



Effects of humidity on the plasma-catalytic removal of low-concentration BTX in air

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ABSTRACT

Effects of relative humidity (30%, 50% and 80% RH) on the removal of low-concentration benzene, toluene and *p*-xylene (BTX mixture) in air by non-thermal plasma (NTP) and the combination of NTP and MnO_x/Al₂O₃ catalyst (CPC) were systematically investigated in a link tooth wheel-cylinder plasma reactor. A long-term (150 h) CPC experiment under 30% RH was also conducted to investigate the stability of the catalyst. Results show that increasing humidity inhibits the O₃ production in plasma and its decomposition over the catalyst. As for BTX conversion, increasing humidity suppresses the benzene conversion by both NTP and CPC; although higher humidity slightly promotes the toluene conversion by NTP, it negatively influences that by CPC; while the conversion of *p*-xylene by both NTP and CPC is insensitive to the humidity levels. Irrespective of the RH, the introduction of MnO_x/Al₂O₃ catalyst significantly promotes BTX conversion and improves the energy efficiency. On the other hand, CPC under 30% RH shows the best performance towards CO_x formation during BTX oxidation processes. However, for a specific input energy of 10 J L⁻¹ in this study, organic intermediates generated and accumulated over the catalyst surface, resulting in a slight deactivation of the MnO_x/Al₂O₃ catalyst after 150-h reactions.

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1. Introduction

Low-concentration volatile organic compounds (VOCs) in indoor environments, mainly including benzene, toluene and xylenes (BTX) [1–3], have been correlated to adverse health effects such as allergic reactions; headache; eye, nose or throat irritation; dry cough; dizziness and nausea; tiredness and even cancer [4,5]. As a result of “sick building syndrome”, the productivity in offices decreases by 6.5% in average [6].

A combined technique of non-thermal plasma (NTP) and heterogeneous catalysis appears to be the best choice for indoor VOCs purification due to the synergetic effects between NTP and catalysts at room temperature [7–10]. During our previous study [9], a combined plasma catalysis (CPC) system was constructed by introducing MnO_x/Al₂O₃ catalyst after the discharge zone of a link tooth wheel-cylinder plasma reactor for removal of low-concentration BTX in air, with a relative humidity (RH) of 25%. Compared with values obtained by NTP alone, BTX conversion, energy efficiency (EE), CO₂ yield and O₃ reduction were significantly improved in CPC configuration. And newly formed active oxygen species from catalytic decomposition of O₃ were considered to be mainly responsible for the promotion effects [11].

On the other hand, indoor environments have variable humidity levels. For example, Maki and Aoki [12] measured humidity ranging from 38% to 78% in reinforced-concrete-building rooms. For practical applications, the effects of humidity on indoor VOC removal must be considered. To our knowledge, however, only Van Durme et al. [7,13] have reported that humidity has adverse effects on the plasma-catalytic removal of toluene from indoor air, with Cu–Mn/TiO₂ or Pd/Al₂O₃ as the catalyst.

In the present study, the effects of humidity on the removal of low-concentration BTX (mixture of benzene, toluene and *p*-xylene) in air were systematically investigated based on the previously constructed NTP and CPC systems [9]. The effects of RH (30%, 50% and 80%) on O₃ production and catalytic decomposition, BTX conversion, EE concerning BTX conversion, and CO_x (CO + CO₂) formation were investigated. Besides, a long-term (150 h) CPC experiment under 30% RH was also conducted to investigate the stability of the MnO_x/Al₂O₃ catalyst. And in order to better understand the observed deactivation result, organic products accumulated over the used catalyst were analyzed by FT-IR method and research on regeneration of the catalyst was conducted.

2. Experimental

2.1. Experimental setup

The experimental system consists of a link tooth wheel-cylinder plasma reactor with a 25 kV/5 mA positive DC high voltage

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power supply, reaction gas supply and analytical instrumentation. $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalyst was introduced downstream of the discharge zone. Details of the experimental setup can be found in Fan et al. [9]. Nevertheless, it should be noticed that the number of discharge teeth wheels was reduced to 5 in this study, resulting in an effective discharge length of only 45 mm.

