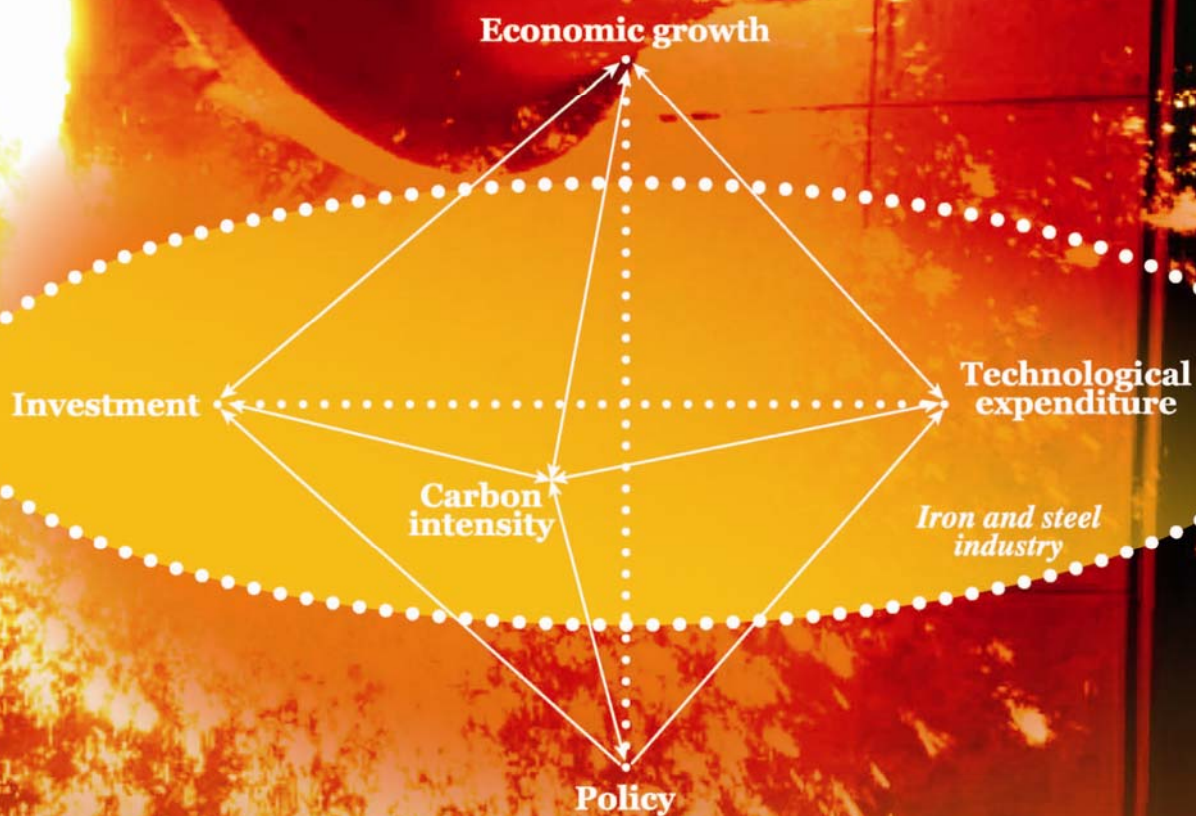


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# Toluene decomposition performance and NO<sub>x</sub> by-product formation during a DBD-catalyst process

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## ABSTRACT

Characteristics of toluene decomposition and formation of nitrogen oxide (NO<sub>x</sub>) by-products were investigated in a dielectric barrier discharge (DBD) reactor with/without catalyst at room temperature and atmospheric pressure. Four kinds of metal oxides, i.e., manganese oxide (MnO<sub>x</sub>), iron oxide (FeO<sub>x</sub>), cobalt oxide (CoO<sub>x</sub>) and copper oxide (CuO), supported on Al<sub>2</sub>O<sub>3</sub>/nickel foam, were used as catalysts. It was found that introducing catalysts could improve toluene removal efficiency, promote decomposition of by-product ozone and enhance CO<sub>2</sub> selectivity. In addition, NO<sub>x</sub> was suppressed with the decrease of specific energy density (SED) and the increase of humidity, gas flow rate and toluene concentration, or catalyst introduction. Among the four kinds of catalysts, the CuO catalyst showed the best performance in NO<sub>x</sub> suppression. The MnO<sub>x</sub> catalyst exhibited the lowest concentration of O<sub>3</sub> and highest CO<sub>2</sub> selectivity but the highest concentration of NO<sub>x</sub>. A possible pathway for NO<sub>x</sub> production in DBD was discussed. The contributions of oxygen active species and hydroxyl radicals are dominant in NO<sub>x</sub> suppression.

