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<th>Title</th>
<th>Abatement of toluene in the plasma-driven catalysis: Mechanism and reaction kinetics</th>
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Abstract—The mechanism and reaction kinetics of toluene destruction in a plasma-driven catalysis (PDC) system were studied. The results show that the toluene removal efficiency (TRE) is greatly increased while the level of O\textsubscript{3} by-product is significantly reduced in PDC as compared with that in nonthermal plasma (NTP). The rate constant of toluene destruction in the PDC is more than twice than that in NTP. Among the multiple reactive species responsible for toluene destruction in the PDC, hydroxyl radicals (•OH) had a small contribution, whereas energetic electrons and atomic oxygen (O) were the most important. The enhanced performance of toluene destruction by PDC was mainly due to greater amounts of O formed during the process. The catalysts improved toluene destruction by catalytic decomposition of O\textsubscript{3} and generation of O. Essentially, better toluene abatement can be achieved by focusing on the increased energy density and improved performance of the catalyst for O\textsubscript{3} decomposition.

Index Terms—Mechanism, nonthermal plasma (NTP), ozone catalytic decomposition, plasma-driven catalysis (PDC), reaction kinetics.

I. INTRODUCTION

THE EMISSION of volatile organic compounds (VOCs) from various industrial and automobile sources is harmful to both human health and the global environment [1], [2]. Plasma-driven catalysis (PDC) has attracted much attention over the past few decades for its capacity to degrade VOCs [3]–[5]. This technique combines the advantages of high selectivity from catalysis and fast ignition/response from the plasma technique [4]. It is a promising technology with high energy efficiency and mineralization rate and low by-product formation [6], [7]. In nonthermal plasma (NTP) systems, many reactive species, such as energetic electrons, ions, ozone, hydroxyl radicals (•OH), and atomic oxygen (O), are involved in destroying pollutants [8]. The PDC system has characteristics of both NTP and catalysis: A homogeneous reaction in the gaseous phase and a heterogeneous reaction on the catalysts coexist in this system. To date, reports on PDC mainly focus on the increase in energy and removal efficiencies [2], [3]. However, few studies have been conducted to investigate the destruction mechanism in PDC due to the complexity of the system and the difficulty in detecting energetic electrons and radicals. Specifically, two important questions should be addressed to characterize the mechanism in PDC. First, what are the dominant species responsible for the abatement of pollutants? Studying all of the reactive species is a difficult task; the dominant reactive that make the greatest contribution to pollutant removal should be identified. Second, how does the catalyst enhance the performance of the system? Catalysts can greatly improve both the energy efficiency of the process and the efficiency of pollutant removal, but the mechanism of this process is not well understood.

This paper aims to address these questions. The mechanism and reaction kinetics of toluene destruction in a PDC system were studied. The contribution of reactive radicals, such as energetic electrons, •OH, and O, was evaluated. Mechanisms for enhanced toluene destruction in PDC were investigated. To our best knowledge, this is the first study that identifies the contribution of dominant oxidants responsible for toluene abatement in PDC. Additionally, it provides insight into the mechanism of toluene destruction by PDC and a valuable basis for the improvement and application of the PDC process.

II. EXPERIMENTAL SECTION

The experimental setup and the preparation of TiO\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3}/nickel foam were described in the previous study [9]. TiO\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3}/nickel foam was placed in a plasma or post-plasma area to carry out the PDC and plasma-assisted catalysis (PAC) process, respectively. The experiment was carried out at room temperature and atmospheric pressure.

The air flow rate, initial toluene concentration, and water vapor content at the inlet of the reactor were 0.2 L/min, 50 ppm, and 1wt%, respectively. Gas samples from the outlet were analyzed online by a gas chromatograph (GC, Kechuang Chromatograph, GC-900A) equipped with two FID detectors. One detector was for organic compound detection with a 50-m SE-30 capillary column (80 °C), and the other, equipped with a methanizer, was for carbon monoxide and carbon dioxide analysis using a 2-m carbon molecular sieve stainless-steel column (65 °C). Air samples from the DBD reactor were collected by Summa Canisters and analyzed by a GC-MS (5973N, Agilent) with an HP-5MS capillary column (Agilent, USA). The O\textsubscript{3} concentration was monitored by an ozone analyzer (Lida Instrument, DCS-1).

