



Detection of hydroxyl radical in plasma reaction on toluene removal

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Abstract

A new method was introduced to detect the concentration of OH radical in dielectric barrier discharge (DBD) reaction. A film, which was impregnated with salicylic acid, was used to detect OH radical in plasma reaction at room temperature and atmospheric pressure. Salicylic acid reacts with OH radical and produces 2,5-dihydroxybenzoic acid (2,5-DHBA). Then, a high performance liquid chromatography (HPLC) was carried out to detect the concentration of 2,5-DHBA. Therefore, OH radical in nonthermal plasma reaction could be calculated. In this plasma reaction, the applied voltage was controlled at 10 kV, the initial concentration of toluene was 400 mg/m³, and the gas flow rate was 300 ml/min. It was observed that when the film was placed away from the plasma area, 2,5-DHBA could not be detected by HPLC, although the sampling time lasted for 48 h. On the other hand, when the film was placed in the plasma area and the sampling time being too long (> 4 h), the concentration of 2,5-DHBA was also below detection limit, and it could not be detected by HPLC. However, when the film was placed in the plasma reaction field with the sampling time being 3 h, the concentration of OH radical was calculated to be $10.54 \times 10^{12} \text{ cm}^{-3}$. In addition, concentration of OH radical was investigated under different humidity, such as 0.2%, 0.4%, 0.6%, 0.8%, and 1.0%. The results showed that the amount of OH radical stayed at order of magnitude of 10^{12} cm^{-3} and increased with the increase of humidity.

Key words: OH radical detection; nonthermal plasma; toluene

Introduction

Nonthermal plasma in air and nitrogen generated by electrical discharges presents considerable interest for a wide range of environmental, biomedical, and industrial applications, such as air pollution control, wastewater cleaning, biodecontamination and sterilization, material and surface treatment, electromagnetic wave shielding, carbon beneficiation and nanotube growth, and element analysis. Plasma chemical processes can be highly effective in promoting oxidation or reduction, enhancing molecular dissociation, or producing free radicals to simulate chemical reactions.

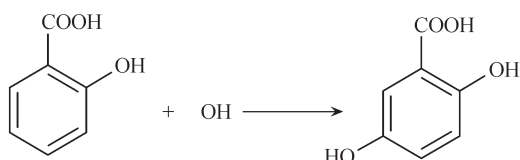
In plasma reactions, to analyze the mechanism of pollutants removal, a diagnosis of the atmospheric pressure nonthermal plasma processing is very important to develop that technology in practice (Oda, 2003). One of the plasma diagnoses is the detection of radical and active species produced in the atmospheric pressure plasma. It would give an insight for plasma chemical processes. This enables understanding and optimizing the air or water pollution control processes. Excited states are produced mostly by collisions with energetic electrons, and thus it is assumed as a measurement of the plasma

active size. Also it can enable calculating basic discharge characteristics. Therefore, it provides understanding of the physical mechanisms. However, because the lives of plasma radicals are very short (some less than 10^{-9} s), the detecting work becomes difficult. In the last few years, some researchers investigated several methods to study the radicals in plasma reaction. For example, Oda (2003) identified that laser-induced fluorescence (LIF) was a very useful technique to observe the radical behavior, and two-dimensional distribution of OH radicals were observed by LIF and photo emission distribution from nitrogen excited by a positive pulse discharge. The LIF detection of the OH radicals was performed in a nozzle-to-plane electrode system, and the two-dimensional OH distribution in the direct current (DC) streamer corona discharge was observed (Kanazawa *et al.*, 2007). Magne and Pasquiers (2005) used LIF to bring an irreplaceable contribution to the study of atmospheric pollutant removal kinetics and monitoring of key species involved in this nonequilibrium gas phase chemistry. Laser-induced fluorescence had been already used for studying NO removal process (Hazama *et al.*, 2000) and measuring the OH radicals (Ono and Oda, 2002) in various nonthermal plasma reactors. A discharge that was generated using planar microelectrode arrays (MEAs) with electrode distances between 50 and 250 μm

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was characterized via optical emission spectroscopy (OES) (Gerick *et al.*, 2002). Machala *et al.* (2007) demonstrated several ways of using UV-Vis OES for the diagnostics of atmospheric pressure air and nitrogen plasmas. Molecular (OH, NO, CN) and atomic (H, O, N) radicals and other active species, e.g., N_2 (C, B, A), N_2^+ (B), were identified. However, in all these articles, the real amount of radicals had not been affirmed.

