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Article

Synergetic effect between non-thermal plasma and photocatalytic oxidation on the degradation of gas-phase toluene: Role of ozone

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ABSTRACT

In this study, a hybrid process using non-thermal plasma (NTP) and photocatalytic oxidation (PCO) was adopted for the degradation of gas-phase toluene using TiO₂ as the photocatalyst. To discover the synergetic effect between NTP and PCO, the performances of both sole (O₃, UV, NTP, and PCO) and combined (O₃ + TiO₂, O₃ + UV, NTP + UV, O₃ + PCO, and NTP + PCO) processes were investigated from different perspectives, such as the toluene removal efficiency, selectivity of CO₂, mineralization rate, ozone utilization, and the generation of by-products. The toluene removal efficiency of the combined NTP + PCO process was 80.2%, which was much higher than that of a sole degradation process such as NTP (18.8%) and PCO (13.4%). The selectivity of CO₂ and the ozone utilization efficiency also significantly improved. The amount of by-products in the gas phase and the carbon-based intermediates adsorbed on the catalyst surface dramatically reduced. The improvement in the overall performances of the combined NTP + PCO process was mainly ascribed to the efficient utilization of ozone in the photocatalytic oxidation, and the ozone further acting as an electron acceptor and scavenger, generating more hydroxyl radicals and reducing the recombination of electron-hole pairs.

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1. Introduction

Emissions of volatile organic compounds (VOCs) are an important cause of air pollution, not only harming the human health and the ecological environment directly, but also leading to the formation of PM_{2.5}, ozone, and photochemical smog [1–4]. Advanced oxidation processes such as thermal catalytic oxidation [5–7], non-thermal plasma (NTP) [8–13], and photocatalytic oxidation (PCO) [14–18] have been deemed efficient

technologies for air purification. Although NTP technology exhibits high efficiency with regard to the removal of VOCs with a short residence time and relatively low energy consumption, it also suffers from the disadvantages of low selectivity in the mineralization of VOCs and the generation of undesirable by-products such as ozone [8,14]. When applied to the PCO process, it possesses high activity toward various contaminants and benign final products (CO₂, H₂O) through the use of hydroxyl radicals (OH•) as the principal species for the complete

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oxidization of VOCs. However, the application of the PCO process is limited by its low quantum efficiency, a fast recombination of the electron-hole pairs, and photocatalyst deactivation during a lengthy operation time [15,18–20].

The combination of NTP and PCO as a way to deal with VOCs has recently attracted significant attention [1,21–26] because both technologies can be applied under ambient temperature and atmospheric pressure. Previous studies have emphasized that such a combination can improve the removal efficiency of VOCs and prompt the formation of carbon dioxide [22,25,27,28]. Although the generated ozone is the main oxidizer in a combined system, the residual ozone is a serious problem with regard to plasma [1,25,29]. Previous researches have mainly focused on the degradation efficiency of VOCs, and few studies have paid attention to the mineralization rate of VOCs in the entire system. Moreover, the ozone consumption in a combined system has not been clearly studied, and what role ozone plays in the combined system has yet to be well determined.

In this study, the NTP and PCO processes were combined to achieve a degradation of gas-phase toluene, which is a representative VOC that occurs from architectural coatings, motor vehicles, and various industrial processes [11,21,23,30,31]. Anatase TiO_2 with a mesoporous network was synthesized for use as a photocatalyst owing to its physical and chemical stability, high photocatalytic activity, non-toxicity, and low cost [18–20]. The combination of NTP and PCO was achieved by placing a PCO reactor with an external UV lamp downstream from the NTP reactor with the aim of the better control and utilization of ozone [1,23,24,26]. The performances of sole (O_3 , UV, NTP, and PCO) and combined ($\text{O}_3 + \text{TiO}_2$, $\text{O}_3 + \text{UV}$, NTP + UV, $\text{O}_3 + \text{PCO}$, and NTP + PCO) processes were studied for comparison. The toluene removal efficiency, mineralization rate of toluene, generation of by-products, ozone utilization efficiency, and carbon balance of the system were investigated to explore the synergetic effect in the combined system and the role that ozone plays.

