) The formation of $NO_2$ showed quadratic increase with SIE, while the $N_2O$ formation was linear. Formation of $N_2O$ and $NO_2$ indicated that the maximum SIE applicable to the PDC reactor will be limited to below 150 J/L.

## References

[1] A. Mizuno, J.S. Clements and R.H. Davis, IEEE Trans. Ind. App. 22 (1986) 516.
[2] C.M. Nunez, G.H. Ramsey, W.H. Ponder, J.H. Abbott, L.E. Hamel and P.H. Kariher, J. Air & Waste 42 (1993) 242.
[3] D.G. Storch and M.J. Kushner, J. Appl. Phys. 73 (1993) 51.
[4] B. Eliasson, M. Hirth and U. Kogelschatz, J. Phys. D: Appl. Phys. 20 (1987) 1421.
[5] G. Dinelli, L. Civitano and M. Rea, IEEE Trans. Ind. Appl. 26 (1990) 535.
[6] S. Futamura, Z. Zhang and T. Yamamoto, IEEE Trans. Ind. Appl. 35 (1999) 760.
[7] B.M. Penetrante, M.C. Hsiao, B.T. Merritt, G.E. Vogtlin and P.H. Wallman, IEEE Trans. Plasma Sci. 23 (1995) 679.
[8] K. Yan, E.J.M.V. Heesch, A.J.M. Pemen and P.A.H.J. Huijbrechts, Plasma Chem. Plasma Proc. 21 (2001) 107.
[9] A. Ogata, D. Ito, K. Mizuno, S. Kushiyama and T. Yamamoto, IEEE Trans. Ind. Appl. 37 (2001) 959.
[10] A. Ogata, H. Einaga, H. Kabashima, S. Futamura, S. Kushiyama and H.-H. Kim, Appl. Catal. B: Environ. 46 (2003) 87.
[11] H. Lee and M.B. Chang, Plasma Chem. Plasma Proc. 21 (2001) 329.
[12] H.-H. Kim, K. Takashima, S. Katsura and A. Mizuno, J. Phys. D: Appl. Phys. 34 (2001) 604.
[13] H. Sekiguchi, Can. J. Chem. Eng. 79 (2001) 512.
[14] Y.-H. Song, S.-J. Kim, K.-I. Choi and T. Yamamoto, J. Electrostat. 55 (2002) 189.
[15] F. Holzer, U. Roland and F.-D. Kopinke, Appl. Catalysis B: Environ. 38 (2002) 163.
[16] A. Gervasini, G. Vezzoli and V. Ragaini, Catal. Today 29 (1996) 449.
[17] H. Einaga, S. Futamura and T. Ibusuki, Environ. Sci. Technol. 35 (2001) 1880.
[18] K. Sekiguchi, A. Sanada and K. Sakamoto, Catal. Commun. 4 (2003) 247.
[19] R.G. Tonkyn, S.E. Barlow and T.M. Orlando, J. Appl. Phys. 80 (1996) 4877.
[20] T. Oda, J. Electrostat. 57 (2003) 293.
[21] H.-H. Kim, Y.-H. Lee, A. Ogata and S. Futamura, Catal. Commun. 4 (2003) 347.
[22] D. Li, D. Yakushiji, S. Kanazawa, T. Ohkubo and Y. Nomoto, J. Electrostat. 55 (2002) 311.
[23] B. Ohtani, R.M. Bowman, P.C. Jr., H. Kominami, H. Noguchi and K. Uosaki, Chem. Lett. (1998) 579.
[24] M.A. Fox and M.T. Dulay, Chem. Rev. 93 (1993) 341.
[25] A. Furube, T. Asahi, H. Masuhara, H. Yamashita and M. Anpo, Chem. Phys. Lett 336 (2001) 424.
[26] K.G. Donohoe, F.H. Shair and O.R. Wulf, Ind. Eng. Chem. Fundam. 16 (1977) 208.
[27] J.S. Levine, R.E. Hughes, W.L. Chameides and W.E. Howell, Geophys. Res. Lett. 6 (1979) 557.