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III. RESULTS AND DISCUSSION

A. Effect of the Catalyst

Fig. 1(a) shows the comparison of the toluene removal efficiency (TRE) of NTP to that of PDC in the air stream. With the increase of energy density from 61 to 1527 J/L, the TRE correspondingly increased from 17% to 74% in NTP alone, while it increased from 20.5% to 94% in the PDC. The combination of the catalyst with NTP significantly improved the TRE in the air stream. However, the TREs of NTP and PDC were almost the same in the N₂ stream, as shown in Fig. 1(b). Based on a comparison of Fig. 1(a) and (b), the catalyst enhanced the toluene abatement only in the presence of oxygen. Although oxygen cannot directly oxidize toluene in this system, it can be ionized by energetic electrons and form O₃. As shown in Fig. 2, the O₃ concentration in air stream containing toluene increased from 21 to 165 ppm, with an increase of energy density from 61 to 1527 J/L in NTP. Clearly, O₃ is a strong oxidant and can be catalytically decomposed. Its concentration was greatly reduced while being decomposed by the catalysts. Accordingly, O₃ could not be completely removed, and some O₃ would be left behind in the effluent. It also can be observed from Fig. 2 that the outlet O₃ concentration was further dropped in PAC as compared with PDC. O₃ formed in the discharge process could be nearly decomposed by the catalysts, while no O₃ was generated in the postplasma. Therefore, the outlet O₃ in PAC is much less than that in PDC. PAC is more efficient for the reduction of O₃ pollution as compared with PDC.

The processes for O₃ catalytic decomposition are described as follows [10]–[12]:

\[
\begin{align*}
O_3 + ^* &\rightarrow O^+ + O_2 \\
O^+ + O_3 &\rightarrow O_2 + O^+ \\
O_2^2 &\rightarrow O_2 + ^*
\end{align*}
\]

where * denotes an active site on the catalyst’s surface.

The formed O can efficiently oxidize toluene and accordingly improve the TRE of PDC. Both energetic electrons and O are the main reactive species responsible for toluene destruction in the air stream, whereas only the former is mainly responsible for toluene destruction in the N₂ stream. As the catalyst is combined with NTP, more pathways and radicals are available for toluene destruction. The number of reactive species can be greatly increased in the presence of catalysts. Therefore, PDC performed better in terms of toluene abatement than NTP alone in the air stream.

Chen et al. [4] suggested that the enhanced performance of the PDC is possibly attributed to the adsorption of the pollutant on the catalyst’s surface. If the catalyst has a significant adsorption capacity, the pollutant retention time would be prolonged and the pollutant concentration in the plasma zone would be increased. Although the TiO₂/γ-Al₂O₃/nickel foam catalyst has a good adsorption capacity, it did not significantly improve toluene abatement in the N₂ stream [see Fig. 1(b)]. Perhaps, the catalyst has a poor adsorption capacity at high voltages because the adsorption of the molecular pollutants would be inhibited by the polarized surface of the catalyst. Observations indicate that pollutants that were absorbed on the catalyst before the discharge could be desorbed during the discharge.
B. Contribution of Radical Species

PDC is a very complicated system. Several radical species, such as energetic electrons, O, and •OH, are responsible for breaking down pollutants. Both energetic electrons and •OH are generally considered as important radicals [13], whereas O has not gotten as much attention in the PDC.

1) Energetic Electrons: As shown in Fig. 1(a), the TRE increased with an increase in energy density in both NTP and PDC processes. Clearly, the increase in energy density improves the formation and energy of energetic electrons. Toluene destruction that occurs in NTP was mainly attributed to the impact of energetic electrons and radical attacks [14], [15]. The mean energy of electrons generally ranges from 1 to 10 eV [10], [16]. The bond energies of the C-H in the methyl group, the C-H in the aromatic ring, the C-C in the methyl group, the C-C in the aromatic ring, and the C = C in the aromatic ring of toluene are 3.7, 4.3, 4.4, 5.0–5.3, and 5.5 eV, respectively [14]. Therefore, the aromatic ring of toluene can be easily broken by energetic electrons.