2.2. Experimental methods

The details of the experimental methods are well described in the previous work [9], and only brief description is given here. Reaction gas containing 470-ppb benzene, 810-ppb toluene, 730-ppb *p*-xylene and a certain content of water vapor was prepared by passing synthetic air through two temperature-controlled bubble towers, containing BTX (liquid mixture) and water, respectively. Gas flow rates were controlled with a set of mass flow controllers. The total gas flow rate was 6.0 L min^{-1} , resulting in the residence time in the discharge zone of 0.6 s. RH of the reaction gas was adjusted to 30%, 50% or 80% by changing the temperature of the water bubble tower. All manipulations were carried out at room temperature and atmospheric pressure.

On the other hand, $\text{MnO}_x/\text{Al}_2\text{O}_3$ (5 wt.% Mn, 2.5–3.5 mm in diameter) prepared by the impregnation method was used as the catalyst in this study. Loading amount of the catalyst was 15.0 g, with the residence time in the catalyst bed being around 0.21 s. When the catalyst was introduced, the reaction was started by energizing the reactor with DC only when the concentrations of BTX at the outlet reached a steady state, meaning that initial adsorption–desorption equilibrium of BTX over the catalyst surface was achieved. Moreover, all the data shown in this work were recorded after the stable state was reached for given condition.

BTX concentrations were analyzed using an Agilent HP-6890N GC (USA), equipped with an FID and a 30-m HP-5 capillary column. The conversion of BTX is calculated based on the inlet and outlet concentrations of BTX. The outlet concentrations of CO and CO_2 were detected by infrared CO and CO_2 analyzers (Shanghai Yingsheng EN-308, China), and the yields of CO_2 (Y_{CO_2}) and CO_x (Y_{CO_x}) were adopted to characterize the oxidation and mineralization degrees of BTX, respectively. O_3 outlet concentrations were determined by the indigo disulphonate spectrophotometric method. Temperature and humidity monitoring was conducted with a SMART SENSOR AR837 device (Hong Kong). As for energy consumption evaluation, specific input energy (SIE, J L^{-1}) and EE (g kWh^{-1}) were selected to value the power deposited into 1 L of reaction gas and the decomposed amounts of BTX per 1 kWh of energy consumption, respectively. Besides, organic compounds over the used catalyst surface were determined by an FT-IR spectrometer (AVATAR360, USA) with the resolution of 4 cm^{-1} at room temperature.

3. Results and discussion

3.1. Effects of humidity on O_3 production and catalytic decomposition

O_3 concentrations at the NTP and CPC outlets were measured in both the presence (Fig. 1) and absence (data are not shown) of BTX in air in this study. Results prove that low levels of BTX in the gas stream hardly influence the O_3 production in NTP and the catalytic O_3 decomposition by CPC. However, measurements show a decrease of O_3 production with increasing humidity (Fig. 1a). For an SIE of 10 J L^{-1} , O_3 concentration at the NTP outlet was 30.0 ppm for 30% RH, while this decreased to 27.3 ppm for 50% RH and 15.1 ppm for 80% RH. O_3 formation mechanisms research showed

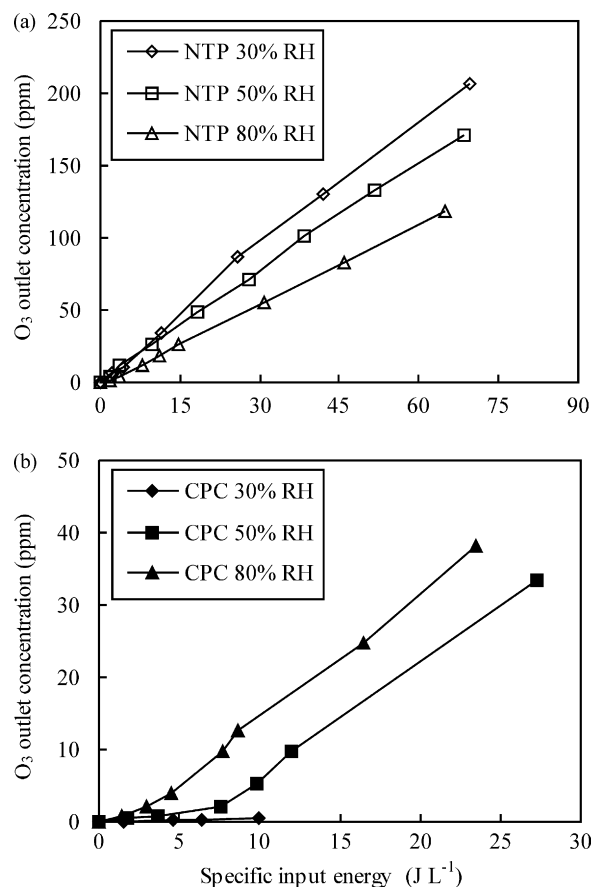


Fig. 1. Effects of humidity on O_3 outlet concentration as functions of specific input energy: (a) NTP and (b) CPC.

that the reduction of O_3 production in humid air could be primarily attributed to the removal of $\bullet\text{O}$ by H_2O [14].

