

REMOVAL OF PHENOL (C₆H₅OH) FROM GAS STREAMS WITH PLASMA CATALYSIS

KUAN LUN PAN, HAN HSUAN PENG, DAI LING CHEN, MOO BEEN CHANG*

No.300, Jhongda Rd, 32001, Jhongli, Taiwan

*Corresponding author's e-mail: mbchang@ncuen.ncu.edu.tw

ABSTRACT

Removal of phenol (C₆H₅OH) by non-thermal plasma (NTP) technology, including NTP-alone and plasma catalysis was investigated. For NTP-alone system, C₆H₅OH removal efficiency increases with increasing input voltage and gas residence time. C₆H₅OH removal efficiency achieved with DBD reaches 100% as 18.75 kV is applied. The inlet C₆H₅OH concentration was 300 ppm while the total flow rate was fixed at 0.6 L/m.

The influence of water vapor is also explored. In the presence of H₂O_(g), the C₆H₅OH removal efficiency and energy efficiency increase, because •OH radical generated can react with C₆H₅OH. On the other hand, C₆H₅OH removal efficiency achieved with plasma catalysis increased from 63 to 82% at same condition (flow rate: 0.6 L/min, voltage: 15 kV, frequency: 110 Hz and H₂O_(g): 0%). Obviously, C₆H₅OH removal efficiency can be significantly enhanced as catalyst is added into the NTP system. In addition, it is noteworthy that CO₂ selectivity significantly increases compared with that of DBD alone.

1. INTRODUCTION

Volatile organic compounds (VOCs) are important contributors to the atmospheric pollution and may have adverse effects on human health [1]. VOCs including aromatic hydrocarbons, alkanes, alcohols, acetates and ketones are commonly utilized for commercial and industrial applications such as paints, chemical plants, and printing industries [2]. Phenol (C₆H₅OH) is one of the most important organic pollutants. Its derivatives are widely distributed in atmosphere, groundwater and surface water, being generated from a number of industrial factories, such as refinery, textiles, pulp and paper, resin and plastics,

pharmaceutical, petrochemical, and so on [3]. Phenol is toxic at low concentration, causing adverse effect on human health through inhalation, ingestion, or eye and skin contact [4]. Additionally, it is also an important odor-causing substance, with a relatively low odor threshold (0.04 ppm).

Conventional methods for VOCs removal include adsorption, direct incineration, absorption, thermal catalytic oxidation (TCO) [5]. Among TCO methods, perovskite-typed catalysts have been extensively studied for VOCs removal and their activities are comparable to noble metal catalysts. However, it must operate at a high temperature (>300°C) for good performance.

Previous studies indicate that non-thermal plasma (NTP) can effectively eliminate VOCs, because it generates numerous free radicals, electrons, ions to react with VOCs [6]. However, NTP technology has some drawbacks need to overcome such as low energy efficiency and selectivity. Therefore, a hybrid system combining non-thermal plasma and perovskite-typed catalyst is developed in this study to improve the removal efficiency of C₆H₅OH and selectivity of CO₂.

2. EXPERIMENTAL

2.1 Activity system measurement

Fig. 1 shows the reaction system for removal of C₆H₅OH with plasma catalysis. Removal of C₆H₅OH was evaluated in a fixed-bed reactor at atmospheric pressure, and the discharge volume is fixed 17 cm³. C₆H₅OH-containing gas stream was generated by passing air through pure liquid C₆H₅OH kept in a water bath at a fixed temperature, and then being diluted with air to get a C₆H₅OH concentration of 300 ppm.

The power source for the plasma was a power meter with a high-voltage transformer. The alternating current voltage was controlled at 15 to 18.75 kV with frequency of 110 Hz. The discharge power was determined by Lissajous diagram (V – Q plot) which was measured by a digital oscilloscope equipped with a high-voltage probe and a voltage probe, and with a 1.0 μ F capacitor connected to the reactor in series. For plasma catalysis system, 6 g perovskite-typed catalyst ($\text{La}_{0.7}\text{Ce}_{0.3}\text{SrNi}$) is placed into the discharge zone. All experimental tests are operated at room temperature, while products are analyzed by GC and FT-IR. The experimental parameters investigated include power, gas flow rate, and water vapor content.