To clarify the contribution of energetic electrons to toluene destruction, the effect of O and •OH should be excluded. Only energetic electrons were responsible for toluene destruction in the dry N₂ stream. As shown in Fig. 1(b), the TRE in NTP alone correspondingly increased from 44.4% to 87.4% with the increase in energy density from 434 to 2240 J/L. This result also proved that energetic electrons could effectively break down toluene and played an important role in toluene abatement in the PDC.

2) O: As previously mentioned, O₃ can be catalytically decomposed into O, which is possibly responsible for the increased TRE in the PDC. The O can also be generated from oxygen activation by energetic electrons in addition to the O₃ catalytic decomposition [17]

\[ e + O₂ \rightarrow e + 2O \].

The reaction occurs in both the NTP and PDC processes. The generation rate of O can be greatly accelerated due to O₃ catalytic decomposition.

To further prove the effect of O generated from O₃ catalytic decomposition, the catalyst was combined in the postplasma instead of in the plasma. The reactive species, except O₃, vanish quickly due to their short lifespan in the postplasma [2]. The O₃ concentrations at the inlet and outlet of the postplasma reactor are equal in NTP. They ranged from 24 to 167 ppm with an increase in energy density from 61 to 1527 J/L, as shown in Fig. 2. As shown in Fig. 3, the TRE in the process with the catalyst in the postplasma was increased by a maximum of 38%, compared with that in NTP alone. Toluene destruction in the latter occurred in two stages. Toluene was primarily broken down by energetic electrons and reactive species in the NTP stage. The unreacted toluene and O₃ entered the postplasma stage, in which the remaining toluene was further destroyed by catalytic ozonation [2]. O₃ can be catalytically decomposed into highly active O in this stage [2], [11]. Therefore, the O₃ concentration in the postplasma stage was consequently reduced, as seen in Fig. 2. Compared with NTP alone, O₃ concentration in the PDC was greatly decreased. Moreover, the resulting O can be further involved in toluene oxidation. Thus, the process with the catalyst in the postplasma had the greatest TRE. The TRE was closely related to the level of O₃ decomposition. The effect of O₃ catalytic decomposition in PDC was similar to that in the postplasma process. The O that was generated from O₃ catalytic decomposition played an important role in toluene destruction in the PDC. This assertion is in agreement with the viewpoint of other researchers [7], [18], [19]. As shown in Fig. 1(b), the TREs in the NTP and PDC processes are similar in the N₂ stream, which also prove the importance of O.

3) •OH: Detecting of •OH in the PDC system is difficult due to its short lifespan and the reaction conditions of high voltage. The •OH concentration can be controlled via the change of reaction conditions, including the air humidity and the catalysts. Thus, the effect of •OH can be clarified.

Clearly, water is essential for •OH formation.

\[ e + H₂O \rightarrow e + •OH + H \] (5)

\[ O(^{1}D) + H₂O \rightarrow 2 •OH \].

Higher humidity should be beneficial to •OH formation and thus improve the TRE if •OH were to play an important role in toluene destruction in the PDC. However, the TRE decreased from 80% to 52% with increased water vapor content from 0% to 2% (see Fig. 4). The result proved that •OH contributed little to toluene destruction. Water vapor has a negative effect
on toluene decomposition since it prevents the adsorption of toluene on the catalyst due to competitive adsorption [20]. It can also deactivate energetic electrons and poison catalytic active sites [21], [22]. In addition, increased humidity is harmful to O₃ decomposition [23]. As demonstrated previously, the O generated from O₃ catalytic decomposition is very important to toluene oxidation in the PDC system. In addition, O₃ can also act as an •OH scavenger [24]

\[ \cdot \text{OH} + \text{O}_3 \rightarrow \text{O}_2 + \text{H}_2\text{O}. \] (7)

Therefore, the •OH concentration would be limited, indicating that •OH could not make a great contribution to toluene destruction in the PDC.