On the other hand, Fig. 1b shows that increasing humidity negatively influences the catalytic O_3 decomposition. For 30%, 50% and 80% RH, O_3 concentrations at the CPC outlet under an SIE of 10 J L^{-1} were 0.6, 5.3 and 14.9 ppm, respectively. This means that 29.4, 22.0 and 0.2 ppm of O_3 were catalytically decomposed at RH of 30%, 50% and 80%, respectively. Considering that O_3 decomposition over the $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalyst begins with dissociative adsorption of O_3 over a surface site [15,16], the decrease in O_3 decomposition under higher humidity can be ascribed to the competitive adsorption of water over the catalyst surface since the $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalyst is hydrophilic. Rakitskaya et al. [17] also proved that the catalysts with increasing amounts of absorbed water showed decreasing activity in O_3 decomposition.

In addition, it is worth mentioning that outlet concentrations of NO and NO_2 were also measured with a Thermo Scientific model42i Chemiluminescent NO– NO_2 – NO_x analyzer (USA) in this work. Similar to the results shown in our previous paper [9], no NO was detected in NTP or CPC process and much lower amount of NO_2 was detected in CPC process as compared to NTP process. On the other hand, the outlet concentration of NO_2 decreased with increasing humidity in both NTP and CPC processes.

3.2. Effects of humidity on BTX conversion

Fig. 2 indicates the conversion profiles of BTX as functions of SIE for NTP and CPC configurations under 30%, 50% and 80% RH. It can be seen that BTX conversion by both NTP and CPC increased with the increase of SIE for all humidity levels, which can be easily

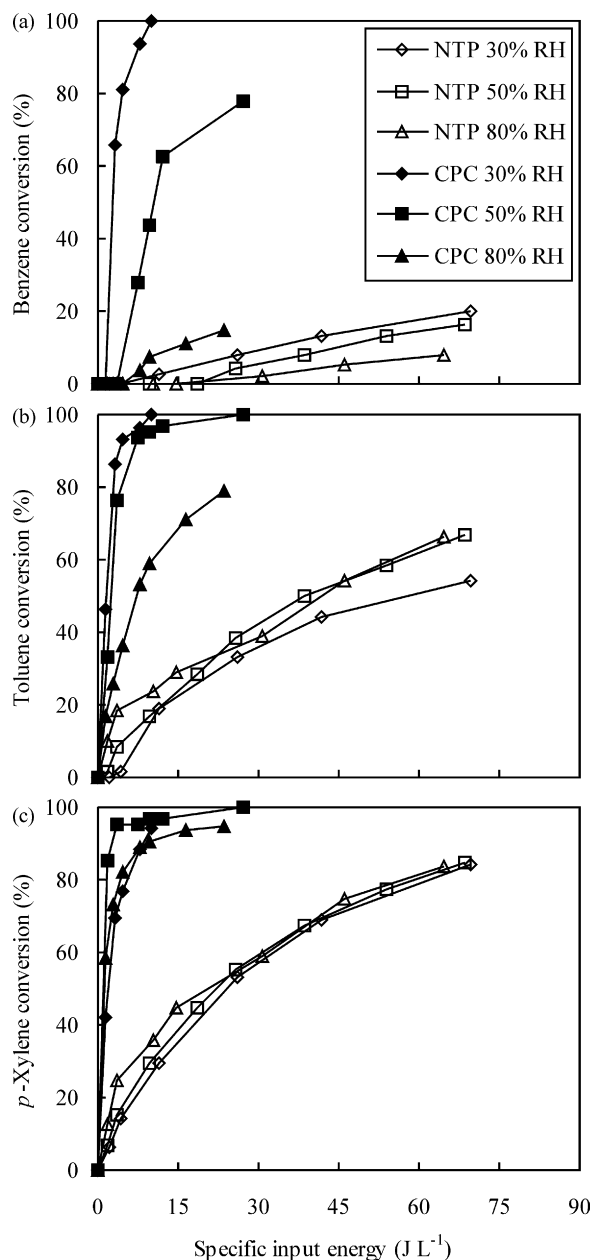


Fig. 2. Effects of humidity on BTX conversion by NTP and CPC as functions of specific input energy: (a) benzene, (b) toluene and (c) *p*-xylene.