In this study, a new technology was introduced to detect the concentration of OH radical in dielectric barrier discharge (DBD) reaction. A film impregnated with salicylic acid was used to collect OH radical in the DBD reaction at room temperature and atmospheric pressure. When salicylic acid reacts with OH radical, 2,5-dihydroxybenzoic acid (2,5-DHBA) is produced. Since the chemical activities of other species are weaker than OH radical, the product of 2,5-DHBA mainly comes from OH radical. For example, the velocity constant of HO_2 radical that reacts with salicylic acid is less for 6 magnitude degree than the OH radical that reacts with salicylic acid, and some other species like O_3 and H_2O_2 almost do not react with salicylic acid. The reaction equation is as follows:



Salicylic acid and 2,5-DHBA could be detected by HPLC. Therefore, the concentration of OH radical could be calculated from that of 2,5-DHBA.

1 Materials and methods

1.1 Experimental setup

The experimental setup was similar to previous reports (Guo *et al.*, 2006a, 2006b, 2007). Background gas of air was generated from an air compressor, and a set of mass flow controllers was used to regulate the gas flow rate. Gaseous toluene was regulated by passing part of air stream through pure toluene liquid (> 99.5%), which was kept in a water bath ($T = 25 \pm 1^\circ\text{C}$). High voltage power was supplied by a booster (0–250 V) cooperated with a high voltage AC transformer (50 Hz, 30 kV, root mean square voltage) in series. A digital power meter (YF9901, China) was connected to a variable voltage transformer to measure the input power. The discharge power (the power deposited to the reactor) was calculated from the applied voltage and the reactor current. The applied voltage was measured by a high voltage probe (HVP-40, Pintek Electronic Co., Ltd., Taiwan, China). The input power included the discharge power and the power consumption on the transformer and the circuit. In this experiment, the discharge power was proportional to the input power by a factor of approximately 0.35 in the DBD system.

Gas samples were obtained from the effluent by an autosampler and were analyzed on-line. Toluene and the

reaction products were analyzed by a gas chromatograph (GC-900A, Kechuang, China) equipped with two hydrogen flame ionization detectors. One was used for the detection of organic compounds (such as methane, benzene, and toluene) with a 50-m capillary column (SE-30, Lanzhou Institute of Chemical Physics AT, China) heated at 80°C , and the other, equipped with a methanizer, and a 2-m carbon molecular sieve stainless steel column heated at 65°C was used for the analysis of carbon monoxide and carbon dioxide. The concentration of ozone was monitored by an ozone analyzer (DCS-1, Shanghai Lida Instrument Factory, China). The experiments were carried out at room temperature and atmospheric pressure.

The toluene removal efficiency (η_t) and carbon dioxide selectivity (S_{CO_2}) in the gas phase were defined as follows:

$$\eta_t = \frac{C_{\text{toluene-inlet}} - C_{\text{toluene-exhaust}}}{C_{\text{toluene-inlet}}} \times 100\% \quad (1)$$

$$S_{CO_2} = \frac{C_{CO_2}}{C_{CO} + C_{CO_2}} \times 100\% \quad (2)$$

1.2 Dielectric barrier discharge reactor

A superimposed wire-plate DBD reactor was used in the reaction. Two epoxy resin boards (200 mm \times 45 mm \times 0.8 mm) were used to form the reactor walls and acted as dielectric barriers (the dielectric constant $\epsilon = 3.6$). A high voltage electrode was made of copper wire with 0.8 mm in diameter. A wire electrode was shaped in a spiral to increase the energy density in the reaction volume. The wire-to-wire distance was 10 mm. Two grounded copper net electrodes were fixed on the two sides of the middle epoxy resin board. The total length of the reactor was 200 mm, whereas the effective length was 150 mm. The gap between the high voltage electrode and the grounded electrode was 8 mm, resulting in a cross-sectional area for the flow channel of 400 mm² and a reaction volume of 60 cm³.

1.3 Preparation of a sampling film

To collect the OH radical produced in the plasma reaction, one piece of filter paper was cut to a calculated size (300 mm \times 45 mm), then a solution, which was made by 0.3 g salicylic acid dissolving in 10 ml anhydrous ethanol (99.9%), was dripped equably by a injector on this filter paper. After that, the paper was dried and weighed until all the solution was loaded on.

1.4 Sampling and sample pick-up

The prepared sampling film was puckered and placed in different area of the DBD reactor. The initial concentration of toluene was controlled to 400 mg/m³, and the gas flow rate was 300 ml/min. The applied voltage was 10 kV. After the plasma reaction was carried out for an appointed time (for example, 2, 8, or 16 h), the sampling film was taken out, cut into fragments and then were dipped in water (15 ml). After that an ultrasonic cleaner was used to accelerate dissolution of the products.