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## Introduction

Emission of volatile organic compounds (VOCs) from various industrial processes is one of the most important sources of air pollution. VOCs are detrimental to both human health and the environment, either directly from their toxicity and malodorous nature or indirectly as ozone and smog precursors (Chen et al., 2009). Toluene, as one of the typical VOCs, is usually chosen as a probe contaminant for treatment because it is difficult to deal with due to the presence of a benzene ring and because it causes respiratory disorders and even carcinogenic and mutagenic effects. It also represents one of the most commonly detected VOCs in many industries, such as those producing lacquers, adhesives, and rubber, as well as in some printing and leather tanning processes (Angel et al., 2008).

Dielectric barrier discharge (DBD) has offered an innovative technology for removing toluene from waste gas characterized by low toluene concentration and high flow rate (Atten et al., 1987; Clements et al., 1989; Yamamoto et al., 1996; Snyder and Anderson, 1998; Pietsch, 2001; Kim et al., 2008; Mista and Kacprzyk, 2008). DBD, which contains at least one dielectric barrier, distributes microdischarges throughout the discharge area. It initiates chemical reactions by electron impact dissociation of organic molecules and ionization of the carrier gas (Magureanu et al., 2007). DBD produces a plasma region characterized by significant non-thermal properties. Electric energy is primarily used for the production of high energy electrons, leaving the bulk of gas at room temperature. The potential for energy-saving is a main advantage of DBD technology.

However, DBD alone usually cannot convert pollutants to ideal products. The main problem for VOC removal in a DBD system is the formation of toxic byproducts, such as CO, O<sub>3</sub>, and NO<sub>x</sub> (Magureanu et al., 2007; Van Durme et

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al., 2008; Delagrangé et al., 2006; Bo et al., 2009; Kalra et al., 2005). These would cause secondary pollution if not subjected to further treatment. Sometimes they are even more harmful than the original VOCs. Notable improvements in inhibition of their formation can be achieved through the plasma-catalysis process, which introduces a catalyst into the discharge zone. Metal oxides have been widely used as active components in the removal of organic compounds (Das and Parida, 2007; Guo et al., 2007; Sano et al., 2006; Karuppiyah et al., 2012; Lahousse et al., 1998).

The byproduct NO<sub>x</sub> can affect reaction rate and even lead to deactivation of a catalyst. Van Durme reported that the deactivation of catalyst materials may be explained by the formation of HNO<sub>3</sub> in the plasma discharge (Van Durme et al., 2008). Subrahmanyam also found that NO<sub>x</sub> could form nitrate, which may cause the deactivation of catalysts (Subrahmanyam et al., 2006). In this study, the formation characteristics of NO<sub>x</sub> during toluene removal were investigated in a DBD-catalyst system at room temperature and atmospheric pressure. Four kinds of metal oxide catalysts, that is, manganese oxide (MnO<sub>x</sub>), iron oxide (FeO<sub>x</sub>), cobalt oxide (CoO<sub>x</sub>) and copper oxide (CuO), supported on Al<sub>2</sub>O<sub>3</sub>/nickel foams, were placed in the discharge area of the reactor. Experimental tests were conducted to determine the effect of the catalysts on toluene oxidation. In addition, exhaust gas was experimentally simulated to determine the influences of humidity, gas flow rate and toluene concentration as well as catalysts on NO<sub>x</sub> formation.

## 1. Experimental

### 1.1. Experimental set-up

A schematic diagram of the experimental system is shown in Fig. 1. The apparatus mainly included a gas supply and regulation system, a DBD reactor with a power supply system and a gas analysis system. The initial toluene concentration ranged from 200 to 800 mg/m<sup>3</sup>. Gaseous toluene was obtained by controlling the air flow rate from a gas cylinder through pure toluene liquid (>99.5%) which was kept in a water bath ( $T = 25 \pm 1^\circ\text{C}$ ). After passing through a mixing chamber, the feed gas entered the DBD reactor. Gas flow rate was controlled to between 150 and 450 mL/min.

Toluene and other volatile organic compounds were analyzed by a gas chromatograph (GC-7890II, Tianmei, China) equipped with a hydrogen flame ionization detector (FID) and a DB-5MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25 mm) heated at 80°C. Humidity was measured by a humidity meter (Center 310,

Shuangxu, Shanghai, China). The concentrations of CO and CO<sub>2</sub> were measured by a CO analyzer (TX2000, Oldham, France) and a CO<sub>2</sub> detector (GXH-3010E, Huayun, Beijing, China), respectively. The concentration of ozone was monitored by an ozone analyzer (DCS-1, Lida, Shanghai, China). NO<sub>x</sub> was detected with a NO analyzer (PGM-1140, Rae, USA) and a NO<sub>2</sub> analyzer (PGM-1150, Rae, USA).