ascribed to the increment of active species such as electrons, $\cdot\text{OH}$ and $\cdot\text{O}$ radicals due to the increased discharge power. Also it can be seen from Fig. 2 that the combination of $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalyst after plasma (CPC) significantly promoted BTX conversion, proving the importance of combined catalysis for BTX removal.

3.2.1. Effects of humidity on BTX conversion by NTP

Generally, VOCs can be removed by discharge plasma via two pathways including (a) direct electron attack and (b) indirect gas phase radical reactions (reactions between VOC molecules and gas phase radicals such as $\cdot\text{OH}$ and $\cdot\text{O}$). Therefore, humidity could affect the VOC conversion by NTP from the following two aspects. On one side, water molecules partially dissociate to form reactive species, such as $\cdot\text{OH}$ radicals, which are important in VOC oxidation [18–20]. On the other side, water negatively influences VOC removal due to its electronegative characteristics. In the presence of high-concentration water, increased plasma attachment processes

limit the electron density in the system and result in a reduced production of activated chemical species [19,21].

In this study, humidity proved to suppress benzene removal by NTP (Fig. 2a), being in agreement with the results obtained with a silent discharge plasma reactor [22]. It is unlikely that $\cdot\text{OH}$ radicals produced from water dissociation are responsible for the benzene removal. In fact, it is well known that benzene molecule is relatively stable with a close π -electron system. Breakage of the benzene ring by high energy electrons probably plays a key role in the NTP benzene removal process. As a result of decreased electron density with increasing RH, benzene conversion decreases. On the contrary, toluene conversion by NTP was slightly promoted by increasing RH from 30% to 50–80% (Fig. 2b), probably due to the enhanced production of $\cdot\text{OH}$ radicals, since the $\text{CH}_3\cdot$ substituent in toluene molecule can be more easily oxidized by radicals as compared to the benzene ring. In fact, toluene reaction kinetics research showed that $\cdot\text{OH}$ induced degradation is one of the most important pathways in toluene oxidation [19]. Despite this, *p*-xylene conversion by NTP was insensitive to water concentration in air (Fig. 2c). This result suggests that for NTP removal of *p*-xylene, the direct electron attack and indirect gas phase radical reaction pathways have equally important roles. A possible explanation is that *p*-xylene can be more easily attacked and decomposed by high energy electrons and active species due to its more vulnerable molecule structure, as compared with benzene and toluene [9]. In fact, results presented in Fig. 2 show that the BTX conversion by NTP alone was in the order of *p*-xylene > toluene > benzene for identical RH and SIE.

3.2.2. Effects of humidity on BTX conversion by CPC

Fig. 2a and b shows that increasing humidity has significantly adverse effects on the conversion of benzene and toluene by CPC. This can be partly ascribed to the decrease in catalytic O_3 decomposition under higher humidity (Fig. 1), since the amount of converted O_3 is directly correlated with the concentration of newly formed active oxygen species ($\cdot\text{O}$ and O_2^{2-}) over the catalyst surface. Another probable reason is that the competitive adsorption of water also inhibits the adsorption and consequently the catalytic decomposition of VOCs. Van Durme et al. [13] reported that the equilibrium adsorption constants (K) of VOCs strongly decreased with increasing humidity. In fact, evidence was also found during our CPC experiments under different humidity levels that the time for initial adsorption–desorption equilibrium of BTX over the catalyst surface was in the order of 30% RH \gg 50% RH > 80% RH. Water covers the surface of the catalyst [21] and poisons the catalyst by occupying the catalytic active sites [22], resulting in a decrease in the catalytic activity. Despite this, no significant difference in *p*-xylene conversion by CPC was observed among the investigated RH (Fig. 2c), indicating that not only the amount of newly formed active species determines the catalytic *p*-xylene conversion, and that the sites reactive for *p*-xylene might be less susceptible to water adsorption as compared with those for benzene and toluene.