1.5 Conditions of HPLC

In this study, HPLC (HP1100, Agilent, USA) experiment was carried out to analyze the sample. HPLC consisted of a vacuum degasser (G1322A, Agilent, USA), a quaternary pump (G1311A, Agilent, USA), an autosampler (G1329A, Agilent, USA), a thermostated column compartment (G1316A, Agilent, USA), and an ultraviolet spectroscopic photometer (300 nm, HP1100, Agilent, USA). The HPLC system was controlled using HP chemstation software. Derivatives were separated on a reversedphase Eclipse XDB-C8 column (150 mm × 4.6 mm, 5 μm, Agilent, USA) by a gradient elution. Eluent A was pure methanol; B was a mixed solvent of methanol, water, and phosphorus acid (methanol/water/phosphorus acid, 40:60:1). Before injection of the next sample, the column was equilibrated with eluent A. The flow rate was maintained constant at 1.0 ml/min, the amount of sample entering the equipment was 20 μl, and the column temperature was set at 30°C.

1.6 Calculation of the concentration of OH radical

After detected by HPLC, the concentration of 2,5-DHBA would be clear. The concentration of OH radical could be calculated by Eq.(3).

$$C_{OH} = \frac{C_{2,5-DHBA} \times V_L \times N}{F_{2,5-DHBA} \times F_g \times t \times \eta \times 1 - \alpha} \quad (3)$$

where, $C_{2,5-DHBA}$ (mol/L) is the concentration of 2,5-DHBA, V_L (L) is the volume of absorbing liquid, N is Avogadro constant, equal to 6.02×10^{23} , $F_{2,5-DHBA}$ is the producing ratio of 2,5-DHBA. In this experiment, almost all salicylic acid reacted with OH radical, therefore, $F_{2,5-DHBA}$ was assumed to be 1. F_g (ml/min) is gas flow rate, t (min) is sampling time, η is pick-up efficiency. In this experiment, almost all 2,5-DHBA was picked up from the film, and was assumed to be 1. The product losing ratio (α) was assumed to be 0 in this experimental condition.

2 Results and discussion

2.1 HPLC chromatogram of salicylic acid and 2,5-DHBA

Figure 1a shows a typical chromatogram of salicylic acid and 2,5-DHBA. The retention time of 2,5-DHBA is 5.604 min and that of salicylic acid is 15.186 min. A standard curve for 2,5-DHBA is shown in Fig.1b according

to Eq.(4).

$$Y = 1249.92X \quad R = 0.99994 \quad (4)$$

where, Y is the peak area, and X (mmol/L) is the concentration of 2,5-DHBA.

2.2 Toluene removal performance in the DBD reaction

In this experiment, the initial concentration of toluene was controlled at 400 mg/m³, the gas flow rate was 300 ml/min, and the applied voltage was 10 kV. Under this condition, the detected toluene removal efficiency was 40%, the concentration of ozone was 60 mg/m³, and the carbon dioxide selectivity was 50%.

2.3 Detection of the concentration of OH radical in different area of DBD reactor

For comparison, a film impregnated with salicylic acid was placed away from the plasma area or in plasma area of the reactor. When the film was placed away from the plasma area (i.e., it was kept out of the reactor), the sampling time varied from 2 to 48 h and 2,5-DHBA could not be detected by HPLC. According to Ono and Oda (2002) and Kanazawa *et al.* (2007), OH radical is still generated or converted from the other radicals or ions inside and afterglow of plasma region. However, when the film was kept out of the plasma area, seldom OH radicals could react with salicylic acid since the life of OH radical was too short (almost 10^{-9} s). Therefore, the radical concentration was below the detection limit.

The film was placed in the plasma area of the reactor (that is, from entrance to back of the plasma reactor), and the sampling time was set at 1, 2, 3, 4, 5, 8, and 16 h. From Table 1, it can be observed that the sampling time could affect the detection of 2,5-DHBA. When the sampling time was less than 2 h, 2,5-DHBA could not be

Table 1 Concentration of OH radical in the plasma area

Sampling time (h)	2,5-DHBA conc. (mmol/L)	OH radical conc. (cm ⁻³)
1	nd	nd
2	0.016	2.68×10^{12}
3	0.063	10.54×10^{12}
4	0.012	2.01×10^{12}
5	nd	nd
8	nd	nd
16	nd	nd

nd: not detected. Conditions: concentration of toluene 400 mg/m³; gas flow rate 300 ml/min; background gas air.