### 1.2. DBD reactor and power supply system

A wire-plate DBD reactor was used in the reaction (Fig. 2). Two epoxy resin boards (200 mm  $\times$  45 mm  $\times$  0.8 mm) were used to form reactor walls and acted as dielectric barriers (the dielectric constant  $\epsilon = 3.6$ ). The high voltage electrode was made of brass wire (diameter 0.6 mm). The brass wire electrode was shaped into a spiral in order to increase energy density in the reaction volume. The wire-to-wire distance was 8 mm. Two grounded copper nets were fixed on the two sides of the middle epoxy resin board. The total length of the reactor was 200 mm, while the effective length was 150 mm. When no catalyst was used, the gap between the high-voltage electrode and the grounded electrode was 8 mm, resulting in a cross sectional area of 400 mm<sup>2</sup> and a reaction volume of 60 cm<sup>3</sup> for the flow channel. To add an in-situ catalyst, it was supported by two pieces of nickel foam (150 mm  $\times$  25 mm  $\times$  2 mm) fixed on the grounded electrodes. This produced a gap of 6 mm, a cross-sectional area for the flow channel of 300 mm<sup>2</sup>, a reaction volume of 45 cm<sup>3</sup> and a catalyst volume of 15,000 mm<sup>3</sup>.

High voltage power was supplied by a booster (0–250 V) combined with a high voltage AC transformer (CTP-2000K, Suman, Nanjing, China) in series. In this experiment the frequency was controlled at 9.512 KHz. The applied voltage and current were measured by a high voltage probe (P6015, Tektronix, USA) and a digitizing oscilloscope (TDS1002, Tektronix, USA). The input power can be detected by the high voltage AC transformer directly. The discharge power (the power deposited to the reactor) was calculated from the applied voltage and the reactor current.

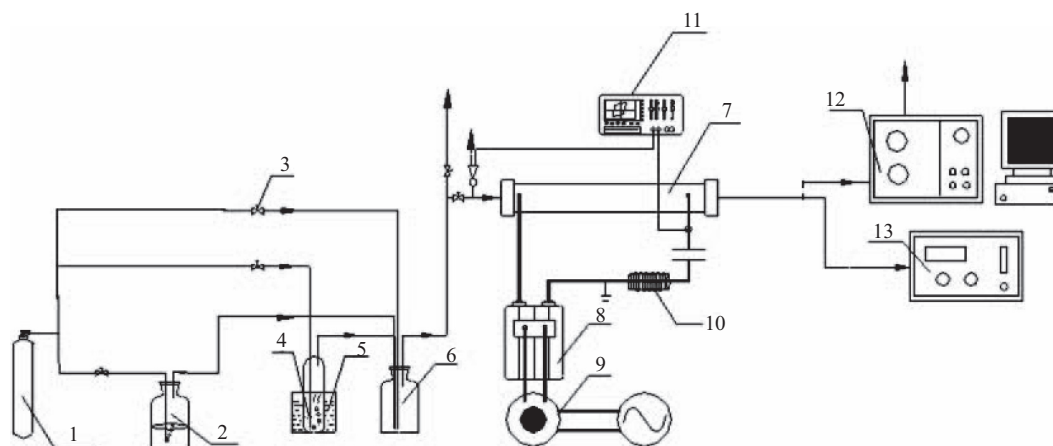
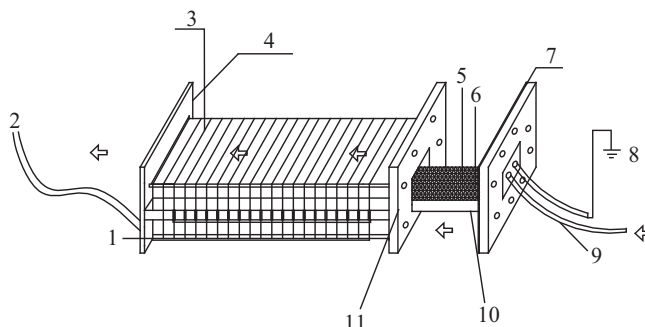


Fig. 1 – Schematic diagram of the experiment. (1) dry air cylinder, (2) bubbling for water vapor preparation, (3) mass flow controller, (4) bubbling for toluene preparation, (5) water bath for toluene generation, (6) buffer, (7) DBD reactor, (8) ac transformer, (9) booster, (10) resistance, (11) oscilloscope, (12) gas chromatogram, (13) ozone analyzer.



**Fig. 2 – Structure of the DBD reactor with catalyst.** (1) high voltage electrode, (2) polyethylene tube (gas out), (3) brass wire, (4) epoxy resin board (1 mm), (5) nickel foam, (6) copper net, (7) silicone pad, (8) ground electrode, (9) polyethylene tube (gas in), (10) epoxy resin board (2 mm), (11) drilled hole for a screw.