Fig. 2 also shows that for CPC removal of benzene and toluene (Fig. 2a and b), the heterogeneous oxidation reactions are much more important than the homogeneous reactions under 30% and 50% RH while under 80% RH the homogeneous reactions become equally important; and that for CPC removal of *p*-xylene (Fig. 2c), the heterogeneous and homogeneous reactions are of the equivalent significance irrespective of the humidity levels. Moreover, the fact that increasing humidity promotes the toluene conversion by NTP but suppresses that by CPC strongly implies that the heterogeneous oxidation reactions do not follow the homogeneous patterns.

On the other hand, in order to better understand the effects of humidity on BTX removal by CPC, a three-stage CPC experiment was also conducted at an SIE of 10JL^{-1} in this study, varying RH of the reaction gas from 30% (Stage I) to 80% (Stage II) and back to

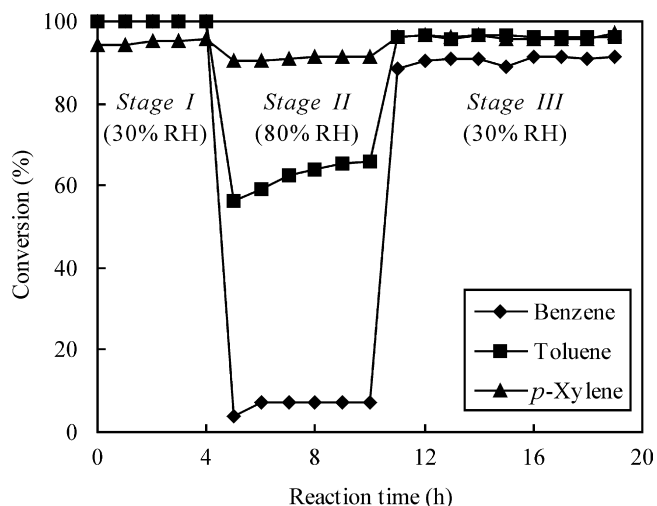


Fig. 3. Time course for BTX conversion during the three-stage CPC experiment (RH: 30%, 80% and 30% for Stages I, II and III, respectively; SIE: 10J L^{-1}).

30% (Stage III) by changing the bubbling temperature of water. The time course for BTX conversion was illustrated in Fig. 3. It was found that although BTX conversion was obviously suppressed under high humidity (Stage II), BTX in Stage III could be removed almost to the same degree as achieved in Stage I, indicating that the catalyst was completely reactivated by lowering the water content in the gas. These results further confirm the strong associations between BTX removal by CPC and RH and prove that optimum BTX conversion can be achieved by adjusting the gas humidity.

In summary, differences in effects of humidity on the conversion of three BTX compounds exist in both NTP and CPC configurations, arising from the different homogeneous and/or heterogeneous decomposition pathways of three compounds. Considering that *p*-xylene was efficiently removed by CPC under all humidity levels, further studies including detailed analysis of the interactions among the catalyst, VOCs and water molecules are desperately required to clarify the influence mechanism of humidity, so as to improve the practical applicability of the CPC technique.

3.3. Effects of humidity on energy efficiency

Fig. 4 shows the effects of RH on the EE for BTX conversion by NTP and CPC as functions of SIE. It is seen that the EE firstly increased to the maximum and then decreased with the increase of SIE, probably