2. Experimental

2.1. Setup

The experimental setup was composed of four parts: polluted gas flow generation, an NTP reactor, a PCO reactor, and an analysis system. A schematic diagram of the experimental setup is shown in Fig. 1. The PCO reactor with a mercury lamp is placed downstream from the NTP reactor. The off-gas was analyzed using a gas chromatograph (GC), an ozone analyzer, and an FT-IR spectrometer.

2.1.1. Polluted gas flow generation

A polluted gas flow was generated through the blending of N_2 (78 vol%), O_2 (21 vol%), water vapor, and gas-phase toluene. A total flow rate of 2 L/min was controlled using mass flow meters. Water was used for bubbling, whereas toluene was used for stripping. The concentration of the gas-phase toluene was adjusted to 70 ppm.

2.1.2. NTP reactor

The NTP reactor adopted a dielectric barrier discharge (DBD) to generate plasma. The DBD generator consisted of a quartz glass plate (as a dielectric), a copper plate (as a high-voltage electrode), and a stainless steel net (as a grounded electrode). The DBD plasma was generated using a home-made pulsed power supply, and the power supply, which was based on fast MOSFETs, produced high-voltage pulses with a peak voltage of up to 6 kV and a width of 1–4 μs at a repetition rate of up to 30 kHz [11].

2.1.3. PCO reactor

The PCO reactor was designed to be baffled with the reaction area uniformly divided into four parts, each of which was 10 cm $\times$ 4 cm $\times$ 1.5 cm (length $\times$ width $\times$ height) in size. As an appropriate dose, 0.15 g of a catalyst was loaded onto a frosted glass using a dip-coating method. A 125 W high-pressure mercury lamp with a dominant wavelength of 365 nm was adopted as the external UV light source.

Fig. 1. Schematic diagram of experimental setup.

2.1.4. Analysis system

Fourier transform infrared spectroscopy (FT-IR) was applied using a Bruker ALPHA-G spectrometer (Bruker, Germany). The concentrations of the gas-phase toluene, carbon monoxide, and carbon dioxide were monitored using GC (PuxiG5, China) with two flame ionization detectors and a nickel conversion equipment. The concentration of the ozone was detected using an ozone analyzer (UV 100, Eco Sensors, USA).

The off-gas containing various gaseous products was captured using an adsorption tube (Tenax TA/Tenax GR). The adsorbed compounds were identified using gas chromatograph-mass spectrometry (GC-MS, Agilent 7890A GC, equipped with an Agilent 5975C MS). The atomic ratio of the catalyst was measured using X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) with Al K_{α} X-ray radiation at 150 W as the excitation source. The species of the intermediates on the surface were tested using temperature programmed desorption-mass spectrometry (TPD-MS, TP-5079, Tianjin, Xianquan, equipped with a Hiden QGA portable MS).

2.2. Catalyst preparation

TiO₂ was synthesized using a one-step hydrothermal method. 2 g of TiOSO₄·xH₂SO₄·xH₂O powder was added into 60 mL of tert-butyl alcohol, followed by the addition of 1 mL of benzyl alcohol. The above suspension was magnetically stirred for 30 min. The precursor solution was then transferred into a 100-mL autoclave to achieve a reaction, which was maintained at 110 °C for 48 h. The product was filtered, washed thoroughly with deionized water, and finally dried at 60 °C for 6 h [32,33].