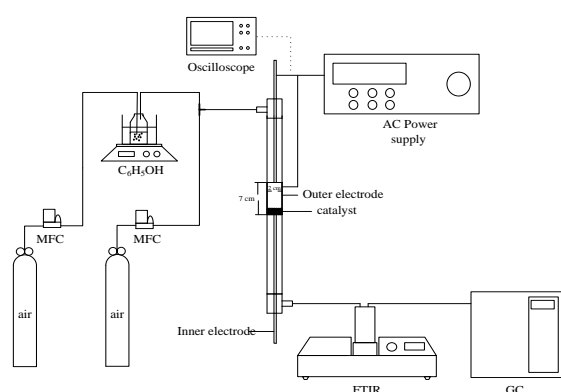


Fig. 1 Reaction system of removal of $\text{C}_6\text{H}_5\text{OH}$ for plasma catalysis

The test data were collected when the reaction reached steady-state conditions. The $\text{C}_6\text{H}_5\text{OH}$ removal efficiency was calculated by Equation (1):

$$\text{C}_6\text{H}_5\text{OH removal (\%)} = \frac{[\text{C}_6\text{H}_5\text{OH}]_{\text{inlet}} - [\text{C}_6\text{H}_5\text{OH}]_{\text{outlet}}}{[\text{C}_6\text{H}_5\text{OH}]_{\text{inlet}}} \times 100\% \quad (1)$$

Where $[\]_{\text{inlet}}$ and $[\]_{\text{outlet}}$ are $\text{C}_6\text{H}_5\text{OH}$ concentrations measured before and after the reactor, respectively.

2.2 Catalyst preparation and analysis

The catalyst ($\text{La}_{0.7}\text{Ce}_{0.3}\text{SrNiO}_4$) was prepared by the Pechini method. The corresponding metal nitrates and citric acid were dissolved in water to form a 1M solution, which was gradually heated to 85°C , and maintained for 1 hour with stirring. The molar ratio of citric acid to the total metal cations was 4 to 1. Then, ethylene glycol was added to the solution at 90°C for 4 hours with stirring. Molar ratio of ethylene glycol was 1:1 with citric acid. The mixed aqueous solution was then heated and stirred to evaporate the water.

Finally, the residual solid composition was dried at 120°C for 24 h, and calcined in air at 950°C for 6 h, then manually milled to powders by using a porcelain mortar and pestle. Subsequently, the synthesized particles were pulverized to the 200 mesh size. Relevant properties of catalyst were analyzed by using Brunauer Emmett Teller (BET), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

3.1 Physicochemical properties of catalyst

Fig. 2 shows the XRD patterns of $\text{La}_{0.7}\text{Ce}_{0.3}\text{SrNiO}_4$, and indicates that it is of perovskite-like phase with A_2BO_4 structure. Its main diffraction peak is mainly assigned to those from LaSrNiO_4 . In addition, there exists one abrupt peak at $2\theta \sim 28^\circ$, it might imply the peak of $\text{La}_{1-x}\text{Ce}_x\text{SrNiO}_4$ in this study. This finding is consistent with the previous study [7] which indicates that oxidative state of catalyst can be changed when Ce partially occupies the La-site for LaSrNiO_4 and the activity of catalyst may increase due to charge compensation.

The specific surface area of $\text{La}_{0.7}\text{Ce}_{0.3}\text{SrNiO}_4$ is $5.2 \text{ m}^2/\text{g}$, and the morphology of catalyst was identified as nano-size and granular particle with abundant pores, but it has some agglomeration on the surface of catalyst due to high calcination temperature, and this result may lead to its low specific surface area.

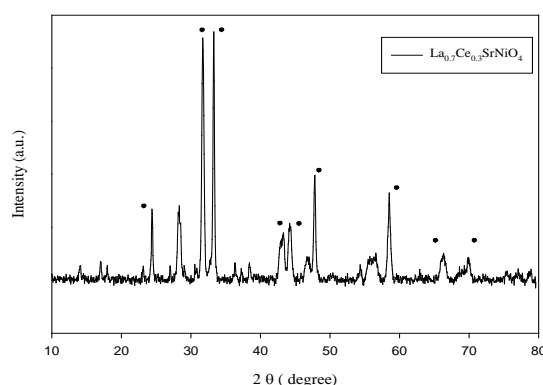


Fig. 2 X-ray diffraction pattern of $\text{La}_{0.7}\text{Ce}_{0.3}\text{SrNiO}_4$ catalysts calcined in air at 950°C (\ast): LaSrNiO