### 1.3. Catalyst

Four kinds of catalysts, i.e. MnOx, FeOx, CoOx and CuO supported on Al<sub>2</sub>O<sub>3</sub>/nickel foam, were prepared by an impregnation method. The detailed process can be obtained in a previous article (Guo et al., 2006).

Toluene removal efficiency ( $\eta$ ), specific energy density (SED, J/L), carbon dioxide selectivity  $S_{\text{CO}_2}$  and energy efficiency ( $\eta_E$ , g/kWh) were calculated as follows:

$$\eta = \frac{[\text{toluene}]_{\text{in}} - [\text{toluene}]_{\text{out}}}{[\text{toluene}]_{\text{in}}} \times 100 \quad (1)$$

$$\text{SED} = \frac{\text{discharge power (W)}}{\text{gas flow rate (L/min)}} \times 60 \quad (2)$$

$$S_{\text{CO}_2}(\%) = \frac{[\text{CO}_2]}{[\text{CO}_2] + [\text{CO}]} \quad (3)$$

$$\eta_E = \frac{[\text{toluene}]_{\text{removal}} (\text{g/m}^3) \times \text{gas flow rate} (\text{m}^3/\text{hr})}{\text{input power (kW)}} \quad (4)$$

## 2. Results and discussion

### 2.1. Toluene removal performance with/without catalyst

#### 2.1.1. Energy yield

The relationship between SED (J/L) and  $\eta_E$  (g/kWh) with/without catalyst presented in Fig. 3a indicates that SED is more dependent on  $E_V$  in a DBD system than in a DBD-catalyst system. For example, the  $E_V$  value was 0.21–1.12 g/kWh in the DBD system compared to 1.24–1.37 g/kWh in the DBD-FeOx catalyst system (SED: 140–320 J/L).

#### 2.1.2. Toluene removal efficiency

The catalytic properties of various metal oxides for toluene oxidation were studied (Fig. 3b). It was found that catalysts promoted toluene decomposition significantly. The following toluene removal efficiency order was found: FeOx catalyst > MnOx catalyst > CuO catalyst > CoOx catalyst > no catalyst. The conversion was only 7.1% without catalyst compared with 45% with the FeOx catalyst (SED: 140 J/L).

#### 2.1.3. Ozone formation

The production of ozone with/without catalyst is indicated in Fig. 3c. It can be seen that metal oxides promoted ozone decomposition. The concentration of O<sub>3</sub> was 34.6 mg/m<sup>3</sup> with the MnOx catalyst, compared to 420 mg/m<sup>3</sup> without catalyst at 320 J/L. By comparing the results presented in Fig. 3c, it can be concluded that the ozone concentration varied in the following order: MnOx catalyst < FeOx catalyst < CoOx catalyst < CuO catalyst < no catalyst. MnOx catalyst exhibited the best performance in terms of O<sub>3</sub> decomposition.

Plasma generates intermediate species having a sufficiently long lifetime to trigger surface reactions on a catalyst placed in the plasma reactor (Hammer et al., 2004). It is clear that most ozone is decomposed catalytically, forming molecular and highly active atomic oxygen (Guo et al., 2007; Magureanu et al., 2005; Delagrangé et al., 2006). Delagrangé reported a mechanism for O<sub>3</sub> decomposition with a MnO<sub>2</sub> catalyst as follows (Delagrangé et al., 2006):