2.3. Catalytic reaction

After the gas-phase toluene achieved adsorption equilibrium and remained stable at 70 ppm, the performances of the sole (O₃, UV, NTP, and PCO) and combined (O₃ + TiO₂, O₃ + UV, NTP + UV, O₃ + PCO, and NTP + PCO) processes were tested. In the sole process of O₃, O₃ was generated using NTP, and the concentrations of toluene at the inlet and outlet of the PCO reactor (without UV-irradiation or a photocatalyst) were detected. In the sole process of NTP, the concentrations of toluene at the inlet and outlet of the NTP reactor were detected when the DBD was on work. Thus, for O₃ and NTP, it was necessary to turn on the power to generate the discharge and adjust the specific input energy. For the sole processes of UV and PCO, the mercury lamp was turned on to launch UV light, and the concentrations of toluene at the inlet and outlet of the PCO reactor (with or without a photocatalyst loaded) were detected. For the combined processes, two types of sole processes, namely, O₃ and NTP, and UV and PCO, were coupled. Therefore, the combined processes included O₃ + TiO₂, O₃ + UV, NTP + UV, O₃ + PCO, and NTP + PCO.

In the decomposition of gas-phase toluene, the toluene removal efficiency was calculated to evaluate the performance of toluene removal through the following equation:

$$\text{Toluene removal efficiency (\%)} = \frac{[\text{toluene}]_{\text{inlet}} - [\text{toluene}]_{\text{outlet}}}{[\text{toluene}]_{\text{inlet}}} \times 100\%$$

The selectivity of CO_x (CO and CO₂) was calculated as follows:

$$\text{Selectivity of CO}_x (\%) = \frac{[\text{CO}_x]_{\text{outlet}} \times 100\%}{7 \times ([\text{toluene}]_{\text{inlet}} - [\text{toluene}]_{\text{outlet}})} \quad (x = 1, 2)$$

The mineralization rate, which represented the complete conversion of toluene into CO₂, was calculated as follows:

$$\text{Mineralization rate (\%)} = \frac{[\text{CO}_2]_{\text{outlet}}}{7 \times [\text{toluene}]_{\text{inlet}}} \times 100\%$$

The ozone utilization efficiency was adopted to assess the extent of ozone utilization in the combined process, and was calculated as follows:

$$\text{Ozone utilization efficiency (\%)} = \frac{[\text{ozone}]_{\text{inlet}} - [\text{ozone}]_{\text{outlet}}}{[\text{ozone}]_{\text{inlet}}} \times 100\%$$

During the NTP process, the specific input energy (SIE) was an important indicator reflecting the energy consumption. The injected energy per cycle (E) was determined through an integration of the product of the current and voltage. Thus, the injected power (P) and SIE were further calculated as follows [11]:

$$E(J) = \int_0^T u(t) \times i(t) dt$$

$$P(W) = E(J) \times \text{frequency(Hz)}$$

$$\text{SIE}(J/L) = P(W) \times 60 / Q(L/min)$$

By adjusting the applied voltage, the SIE was adjusted to an appropriate value of 60 J/L.

3. Results and discussion

3.1. Study on toluene degradation performance

3.1.1. Degradation performance of sole process

First, a blank test was carried out to investigate the effects of the photolysis (UV) and ozonation (O₃) on the degradation of toluene. The results shown in Fig. 2 indicate that individual UV-irradiation or ozone had almost no effect on the toluene removal. The toluene degradation performances of sole NTP and PCO are also shown in Fig. 2. The performance of the NTP showed that the toluene removal efficiency remained relatively stable at 18.8% during the entire reaction time. In the plasma, highly reactive radical species such as e⁻, O•, HO₂•, OH•, N₂•, and O₃ were generated, which could react with toluene. Nevertheless, the performance concluded that NTP exhibited low efficiency in terms of toluene removal under a low energy input. The performance of PCO showed that the toluene removal efficiency was only 13.4% on average. In the PCO, the generation of electron-hole pairs was a crucial step for forming active species such as hydroxyl radicals (OH•) and superoxide radicals (O₂•-), which were principal species to react with toluene. The process is as follows:

The performance indicates that PCO also exhibited low efficiency in terms of toluene removal, which might suffer from

Fig. 2. Toluene degradation performance of sole processes.

limitations of the low quantum efficiency and the recombination of electrons and holes.