In summary, among the multiple reactive species responsible for toluene destruction in the PDC, •OH had a small contribution, whereas energetic electrons and O were the most important. The enhanced performance of toluene destruction by PDC was mainly due to the greater amounts of O formed during the process.

C. Reaction Kinetics

Possible pathways for pollutant destruction in the PDC mainly include the following: 1) electron impacts; 2) ion collisions; 3) gas-phase radical attacks, such as •OH and O; and 4) O₃ [2], [6], [10], [15]. Determining the reaction rates of toluene destruction with each radical is difficult since radicals, the intermediates, and their concentrations during destruction can hardly be detected. However, we can identify the predominant steps during toluene destruction by estimating the reaction rates of radicals.

Previous studies reported that toluene destruction in the NTP and PDC process could be described by first-order reactions [25]. The kinetic equation of toluene destruction can be expressed as follows:

\[ \frac{d[C]}{dt} = (k_e[e] + k_{\text{ion}}[\text{ion}] + k_{\text{O}_3}[\text{O}_3] + k_e[O] + k_{\text{OH}}[\text{OH}])[C] \] (8)

where \([C], [e], [\text{ion}], [\text{O}_3], [O], \) and \([\text{OH}]\) represent the concentrations of toluene, electrons, ions, O₃, O, and •OH, respectively, and \(k_e, k_{\text{ion}}, k_o, k_{\text{O}_3}, \) and \(k_{\text{OH}}\) represent the rate constants of toluene destruction with the corresponding radicals, respectively.

The reaction equations and rate constants of electrons, ions, O₃, O, and •OH with toluene are as follows [26]:

\[ \text{C}_6\text{H}_5 + \text{CH}_3 + e \rightarrow \text{C}_6\text{H}_3 + \text{H}_2\text{O} \] (9)

\[ \text{C}_6\text{H}_5 + \text{CH}_3 + \text{O}_3 \rightarrow \text{C}_6\text{H}_3 + \text{H}_2\text{O} \] (10)

\[ \cdot \text{OH} + \text{O}_3 \rightarrow \text{O}_2 + \text{H}_2\text{O}. \] (11)

\[ \text{C}_6\text{H}_5 \cdot \text{CH}_3 + \text{O} \rightarrow \text{C}_6\text{H}_5 \cdot \text{CH}_2\text{O} + \text{H} \rightarrow \text{Products} \]

\[ k_o = 2.2 \times 10^{-14} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \] (12)

\[ \text{C}_6\text{H}_5 + \cdot \text{OH} \rightarrow \text{C}_6\text{H}_5 \cdot \text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{Products} \]

\[ k_{\text{OH}} \approx 7 \times 10^{-13} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}. \] (13)

Among the energetic species, the concentration of ions is approximately equal to that of electrons [15]; however, its rate constant \((\sim 1.5 \times 10^{-10} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1})\) is much smaller than that of electrons \((\sim 1 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1})\). The direct attack of O₃ on toluene can be ruled out in the PDC [5], [19]. Thus, the effect of ions and O₃ on toluene abatement can be ignored due to their small reaction constants. The rate constant of •OH \((\sim 7 \times 10^{-13} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1})\) is larger than that of O \((\sim 2.2 \times 10^{-14} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1})\) [15], while its concentration \((\sim 5 \times 10^{12} \text{ cm}^3)\) is much smaller than that of O \((\sim 2 \times 10^{18} \text{ cm}^3)\) [27]. Consequently, the effect of •OH on toluene abatement can also be considered negligible. Thus, energetic electrons and O are the main radicals responsible for toluene destruction. Accordingly, (8) can be simplified as

\[ - \frac{d[C]}{dt} = \{k_e[e] + k_o[O]\} [C]. \] (14)

Therefore, the TRE is mostly determined by the \([e]\) and \([O]\). \([e]\) is mostly decided by the energy density, while \([O]\) mainly depends upon the O₃ concentration and the performance of the catalyst in terms of O₃ decomposition. The O₃ concentration is also determined by the energy density. Thus, the TRE can be improved in two ways. One is to increase the energy density for generating more energetic electrons and O₃. The increased energy density can improve the TRE, which is shown in Fig. 1. The other way is to increase the generation rate of \(O\) by improving the performance of the catalyst in terms of O₃ decomposition. The improvement of catalysts regarding this aspect will be addressed in future research.