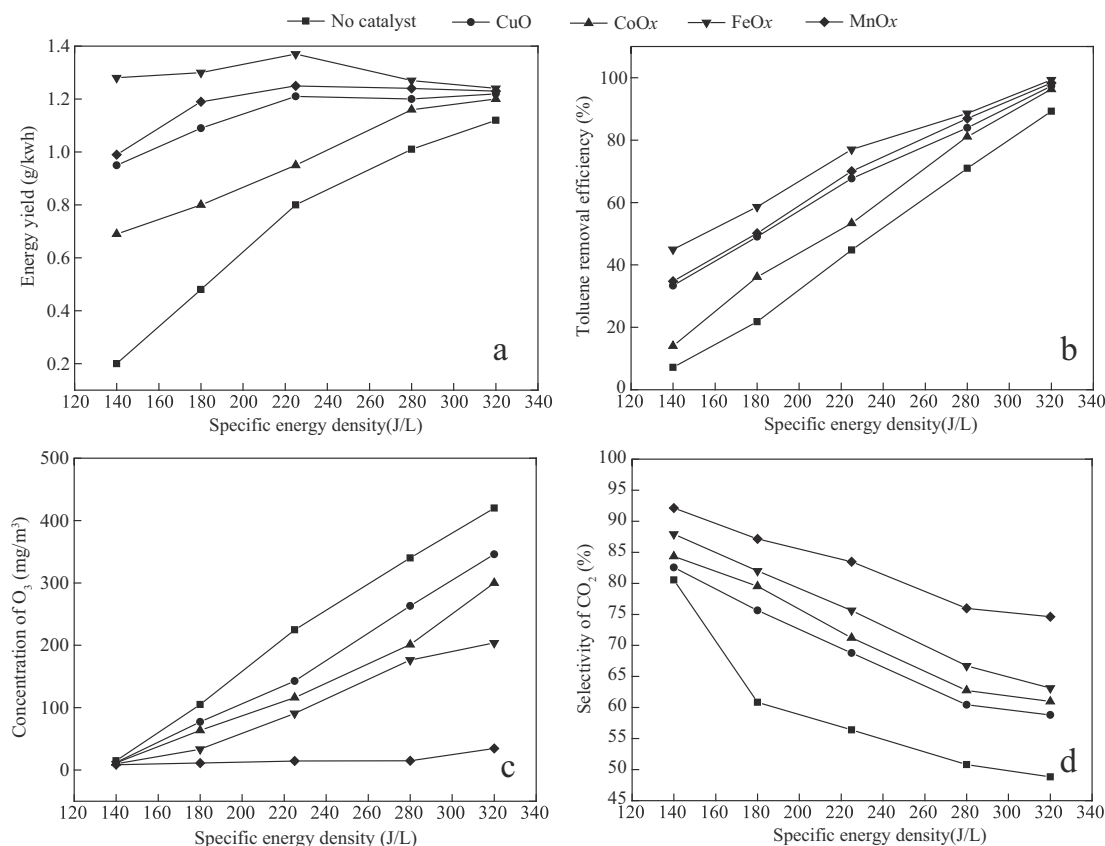


#### 2.1.4. Selectivity of CO<sub>2</sub>

The selectivity of CO<sub>2</sub> decreased with increasing SED (Fig. 3d). The selectivity of CO<sub>2</sub> decreased from 80.56% to 48.84% when SED increased from 140 to 320 J/L without catalyst. The result was the same as in previous reports (Guo et al., 2006, 2010). But this trend was different than that reported in some papers (Magureanu et al., 2007; Karupiah et al., 2012). Maybe differences in catalyst oxidation ability cause this discrepancy.

Fig. 3d also shows that CO<sub>2</sub> selectivity can be greatly enhanced by introducing catalysts. The CO<sub>2</sub> selectivity without catalyst was only 48.84% but it increased to 74.62% with the MnOx catalyst (SED: 320 J/L). Oxygen active species are formed in the decomposition of O<sub>3</sub> on a catalyst surface. Carbon monoxide and toluene (or intermediate reaction products) are oxidized by oxygen active species to CO<sub>2</sub>, which eventually lead to a higher CO<sub>2</sub> selectivity (Chavadej et al., 2007).

The MnOx catalyst exhibited the highest CO<sub>2</sub> selectivity (Fig. 3d) and lowest ozone concentration (Fig. 3c), which



**Fig. 3 – Effect of SED on energy yield with different catalysts (a), and effects of different catalysts on toluene removal efficiency (b), O<sub>3</sub> concentration (c), CO<sub>2</sub> selectivity (d). Gas flow rate: 450 m/min, initial concentration of toluene: 400 mg/m<sup>3</sup>, relative humidity (RH): 20%.**

proved that active species produced from O<sub>3</sub> decomposition oxidized CO into CO<sub>2</sub>. This is in accord with Sano's result, which concluded that a catalyst with a higher O<sub>3</sub> decomposition activity was related to a catalyst with a higher CO oxidation activity (Sano et al., 2006).

## 2.2. NO<sub>x</sub> performance under different conditions

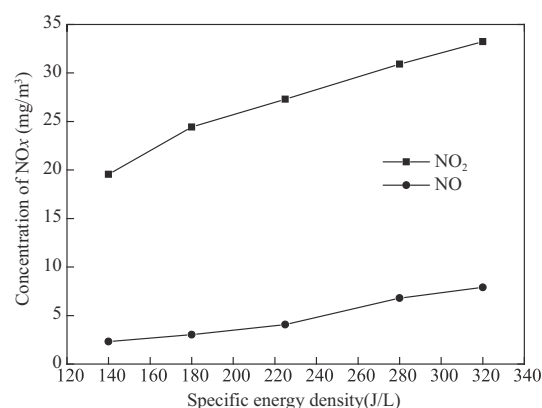
### 2.2.1. Specific energy density effect

The production of the main NO<sub>x</sub> species (NO, NO<sub>2</sub>) as a function of SED is shown in Fig. 4. The concentration of NO and NO<sub>2</sub> both increased with increasing SED. For example, the concentration of NO increased from 2.3 to 7.9 mg/m<sup>3</sup>, and for NO<sub>2</sub> it was 19.56–33.23 mg/m<sup>3</sup> with SED ranging from 140 to 320 J/L. This trend is consistent with the result by Cooray and Rahman (2005). The concentration of NO was much lower than that of NO<sub>2</sub>. The concentration of NO<sub>2</sub> was 33.2 mg/m<sup>3</sup> but for NO it was only 7.9 mg/m<sup>3</sup> (SED: 320 J/L). Some active molecules and radicals such as O<sub>3</sub>, OH and O produced in the discharge are effective in the oxidation of NO to NO<sub>2</sub>, which results in less NO in the effluent.