3.1.2. Degradation performance of combined process

Owing to the complicated factors of the combined NTP + PCO process, which includes free radical ions excited by the NTP, UV-irradiation in the PCO, the photocatalyst, and ozone generated in the NTP, multiple combined processes take place in the system, including catalytic ozonation ($O_3 + TiO_2$), ozone photolysis ($O_3 + UV$), NTP-assisted photolysis (NTP+UV), ozone-assisted PCO ($O_3 + PCO$), and the combined NTP + PCO process (NTP + PCO) [23,30]. Toluene degradation of these combined processes is shown in Fig. 3.

Contrary to previous research [23,30], catalytic ozonation exhibited little activity regarding the degradation of toluene. This might be ascribed to the high flow rate in our system and the different catalyst loading method applied. Thus, the contribution of catalytic ozonation can be nearly neglected in this study. With ozone and NTP-assisted photolysis, the toluene removal efficiency reached 43.6% and 53.8%, respectively, revealing that ozone photolysis might exert an important impact on the toluene removal. Furthermore, the toluene removal efficiency reached 76.5% and 80.2% in the ozone- and

Fig. 3. Toluene degradation performance of combined processes.

NTP-assisted PCO, which were much higher than that of NTP, PCO, ozone photolysis, and NTP-assisted photolysis. This result indicates that the participation of ozone in the photocatalytic process contributes significantly to the degradation of toluene, and the ozone creates an intimate bond between the NTP and PCO processes.

If the NTP and PCO processes are simply coupled together, the toluene removal efficiency can be calculated approximately as follows:

$$1 - (1 - \eta_1)(1 - \eta_2) = \eta_1 + \eta_2 - \eta_1\eta_2 = 29.7\%$$

where η_1 refers to the toluene removal efficiency of NTP (18.8%), and η_2 refers to that of PCO (13.4%). Actually, a distinct enhancement was obtained through the removal of toluene in the combined NTP + PCO process. The toluene removal efficiency reached 80.2%, which was even much greater than the sum of NTP (18.8%) and PCO (13.4%). This indicates that a strong synergetic effect exists in the combined process of NTP and PCO for toluene removal.

3.2. Study on comprehensive degradation performance

3.2.1. Selectivity of CO_x and mineralization

Extensive attention has been paid to the selectivity of CO_2 and mineralization of VOCs [2,3,9,11,34]. In this study, the selectivity of CO_x was calculated to explore whether the removed toluene was completely converted into CO or CO_2 . The carbon balance was carefully calculated to estimate the amount of exhausted carbon-based intermediates in the gas phase. A comparison of the carbon balance among the above processes is shown in Fig. 4(A), followed by the mineralization rate shown in Fig. 4(B).

In the NTP process, the selectivity of CO_x was close to 100% owing to the carbon balance calculation, indicating that the removed toluene was almost completely decomposed into CO and CO_2 . However, the selectivity of CO was the highest among the tested processes, whereas the selectivity of CO_2 was 70%. This illustrates that a portion of the toluene did not achieve deep oxidation, and only oxidized into CO in the NTP. In the PCO, the selectivity of CO_x was clearly lower than that of the NTP, indicating that a greater amount of carbon-based intermediates was generated during the photocatalytic degradation process. Many studies have reported that intermediates such as benzaldehyde, benzyl alcohol, and benzoic acid might be generated [30,35,36]. However, the selectivity of CO_2 during the PCO process was higher than that of the NTP, indicating that CO was easier to be oxidized into CO_2 through this process. In the ozone-assisted PCO and combined NTP + PCO processes, the selectivity of CO_2 was greater than that of the sole NTP and PCO processes, whereas the generation of intermediates also showed the lowest value. It can be concluded that most of the degraded toluene was converted into CO_2 .

For a deeper understanding of the performance of ozone- and NTP-assisted photolysis, the selectivity of CO_x was also determined. The selectivity of CO_2 was much lower, whereas the generation of intermediates appeared to be significantly larger in comparison with the other processes. This indicates that a large portion of toluene was converted into carbon-based

Fig. 4. Selectivity of CO_x (A) and mineralization rate (B) of different processes. (a) NTP; (b) PCO; (c) O₃ + PCO; (d) NTP + PCO; (e) O₃ + UV; (f) NTP + UV.

intermediates during the ozone and NTP-assisted photolysis processes, instead of CO or CO₂.