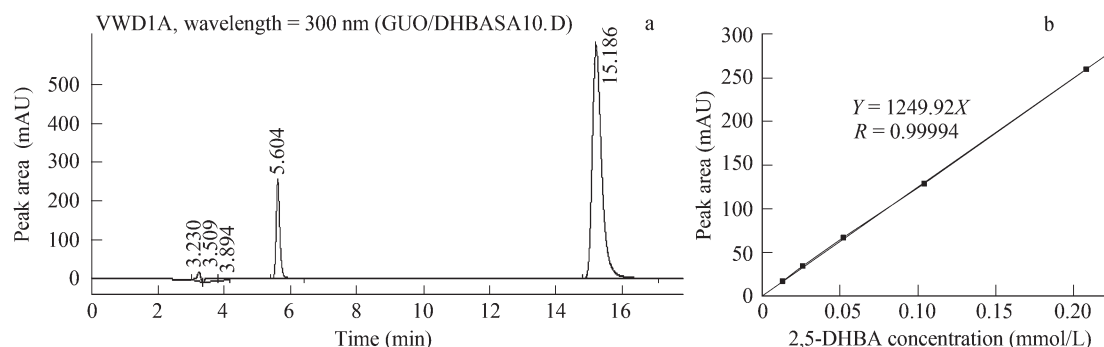


Fig. 1 HPLC chromatogram for salicylic acid and 2,5-dihydroxybenzoic acid (2,5-DHBA) (a) and standard curve (b) for analysis of 2,5-DHBA.

detected by HPLC. It was because when the sampling time was too short, the amount of 2,5-DHBA that was caught on the film was too little, that was below the detecting limit of HPLC. A detection limit of the HPLC was 10^{-9} g. According to Eq.(3), a concentration limit of 7.23×10^7 cm^{-3} for OH radical could be calculated. However, when the sampling time was too long (> 4 h), 2,5-DHBA also could not be detected by HPLC. One possible reason was that when the sampling time was too long, the collected 2,5-DHBA would react with other species under plasma area and decomposed. After sampling for more than 4 h, some yellow solids could be seen on the filter paper. Therefore, at this time, the concentration of 2,5-DHBA was too low to be detected.

2.4 Humidity effect in the detection of concentration of OH radical

On the basis of the former experiments, the sampling time was controlled at 3 h, and the sampling filter paper was placed in the plasma area. Under different humidity, the concentration of OH radical was detected and the results are shown in Table 2. The humidity increased from 0.2% to 1.0%. It shows that OH radical increased with the increase of humidity. The amount of OH radical stayed at order of magnitude of 10^{12} cm^{-3} . The result was consistent with that of Ono and Oda (2002).

Water plays a very important role in the reaction since it decomposes into OH and H free radicals in the plasma system. The initiating reactions involving the H_2O excitation are given in Reactions (5)–(8) (Drzewicz, 2004). When the humidity is high, more H_2O molecules collide with high-energy electrons and OH radicals are formed. However, water also has an adverse effect on toluene removal due to its electronegative characteristics. Increasing the humidity limits the electron density in the system and quenches some activated chemical species. Therefore, because of the electronegative characteristics of water, in this experiment, OH radical does not play a dominant effect in plasma reaction. Other species produced in electron impacting ionization, for example, O radical have more important effects on toluene removal. The amount of such species affects toluene removal at a great extent. Therefore, in reference (Guo *et al.*, 2006c), an optimal humidity existed for toluene destruction.

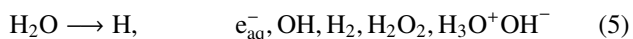
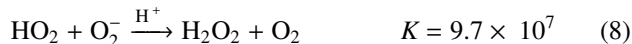


Table 2 Concentration of OH radical in the plasma area with different humidity

Humidity (%)	2,5-DHBA conc. (mmol/L)	OH radical conc. (cm^{-3})
0.2	0.011	1.84×10^{12}
0.4	0.023	3.85×10^{12}
0.6	0.031	5.19×10^{12}
0.8	0.041	6.86×10^{12}
1.0	0.049	8.20×10^{12}

Conditions: sampling time 3 h; concentration of toluene 400 mg/m^3 ; gas flow rate 300 ml/min ; background gas air.



where, K ($\text{L}/(\text{mol}\cdot\text{s})$) is rate constant.

3 Conclusions

A new method was used to detect the concentration of OH radical in DBD reaction. In this method, a film impregnated with salicylic acid was introduced to collect OH radical in reaction and an HPLC was associated to detect the concentration of 2,5-DHBA. It was found that when the film was placed in the plasma reaction field and the sampling time was 3 h, the concentration of OH radical was about 10.54×10^{12} cm^{-3} . In addition, OH radical concentration was detected under different humidity. The results showed that the amount of OH radical increased with the increase in humidity and stayed at order of magnitude of 10^{12} cm^{-3} .

Acknowledgments

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