### 2.2.2. Humidity effect

Since practical oxidation of VOCs in air usually occurs in the presence of water vapor, the effect of humidity on the formation of NO<sub>x</sub> was investigated as shown in Fig. 5a. The results suggested that the addition of water vapor caused a remarkable

suppression of NO<sub>x</sub>. Close to 65.0 mg/m<sup>3</sup> of NO<sub>2</sub> was detected under dry conditions at SED of 320 J/L, whereas, it decreased to 30.1 mg/m<sup>3</sup> (relative humidity/RH: 20%) and 28.0 mg/m<sup>3</sup> (RH: 40%). This is in agreement with the report of Van Durme et al. (2007).



**Fig. 4 – Effect of SED (J/L) on NO<sub>x</sub> formation. Gas flow rate: 450 mL/min, initial concentration of toluene: 400 mg/m<sup>3</sup>, RH: 20%.**

### 2.2.3. Effect of gas flow rate

Gas flow rate had a significant effect on NO<sub>x</sub> generation (Fig. 5b). When flow increased from 150 to 450 mL/min, the concentration of NO<sub>2</sub> decreased from 51.7 down to 33.23 mg/m<sup>3</sup> and NO decreased from 15.8 to 7.9 mg/m<sup>3</sup> (SED: 320 J/L). The increase of gas flow rate decreases the concentration of discharging electrons and the probability of collision rate with electrons. Therefore fewer N and O atoms are generated and NO<sub>x</sub> is depressed.

### 2.2.4. Effect of initial toluene concentration

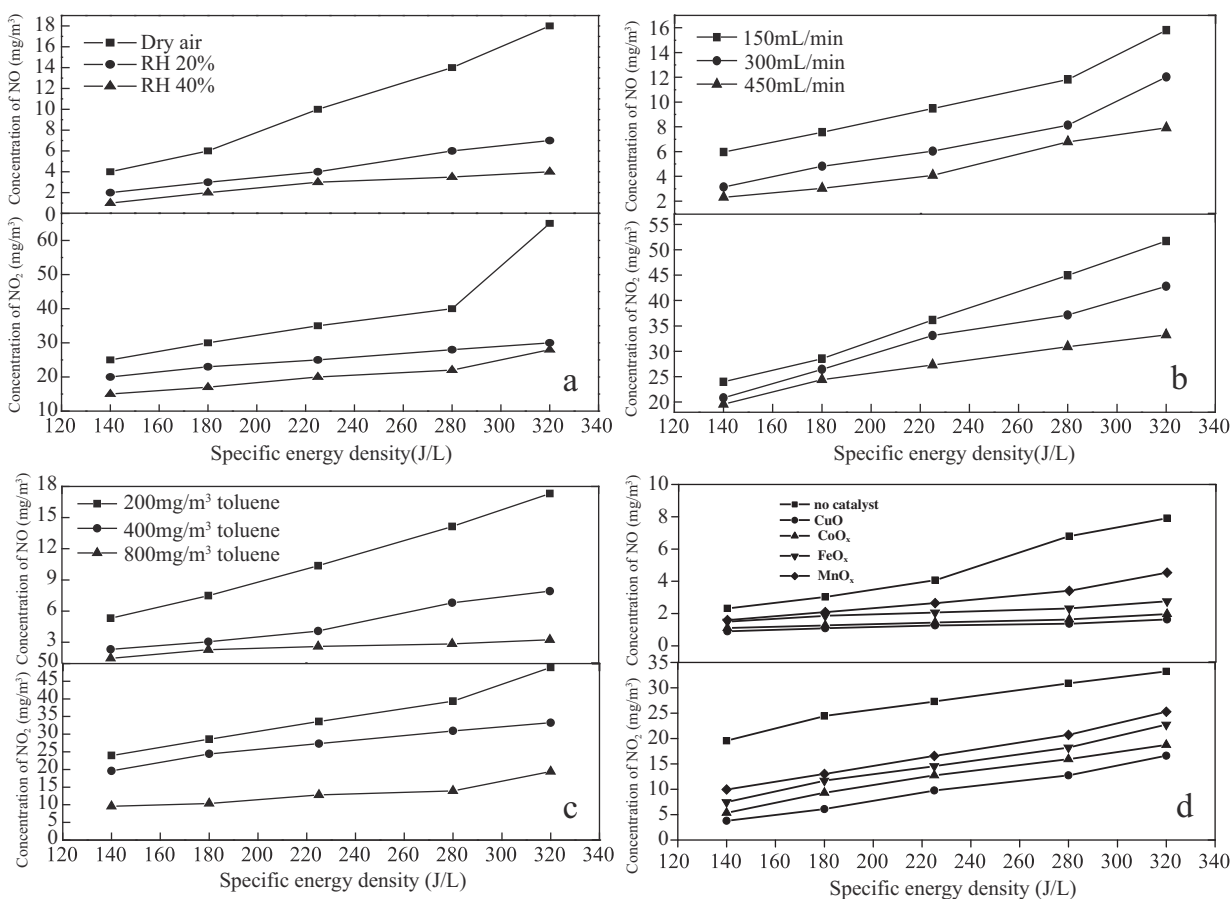
Fig. 5c shows the concentration of NO<sub>x</sub> under different initial toluene concentrations. A better performance in suppressing NO<sub>x</sub> was identified when the toluene concentration was higher. NO<sub>2</sub> concentration decreased from 48.88 to 19.39 mg/m<sup>3</sup> with the increase of toluene concentration from 200 to 800 mg/m<sup>3</sup> (SED: 320 J/L).