In terms of the mineralization rate, among the tested processes, the ozone-assisted PCO and combined NTP + PCO system also showed the best performances. This indicates that a strong synergetic effect of NTP and PCO, which is mainly contributed to by ozone, not only influences the toluene removal efficiency, but also affects the selectivity of CO_x and the mineralization rate.

3.2.2. Ozone utilization

Ozone generated in the NTP is considered to have a longer lifetime than other radical species, which was also deemed a type of harmful by-product owing to its leakage in the exhausted gases. Ozone was formed through oxygen radicals combined with oxygen molecules as follows [37]:

A blank test was carried out when the gas flow of pure air (without toluene) passed the NTP reactor, which was turned on. The concentration of ozone gradually and steadily approached 340 ppm, which is denoted as the concentration of ozone at the inlet. The ozone utilization efficiency during the ozone-related processes is shown in Fig. 5.

Fig. 5. Ozone utilization efficiency of ozone-related processes.

The ozone utilization efficiency of the NTP was shown to be only 21.2%, which is the lowest among these processes. It is concluded that ozone has seldom been utilized in the NTP process, which might be ascribed to the short duration time of the NTP process. For the ozone and NTP-assisted photolysis processes, the ozone utilization efficiency arrived at 51.1% and 61.5%, respectively. Although the performance was significantly improved compared with that of the NTP, a large amount of ozone was still emitted in the off-gas. During the ozone-assisted PCO and combined NTP + PCO processes, the ozone utilization efficiency reached approximately 87.4% and 90.1%, indicating that ozone was efficiently utilized during the toluene degradation process.

These results further indicate that the synergetic effect of NTP and PCO is comprehensive, which is reflected in the toluene removal efficiency, the selectivity of CO_x, the mineralization rate, and the ozone utilization performance. It also indicates that a strong synergetic effect occurs among the coexistence of ozone, UV-irradiation, and the photocatalyst. The results are also consistent with the report indicating that the toluene oxidation rate, CO₂ yield rate, and ozone removal efficiency in the UV/O₃/TiO₂ process are greater than those in the UV/O₃ process [21]. The results are also identical with previous research [23,30,38,39].

3.3. By-products in the gas phase

3.3.1. Analysis of FT-IR spectra

To further understand the synergetic effect of NTP + PCO, an FT-IR spectrometer analysis was applied to test the by-products generated during the toluene degradation process, the results of which are shown in Fig. 6.

Fig. 6(a) shows the FT-IR spectra of toluene. The bands appearing at 3013 and 2941 cm⁻¹ were assigned to the C-H stretching mode of the aromatic ring and methyl group, respectively. The bands at 1611 and 1499 cm⁻¹ were assigned to the skeleton vibrations of the aromatic ring [40,41]. The band located at 728 cm⁻¹ can be identified as toluene as well. In the spectra of the exhausted gases of the NTP (Fig. 6(b)) and combined NTP + PCO (Fig. 6(c)) processes, the above-mentioned bands decreased and even disappeared, indicating that the

Fig. 6. FT-IR spectra of toluene (a), NTP (b), and combined NTP + PCO (c) processes regarding the degradation of toluene.

toluene was dramatically degraded. In the spectrum for the exhausted gases from the NTP process (Fig. 6(b)), bands at 1053 and 1037 cm^{-1} for ozone [42] sharply emerged, indicating that a significant amount of ozone was generated and emitted. Weak bands appearing at 2357 and 2341 cm^{-1} were assigned to CO_2 , whereas those at 2123 and 2101 cm^{-1} were assigned to CO [43], indicating that a proportion of the toluene was oxidized into CO and CO_2 . In addition, the small bands at 2238 and 2212 cm^{-1} were assigned to N_2O [44], which is a by-product of the plasma process. In the spectrum of the exhausted gases from the combined NTP + PCO process (Fig. 6(c)), the bands at 2357 and 2341 cm^{-1} are attributed to CO_2 , which became much stronger in comparison with the sole processes, whereas the bands at 2238 and 2212 cm^{-1} (N_2O) 2123 and 2101 cm^{-1} (CO) and 1053 and 1037 cm^{-1} (O_3) disappeared. The new band at 669 cm^{-1} attributed to CO_2 [43], appeared when CO_2 was present at a high concentration. This indicates that toluene is dramatically oxidized into CO_2 through the combined NTP + PCO process. Ozone was fully taken advantage of in the arrangement of the PCO downstream NTP. In addition, by-products such as N_2O and CO were also effectively removed. To summarize, the combined NTP + PCO process exhibited high efficiency in terms of the degradation of toluene into CO_2 .