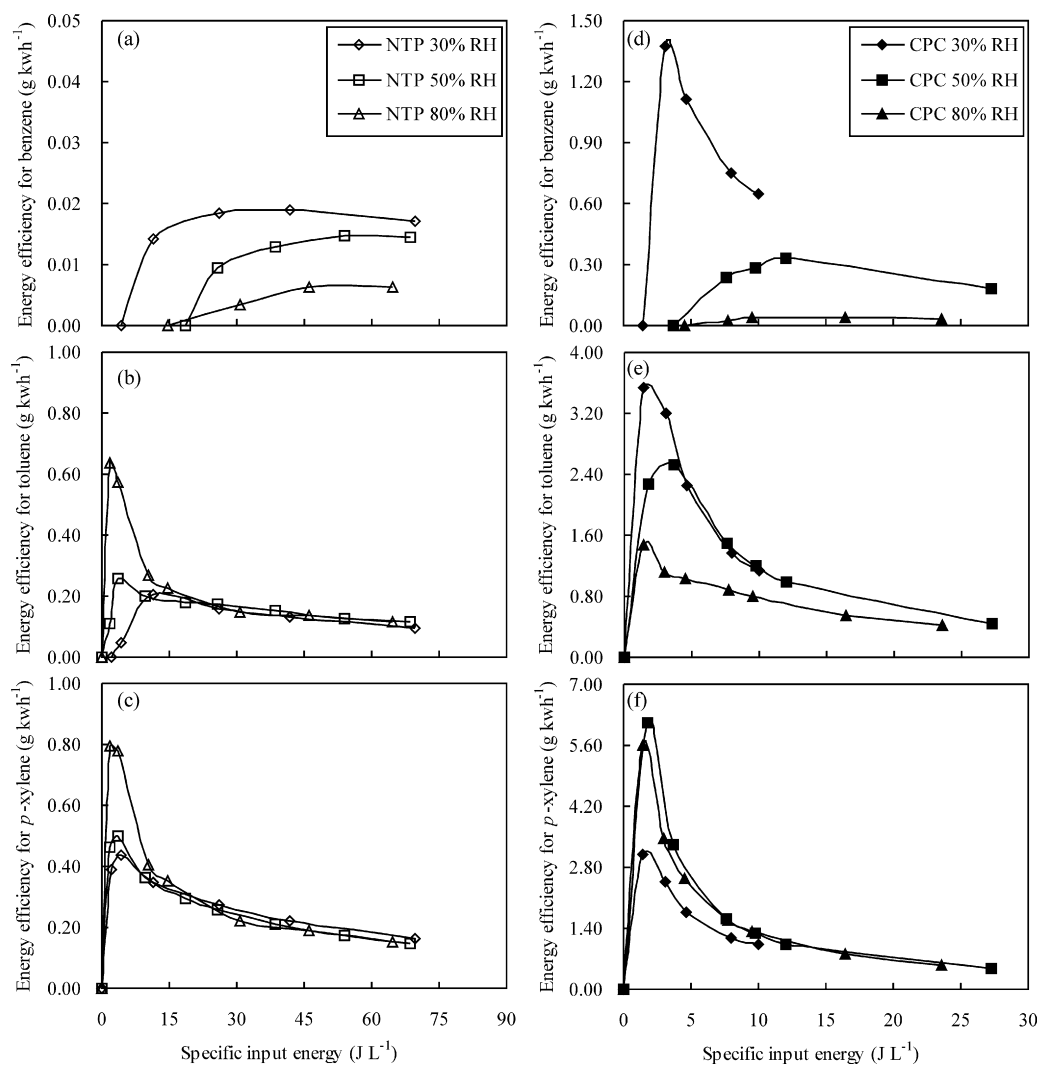


Fig. 4. Effects of humidity on energy efficiency for BTX conversion by NTP and CPC as functions of specific input energy: (a and d) benzene, (b and e) toluene and (c and f) *p*-xylene.