Toluene destruction occurs in multiple steps, including H-abstraction, rupture of the C-C in the methyl group, and the breaking of the aromatic ring, all of which results in intermediates with small molecular fragments. The trace hydrocarbon intermediates identified by GC-MS in the PDC included acetic acid, formic acid, benzene, and benzaldehyde. The intermediates are further oxidized by oxidants and finally oxidized to COₓ (CO₂ and CO) with selectivity close to 100%. Toluene destruction by energetic electrons and O are inseparable and cooperative due to their coexistence in the PDC.

The concentration of electrons and O is constant under conditions of identical electric field and air pressure. Equation (14) can be simplified as

\[ - \frac{d[C]}{dt} = k_e[e] [C]. \] (15)

where \(k_e \) \((= k_e[e] + k_o[O])\) is defined as the apparent rate constant, in per second.

Integrating (15) (integral boundary conditions: \(C = [C_0]\), \(t = 0\), and \(C_0\) is the inlet toluene concentration) results in

\[ \text{C}_6\text{H}_5 \cdot \text{CH}_3 + \text{O} \rightarrow \text{C}_6\text{H}_5 \cdot \text{CH}_2\text{O} + \text{H} \rightarrow \text{Products} \]

\[ k_o = 2.2 \times 10^{-14} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \] (12)

\[ \text{C}_6\text{H}_5 + \cdot \text{OH} \rightarrow \text{C}_6\text{H}_5 \cdot \text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{Products} \]

\[ k_{\text{OH}} \approx 7 \times 10^{-13} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}. \] (13)
TABLE I

<table>
<thead>
<tr>
<th>Air-flow rate (L/min)</th>
<th>retention time (s)</th>
<th>NTP</th>
<th>PDC</th>
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<td>TRE, η (%)</td>
<td>-ln(1-η)</td>
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<tr>
<td>0.2</td>
<td>10</td>
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</tbody>
</table>

Fig. 5. Rate constants of toluene destruction in the NTP and PDC processes.

the following:

\[
-ln \left( \frac{C}{C_0} \right) = k_s t. \tag{16}
\]

According to the definition of \( \eta = \frac{C_0}{C} \) (TRE)

\[
\eta = 1 - \frac{C}{C_0}. \tag{17}
\]

Substituting (17) into (16) and rearranging the resulting equation creates the following:

\[
-ln(1-\eta) = k_s t. \tag{18}
\]

To calculate the reaction rate constant, TRE (\( \eta \)) was measured at a series of residence times, as shown in Table I. The term \( -ln(1-\eta) \) is worked out in Table I.

Based on the data in Table I, the rate constants for toluene destruction in the NTP and PDC processes can be determined, as shown in Fig. 5. The slopes of the lines are the apparent rate constants \( k_s \), which were 0.425 and 0.198 s\(^{-1}\) in NTP and PDC, respectively. The rate constant in the PDC is much greater than that of NTP, indicating that the catalyst can significantly improve toluene destruction.

IV. CONCLUSION

As compared to NTP, the TRE is greatly increased while the amount of \( \text{O}_3 \) by-product is significantly reduced in the PDC system. The rate constant of toluene destruction in the PDC is more than twice that in NTP. Among the multiple reactive species responsible for toluene destruction by PDC, energetic electrons and \( \text{O} \) were the most important, while the contribution of \( \bullet \text{OH} \) is small. The enhanced performance of toluene destruction by PDC is mainly attributed to the \( \text{O} \) formed in the process. The catalysts improved toluene destruction via \( \text{O}_3 \) catalytic ozonation. The increased energy density and improved performance of the catalyst for \( \text{O}_3 \) decomposition should be considered as means to achieve better toluene abatement.

REFERENCES