3.3.2. Analysis of GC-MS spectra

Further, GC-MS was adopted to identify the by-products in the exhausted gases during the gas phase. The results of NTP-assisted photolysis and the combined NTP + PCO process were analyzed for comparison, the results of which are shown in Fig. 7.

As shown in Fig. 7(a), a sharp peak of benzene appears next to the peaks of toluene, CO_2 , and H_2O . In addition, small peaks of isobutylene and acetone also appear. This indicates that a portion of the degraded toluene was not completely oxidized into CO_2 and H_2O , but was converted into benzene and small amounts of isobutylene and acetone during the NTP-assisted photolysis. In contrast, Fig. 7(b) shows that the peak of benzene decreased dramatically, indicating that the removed toluene was almost completely oxidized into CO_2 and H_2O during the combined NTP + PCO process. These results correspond well with the selectivity of CO_x .

3.4. Adsorbed intermediate products on catalyst surface

3.4.1. Analysis of XPS

Clearly, the apparent color of the TiO_2 photocatalysts changed after the above toluene degradation processes were applied. The color of the pure TiO_2 was white. The color of the used photocatalyst changed thoroughly into yellow during the PCO process (called PCO- TiO_2 herein) and changed slightly into yellow during the combined NTP + PCO process (called combined- TiO_2). This clearly indicates that some intermediates were adsorbed on the surface of the TiO_2 and were not desorbed in time. A type of in situ treatment was introduced in our study. The flow of toluene was cut off, and only air continued to flow through. Both NTP and PCO were turned on. The apparent color of PCO- TiO_2 returned to white after the in situ treatment (called treated- TiO_2). The result of apparent colors of the samples was shown in Fig. 8.

To find the differences among the four samples above, an XPS was conducted to analyze the atomic ratios of Ti on the catalyst surface. The results are shown in Table 1. The atomic ratios of Ti 2p were 19.10%, 17.77%, 18.16%, and 18.26%, respectively. The smaller the atomic ratio of Ti 2p was, the greater the amount of carbon-based intermediates that were deposited onto the surface of the sample. These results indicate

Fig. 7. GC-MS spectra of the exhausted gases of NTP + UV (a) and NTP + PCO (b) processes.

Table 1

XPS analysis results (atomic ratio of Ti of the four samples).

Atomic %	Pure TiO ₂	PCO-TiO ₂	Combined-TiO ₂	Treated-TiO ₂
Ti 2p	19.10	17.77	18.16	18.26

that some carbon-based intermediates were deposited onto the TiO₂ during the PCO and combined NTP + PCO processes. The deposition of carbon-based intermediates during the PCO process was more severe. During the combined NTP + PCO process, fewer intermediates were deposited onto the photocatalyst surface, whereas the atomic ratio of Ti 2p of the treated-TiO₂ was greater than that of PCO-TiO₂ and combined-TiO₂, indicating that carbon-based intermediates on the catalyst were decomposed to a certain degree. These results are consistent with previous research [26].

3.4.2. Analysis of TPD-MS

Previous studies have reported that benzaldehyde, benzyl alcohol, benzoic acid, benzene, phenol, and acetone are the most common intermediates in the photocatalytic oxidation of toluene [30,35,36,45,46]. To determine the specific species deposited on the surface of a photocatalyst, TPD-MS was adopted for a semi-quantitative analysis to test the amounts of the above compounds. The above four samples were analyzed, the results of which are shown in Fig. 9.