More chemical species compete for radicals generated by a fixed amount of plasma energy under a higher toluene concentration. The detailed reactions were discussed by Guo et al. (2006). Moreover, detection of polymers containing N in the effluent supports the idea that N<sub>2</sub> can be broken, and radicals that are dissociated from toluene would compete for energy with N<sub>2</sub> (Subrahmanyam et al., 2006; Bo et al., 2007).

### 2.2.5. Effect of different catalysts

Catalysts had a positive effect on the suppression of NO<sub>x</sub> (Fig. 5d). The NO<sub>2</sub> concentration was 33.23 mg/m<sup>3</sup> without catalyst, but it decreased to 16.6 mg/m<sup>3</sup> with the CuO catalyst (SED: 320 J/L). And, the NO concentration without catalyst was nearly five times higher than that with the CuO catalyst. The concentration of NO<sub>x</sub> follows the trend: CuO catalyst < CoOx catalyst < FeOx catalyst < MnOx catalyst < no catalyst. The CuO catalyst shows excellent performance in the suppression of NO<sub>x</sub>. However, from the results of Fig. 3b, c, d, the CuO catalyst showed a weaker catalytic ability, for example lower toluene decomposition, the highest O<sub>3</sub> concentration and lowest CO<sub>2</sub> selectivity. But actually when we choose a catalyst, catalytic ability is the most important factor. This result in Fig. 5d could give some suggestions for NO<sub>x</sub> suppression.

The MnOx catalyst had the best ability in decomposing O<sub>3</sub>, but the concentration of NO<sub>x</sub> was the highest among the four kinds of catalysts. According to formula (5), with the MnOx catalyst most O<sub>3</sub> is decomposed to O<sub>2</sub> and O atoms, which may combine with N atoms and generate more NO<sub>x</sub> compared with other catalysts. On the other hand, these O atoms also are consumed in the decomposition of toluene. With catalyst, toluene removal efficiency is higher than without catalyst. The



**Fig. 5** – Effect of background humidity (a), gas flow rate (b), toluene concentration (c), different catalysts (d) on NO<sub>x</sub> formation. Gas flow rate: 450 mL/min, initial concentration of toluene: 400 mg/m<sup>3</sup> when they are used in experiments.



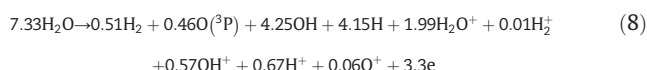
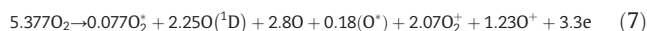
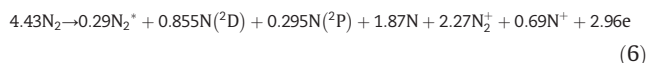
competing reaction of O atoms with toluene causes a decrease in the NO<sub>x</sub> concentration.