3.2 Effect of input voltages on $\text{C}_6\text{H}_5\text{OH}$ removal with DBD

Fig. 3 shows the $\text{C}_6\text{H}_5\text{OH}$ removal efficiencies achieved at various input voltages. The result indicates that $\text{C}_6\text{H}_5\text{OH}$ removal efficiency is only

36% at initial input voltage of 13.5 kV. As input voltage is increased to 18.75 kV, C₆H₅OH achieved with NPT-alone reaches 100%. On the other hand, energy efficiency decreases from 2.1 to 1.6 g/kWh as input voltage is increased from 15 to 18.75 kV. As presented in Fig. 3, C₆H₅OH removal efficiency increases monotonously with increasing input voltage. This result can be explained since potential difference would increase between gap of discharge, further, causing reduced field (E/N) to enhance in the system. The electron energy distribution function (EEDFs) would change as reduced field (E/N) is changed, namely, electron energy is enhanced with increasing reduced field (E/N). Another possibility, electron number can be increased within system as input voltage is increased, causing favour removal of pollutant.

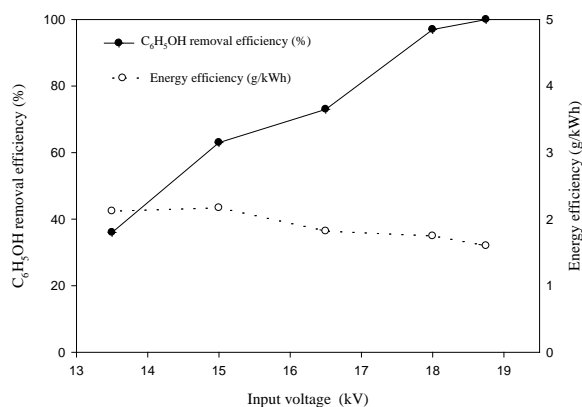


Fig. 3 C₆H₅OH removal efficiency achieved with NTP-alone with various input voltages ($C_{phenol} = 300$ ppm, gas flow rate = 0.6 L/min, frequency = 110 Hz)

3.3 Effect of gas flow rate on C₆H₅OH removal with DBD

Effect of gas flow rate on C₆H₅OH removal is presented at Fig. 4, and the result indicates that C₆H₅OH removal efficiency is 53% at gas flow rate of 1 L/min. further, 100% C₆H₅OH removal efficiency can be reached as the total gas flow rate is lower than 0.3 L/min. Overall, C₆H₅OH removal efficiency and energy efficiency increase with decreasing total gas flow rate. Generally, gas residence time would affect the collision probability between electron and pollutant. As presented in Fig. 4, a higher gas residence time leads to higher C₆H₅OH removal efficiency.

3.3 Effect of water vapor on C₆H₅OH removal with DBD

Fig. 5 shows the effect of water vapor on

C₆H₅OH removal efficiency. C₆H₅OH removal efficiency is 63% in the absence of H₂O_(g). As water vapor is introduced into the gas stream (RH: 60%), C₆H₅OH removal efficiency is significantly increased to 73%, while energy efficiency also increases from 2.1 to 2.5 g/kWh at the gas flow rate of 0.6 L/min. It speculates that •OH radical can be generated with DBD in the presence of H₂O_(g), which can further react with C₆H₅OH, hence, it favors to convert C₆H₅OH into other compounds.

3.4 Removal efficiency of C₆H₅OH with plasma catalysis

Fig. 6 displays the C₆H₅OH removal efficiency achieved with plasma catalysis. C₆H₅OH removal efficiency and energy efficiency increase from 63% to 83% and from 2.1 to 2.9 g/kWh with plasma catalysis operated at 15 kV and 110 Hz. Obviously, C₆H₅OH removal efficiency can be significantly enhanced as catalyst is added into the non-thermal plasma system.

The reaction mechanism is complex as catalyst is introduced into the plasma discharge. Catalysts may affect plasma discharge type or can induce a shift in the distribution of the accelerated electrons. These processes influence the production of excited and short-living reactive plasma species, and new reactive species can also be generated. In addition, temperature can be increased during plasma operation to thermally activate catalyst. Additionally, the presence of highly reactive plasma species and electrons trigger physical changes of the catalyst material and consequently affect VOC surface adsorption [6]. To conclude, several processes are possible when catalysts are combined with non-thermal plasmas. Overall, it can be postulated that VOC removal becomes more efficient, along with a higher mineralization rate.