Fig. 9(a) shows that the compounds were not present on the surface of the pure TiO₂. Fig. 9(b) indicates that benzene and acetone were the main intermediates deposited onto the surface of TiO₂ during the PCO process, whereas toluene, phenol, benzaldehyde, benzyl alcohol, and benzoic acid were scarcely detected. This indicates that intermediates such as benzene and acetone ultimately accumulated on the surface of the TiO₂. Fig. 9(c) showed that the peaks of benzene and acetone decreased significantly compared with that of PCO-TiO₂, revealing that smaller amounts of benzene and acetone were accumulated on TiO₂ during the combined NTP + PCO process. Fig. 9(d) shows that the amounts of benzene and acetone were further decreased during the treatment process, demonstrating that the intermediates on TiO₂ can be decomposed during the NTP and UV-irradiation processes.

3.5. Role of ozone

During the combined NTP + PCO process, the degradation reaction took place separately within the plasma and photocatalytic regions. The free radical species generated in the plasma region had a short life expectancy. Only the by-product

of O₃ was able to cover the plasma and photocatalytic regions. Thus, it can be concluded that ozone had a significant contribution to the synergetic effect of NTP and PCO for the enhancement of the toluene removal efficiency, the selectivity of CO_x, and the rate of mineralization. There are two prevailing ideas explaining the contribution of ozone [24,26,30,38].

As the first idea, ozone might be decomposed through the absorption of photons in the following pathway:

here, O• is generally regarded as an intermediate highly active oxygen species formed from the catalytic and photolysis decomposition of ozone. It acts as a strong oxidant during the photocatalytic oxidation process. Some studies have reported that O•, acting as a strong oxidant, is beneficial for the photocatalytic oxidation of toluene [23,30].

As the second idea, ozone might act as an electron acceptor during the photocatalytic process through the following pathway:

The most important aspect is that the electron affinity of O₃ (2.1 eV) is much higher than that of O₂ (0.44 eV) [21,28]. Therefore, the electrons in the conduction band of TiO₂ activated by UV light are easier to be captured by O₃, and promote the formation of the highly oxidizing species O^{•−}. The process can also decrease the recombination rate of the electron-hole pairs by scavenging photo-induced electrons, thereby accelerating the generation rate of hydroxyl radicals [21,24,30]. The reactions might take the following pathway:

The first idea considered above may be supported by the results of the NTP-assisted photolysis. When ozone absorbs photons and produces the active species of O•, O• can directly participate in the oxidation of toluene during the gas phase. The second idea may be supported based on the results of the combined NTP + PCO process. When the separated electrons are captured by ozone, more hydroxyl radicals are generated on the surface of TiO₂ and participate in the oxidation of toluene. The above comparison indicates that the second idea appears to be more important. The contribution of ozone during photocatalytic oxidation is mainly as an electron acceptor and scavenger.

Based on a comparison of the degradation performance of different combined processes, it was concluded that the contribution of ozone in the combined NTP + PCO process was mainly its participation in the photocatalytic oxidation and its acting as an electron acceptor and scavenger, generating more hydroxyl radicals and reducing the recombination rate of electron-hole pairs. Only a small amount of ozone took part in the photolytic oxidation. The process can be described in Fig. 10.

4. Conclusions

In this study, the combined NTP + PCO process was used for

Fig. 8. Apparent colors of the samples.

Fig. 9. TPD-MS spectra of the four samples.

the degradation of gas-phase toluene, and the degradation performances of sole (O_3 , UV, NTP, and PCO) and combined (O_3 + TiO_2 , O_3 + UV, NTP + UV, O_3 + PCO, and NTP + PCO) processes were all investigated to discover the synergetic effect between NTP and PCO.