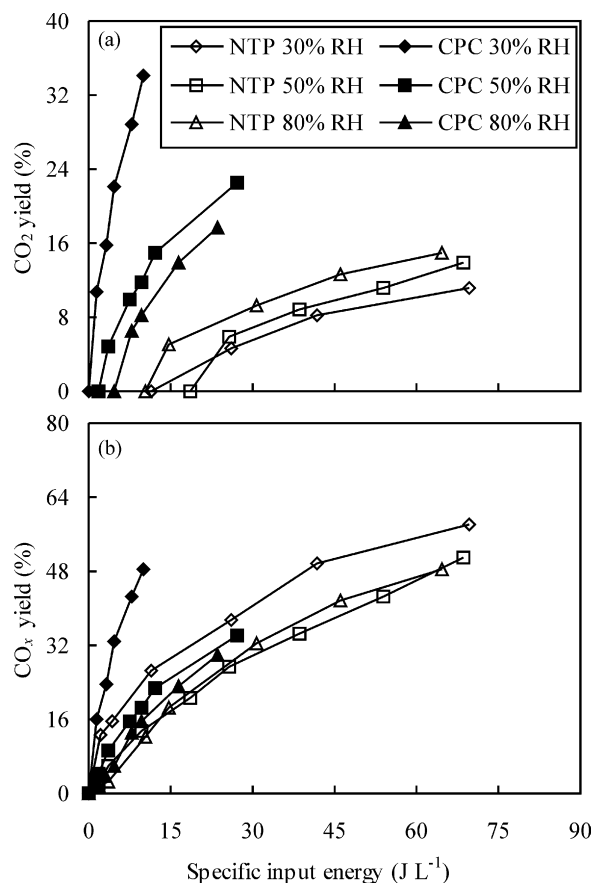


Fig. 5. Effects of humidity on the yields of CO₂ and CO_x by NTP and CPC as functions of specific input energy: (a) CO₂ and (b) CO_x.

due to the increased energy consumption for production of heat, photons and discharge byproducts (O₃) at higher SIE. Also it is seen from Fig. 4 that the EE was greatly improved by combining NTP with MnO_x/Al₂O₃ catalyst, meaning that higher amounts of BTX can be removed by CPC for identical energy consumption. On the other hand, the effects of humidity on the EE are consistent with those on the BTX conversion (Fig. 2), since the EE is directly proportional to the BTX conversion for given SIE.

3.4. Effects of humidity on CO_x formation

Fig. 5a shows the dependence of CO₂ yield on SIE for NTP and CPC configurations with different RH. It can be seen that the CO₂ yield by both NTP and CPC increased with the increase of SIE under all humidity levels, indicating that higher discharge power promotes BTX conversion towards total oxidation. On the other hand, it is also seen from Fig. 5a that the CO₂ yield by NTP increased while that by CPC decreased with the increase of RH. Water molecules promote the homogeneous oxidation of BTX to CO₂, but suppress the heterogeneous CO₂ formation reactions. However, even for the highest RH (80%), significantly positive effects of combined catalysis on the CO₂ yield were observed, suggesting that during CPC processes, the heterogeneous oxidation reactions are much more important than the homogeneous reactions for CO₂ formation.

Fig. 5b shows the yields of CO_x as functions of SIE under different RH. It is seen that the CO_x yield by both NTP and CPC increased with increasing SIE, implying that increased discharge power favors the mineralization of BTX. Also it is seen from Fig. 5b that the yield of CO_x was enhanced by combining MnO_x/Al₂O₃ catalyst after plasma, especially under 30% RH. In fact, results presented in Fig. 5a and b prove that the CPC configuration under 30% RH shows the best per-

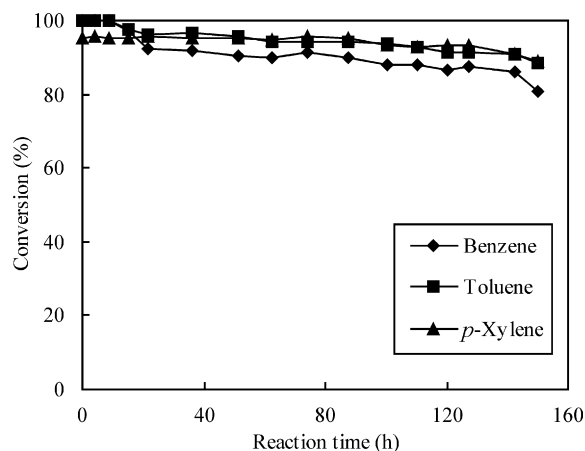


Fig. 6. Time course for BTX conversion during the long-term CPC experiment (RH: 30%; SIE: 10 J L⁻¹).

formance towards total oxidation and mineralization of BTX, having the highest yields of CO₂ and CO_x for given SIE. However, it should be noticed that for CPC with 30% RH and an SIE of 10 J L⁻¹, the BTX conversion reached more than 95% (Fig. 2) while the CO_x yield was only 49% (Fig. 5b), meaning that part of the removed BTX were converted to organic intermediates (incomplete oxidation products).

3.5. Deactivation of the catalyst

From the results described above, it can be concluded that the CPC configuration under 30% RH exhibits the best performance in terms of O₃ reduction, BTX conversion as well as CO_x formation. Accordingly, the stability of the MnO_x/Al₂O₃ catalyst during 150-h continuous removal of BTX by CPC was investigated under 30% RH and an SIE of 10 J L⁻¹ in this study. As shown in Fig. 6, no deactivation was observed during the first 9 h, after which BTX conversion slightly decreased with the reaction time. The conversion of benzene, toluene and p-xylene decreased from 100%, 100% and 95% at 9 h to 81%, 88% and 89% at 150 h, respectively. This deterioration of catalytic activity might result from accumulation of organic intermediates over the catalyst surface. In fact, organic compounds over the 150-h used MnO_x/Al₂O₃ catalyst were extracted with ethanol and analyzed by FT-IR, with the spectrum presented in Fig. 7.