3.5 Product analysis

The by-products of C₆H₅OH removal are mainly CO₂, HNO₃, and O₃ after DBD-alone treatment. For plasma catalysis system, the amounts of HNO₃ and O₃ decrease if compared with DBD-alone system. Specifically, selectivity of CO₂ can be significantly improved as catalyst is added into DBD system, with the value being increased from 55% to 80%. Indeed, it can bring positive effect on VOC removal.

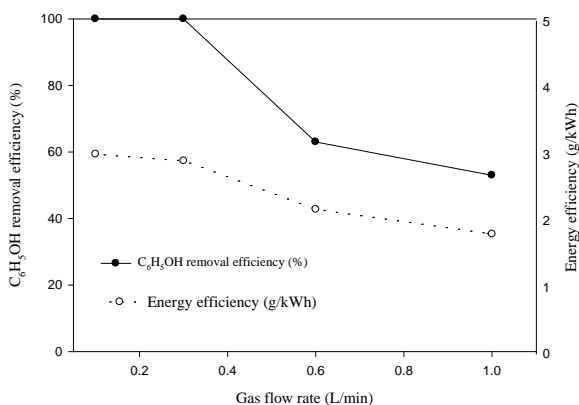


Fig. 4 C₆H₅OH removal efficiency with NPT-alone with various total flow rate ($C_{phenol} = 300$ ppm, input voltage = 15 kV, frequency = 110 Hz)

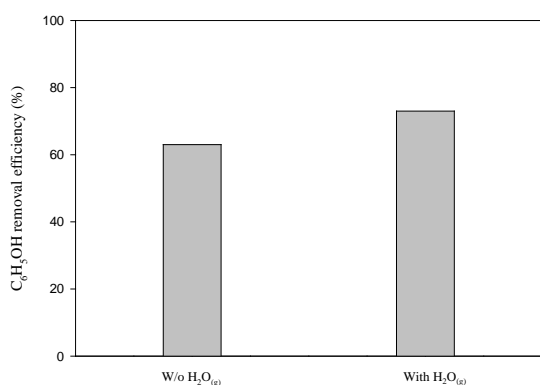


Fig. 5 Effect of water vapor on C₆H₅OH removal efficiency for DBD system ($C_{phenol} = 300$ ppm, input voltage = 15 kV, frequency = 110 Hz, flow rate = 0.6 L/min, RH = 60%)

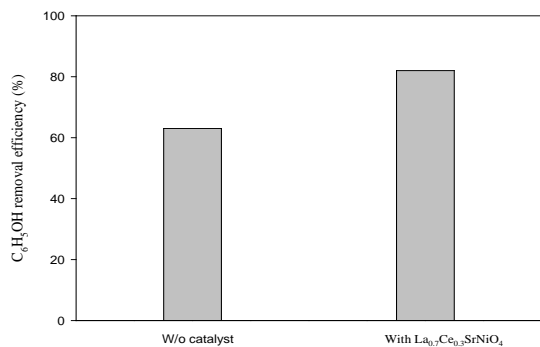


Fig. 6 C₆H₅OH removal efficiency achieved with plasma and plasma catalysis, respectively ($C_{phenol} = 300$ ppm, input voltage = 15 kV, frequency = 110 Hz, gas flow rate = 0.6 L/m)

4. CONCLUSIONS

This work indicates that C₆H₅OH removal efficiency increases with increasing input voltage. The C₆H₅OH removal efficiency achieved with NPT-alone reached 100% at 18.75 kV and 110 Hz. In addition, the C₆H₅OHO removal efficiency increased monotonously with decreasing total gas flow rate, with applied 15 kV and frequency 110 Hz.

C₆H₅OH removal efficiency and energy efficiency are increased as water vapor is introduced into the stream (RH: 60%), because additional radical can be generated, which favors C₆H₅OH removal. C₆H₅OH removal efficiency achieved with plasma catalysis system is 83% at 15 kV and 110 Hz of frequency, the same removal efficiency was obtained when plasma-alone was operated at input voltage higher than 16.5 kV. Overall, plasma catalysis can bring positive benefits and increase performance of C₆H₅OH removal.

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