Through a combination of NTP and PCO, a significant synergetic effect was obtained on the toluene removal efficiency, selectivity of CO_x , mineralization rate, ozone utilization efficiency, and the generation of by-products. The toluene removal efficiency of the combined NTP + PCO process was 80.2%, which was much greater than that of NTP (18.8%) and PCO (13.4%) alone. Furthermore, the mineralization rate, selectivity of CO_x , and ozone utilization efficiency were 83.8%, 96.2%, and 90.1%, which were also significantly greater than those in the sole processes of NTP or PCO. The results of FT-IR and GC-MS

indicated that by-products in the gas phase were dramatically reduced and that the mineralization rate was significantly improved during the combined NTP + PCO process. Additionally, the combined NTP + PCO process can dramatically reduce the amount of carbon-based intermediates on TiO_2 surface, such as benzene and acetone. It was also verified that the coexistence of UV-irradiation, ozone, and a catalyst can decrease the amount of carbon-based intermediates adsorbed on the catalyst surface. These results indicate that the emergence of ozone had a significant contribution to the performance enhancement, and was most likely to act as an electron acceptor and scavenger, generating more hydroxyl radicals and reducing the recombination rate of the electron-hole pairs.

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Fig. 10. Role of ozone in the combined NTP + PCO process.

Graphical Abstract

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Synergetic effect between non-thermal plasma and photocatalytic oxidation on the degradation of gas-phase toluene: Role of ozone

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During the combined NTP + PCO process, ozone mainly acted as an electron acceptor and scavenger, generating more hydroxyl radicals and reducing the recombination of electron-hole pairs.

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低温等离子体组合光催化氧化降解气相甲苯的协同效应：臭氧的作用

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摘要: 挥发性有机物(VOCs)是导致大气污染的重要成因, 它不仅会直接威胁到人体健康和生态环境, 而且是PM_{2.5}、臭氧和光化学烟雾的重要前驱体。近年来, 低温等离子体(NTP)技术与光催化氧化(PCO)技术等被视作降解VOCs的有效技术而得到广泛关注。NTP技术的停留时间短, 能耗低, 对于VOCs的降解具有较高的效率, 但是其矿化率较低, 而且会产生臭氧等副产物。PCO技术能够通过羟基自由基将VOCs完全氧化为CO₂和H₂O, 但是受限于低量子效率, 电子空穴对的快速复合以及光催化剂的失活。因此, 将NTP与PCO相结合是提升VOCs的去除率和矿化率, 降低副产物产量的有效策略。

本文以甲苯为VOCs的典型物, TiO₂为光催化剂, 采用NTP与PCO的组合工艺降解气相甲苯。为了探索NTP与PCO之间的协同效应, 我们对单一工艺(O₃, UV, NTP, PCO)与组合工艺(O₃ + TiO₂, O₃ + UV, NTP + UV, O₃ + PCO, NTP + PCO)在甲苯去除率、CO与CO₂选择性、臭氧利用率以及副产物的产生等方面的性能进行了深入考察。结果表明, NTP与PCO组合工艺的甲苯去除率为80.2%, 远高于单一工艺中NTP的18.8%和PCO的13.4%, 同时也明显高于其他组合工艺。此外, NTP与PCO组合工艺的CO₂选择性、矿化率和臭氧利用率也是所有工艺中最优的。傅里叶透射红外光谱和气相色谱-质谱联用结果表明, 气相中副产物的产量显著减少; X射线光电子能谱和程序升温脱附-质谱联用的结果表明, 吸附于催化剂表面的碳基中间产物的含量也显著下降。结果证明了NTP与PCO两者存在着协同效应, 且只有在臭氧、紫外光源和光催化剂三者均存在的情况下才能表现出上述的优异性能。综上, NTP与PCO组合工艺中所展现的协同效应主要归功于NTP中产生的臭氧在PCO中获得有效利用。在这个过程中, 臭氧最重要的作用是充当了电子接收剂和牺牲剂, 因而能够产生更多的羟基自由基并降低电子-空穴对的复合, 从而提升甲苯去除率、CO₂选择性、矿化率和臭氧利用率, 并且降低副产物的含量。

关键词: 低温等离子体; 光催化氧化; 协同效应; 臭氧; 甲苯

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