Metal oxides have been reported to be highly effective for NO<sub>x</sub> removal in combination with non-thermal plasma (Rappé et al., 2004; Sun et al., 2005). This can be explained as follows. First, microdischarges are generated inside the catalyst pores, resulting in more discharge per volume and energy density of the discharge (Hensel et al., 2005; Holzer et al., 2005). Catalysts may induce a shift in the distribution of accelerated electrons (Van Durme et al., 2008). Then, partially oxidized hydrocarbons and peroxy radicals (RO<sub>2</sub>) are generated, which react with NO and strongly influence NO<sub>2</sub> formation rates (Rappé et al., 2004). In addition, NO<sub>2</sub> reacts over the catalyst while partially oxidized hydrocarbons are consumed during selective catalytic reduction, producing CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O. On the other side, adsorption is another reason for the lower amount of NO<sub>x</sub> detected with catalysts (Kwak et al., 2006).

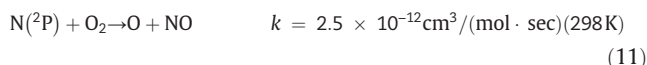
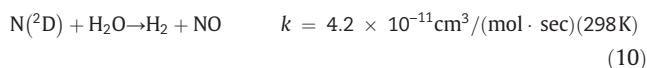
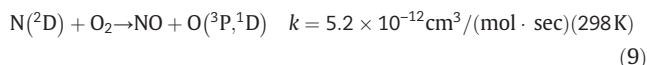
### 2.3. Possible formation pathways of NO<sub>x</sub>

#### 2.3.1. Nitrogen atom reaction pathway

Since in this study no nitrogen was contained in the pollutant, it could be assumed that NO<sub>x</sub> came from the air that was used as carrier gas. Electrons, ions, excited molecules and free radicals are formed during the DBD process. When fast electrons are absorbed in the carrier gas, they cause ionization and excitation of N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O in the carrier gas. Primary species and secondary electrons are formed. The G-values (molecules/100 eV) of the primary species are simplified as follows (Mätzing, 1989).

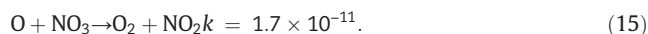
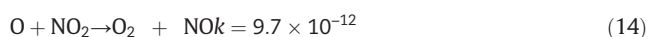
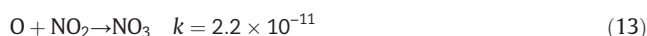


N(<sup>2</sup>D) and N(<sup>2</sup>P) as the first two electronically excited states of atomic nitrogen react with O<sub>2</sub> and H<sub>2</sub>O, then NO is formed (Herron, 1999).



#### 2.3.2. Oxygen atom reaction pathway

NO<sub>x</sub> reactions involving O atom are as follows:



The rate constants are taken from the literature (Atkinson et al., 1992, 1997). The units of the reactions are: sec<sup>-1</sup>, cm<sup>3</sup>/(mol·sec) and cm<sup>3</sup>/(mol·sec) for first-, second- and third-order reactions, respectively. Kim indicated that the increase of oxygen partial pressure can reduce the formation of nitrogen oxide (Kim et al., 2008).

#### 2.3.3. OH radical reaction pathway

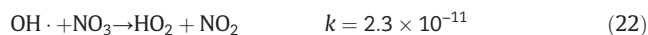
Water mainly came from the oxidation of toluene with air and the water contained in the background gas.



Fast electrons from the electron beam ionize H<sub>2</sub>O and produce OH radical (Chae, 2003).



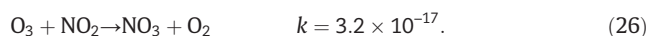
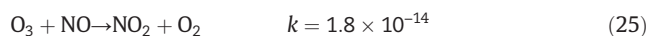
OH radicals react with NO and NO<sub>2</sub> to form HNO<sub>2</sub> and HNO<sub>3</sub>. The reactions are as follows (Chmielewski et al., 2002):



Reactions (20) and (21) are critical for NO<sub>x</sub> removal. The results shown in Fig. 5a demonstrate the suppression of NO<sub>x</sub> with the addition of water.

#### 2.3.4. O<sub>3</sub> reaction pathway

O<sub>3</sub>, which is formed from the reaction of O<sub>2</sub> and O atoms, is involved in the NO<sub>x</sub> reduction reaction as follows (Chmielewski et al., 2002):



Comparing the rate constant from reactions (12)–(15), (20)–(26), it can be seen that O atoms and OH radicals play a more important role than that of O<sub>3</sub> in this process.

### 3. Conclusions

(1) The concentration of NO<sub>2</sub> was much higher than that of NO since NO could be oxidized to NO<sub>2</sub> easily in a DBD reactor. (2)

Catalysts can suppress NO<sub>x</sub> production due to the fact that catalysts could affect some characteristics of the DBD and adsorb NO<sub>x</sub>. Long-lived species are useful to further decompose toluene on the surface of the catalyst. Among the four kinds of catalysts, the CuO catalyst showed the best performance in NO<sub>x</sub> suppression. (3) Oxygen active species and hydroxyl radicals are more important than ozone in suppressing NO<sub>x</sub>.

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