The broad band in the range of 3650–3100 cm⁻¹ with the maximum intensity at 3360 cm⁻¹ may be the overlapping of sev-

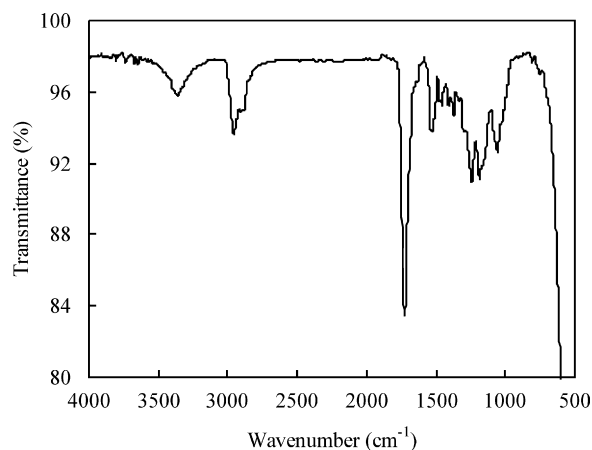


Fig. 7. FT-IR spectrum of organic compounds extracted from the deactivated MnO_x/Al₂O₃ catalyst.

eral bands including N–H stretching of amine and O–H stretching of organic intermediates such as carboxylic acids, phenols and alcohols. The bands at 2960, 2880, 1460 and 1370 cm^{-1} are the characteristic peaks of methyl. The band at 1730 cm^{-1} is assigned to the C=O stretching of saturated aldehydes and/or ketones, overlapped with the C=O stretching bands of carboxylic acids (1820–1750 cm^{-1}) and/or acid amides (1690–1650 cm^{-1}). Besides, the band at 1520 cm^{-1} can be the overlapping of the skeleton vibration of aromatic rings and the N=O stretching of nitro-aromatic compounds. The band at 1410 cm^{-1} is ascribed to the O–H bending, overlapped with the C–N stretching of acid amides. The bands at 1240, 1190 and 1050 cm^{-1} correspond to the C–O stretching of carboxylic acids, phenols and primary alcohols, respectively.

These IR absorption results show that the probable organic intermediates produced during the CPC BTX removal process include saturated aldehydes and/or ketones, carboxylic acids, phenols, primary alcohols, acid amides and nitro-aromatic compounds. These organic intermediates may occur for the following two reasons. Firstly, BTX molecules often undergo a series of intermediate reactions before they are completely oxidized by radicals such as $\bullet\text{OH}$ and $\bullet\text{O}$ in plasma or over the catalyst surface. Secondly, BTX molecular fragments such as phenyl and benzyl radicals, which resulted from the collision of electrons with BTX molecules, often recombine with gas phase radicals such as $\bullet\text{OH}$, $\bullet\text{O}$, $\bullet\text{N}$ and $\bullet\text{H}$ in NTP. Similar carbon-containing intermediates were also detected during the destruction of benzene and toluene with dielectric barrier discharge [23,24].

On the other hand, in order to better understand the reason of catalyst deactivation in this study, the deactivated $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalyst was calcined in air stream at 773 K for 4 h. Then, the long-term CPC removal of BTX with the re-calcined catalyst was carried out (under 30% RH and an SIE of 10 J L^{-1}) and results showed that the catalyst was fully regenerated: the time course for BTX conversion was almost the same as that obtained with the fresh catalyst (Fig. 6). These findings further support that the accumulation of organic intermediates over the catalyst surface is the main cause of catalyst deactivation. To prolong the service life of the $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalyst for practical applications, a higher SIE or a moderate heating of the catalyst might be needed [25].

4. Conclusions

Effects of humidity on the NTP and CPC removal of low-concentration BTX in air were systematically investigated in a link tooth wheel-cylinder plasma reactor in this study. And the stability of the $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalyst was studied under 30% RH and an SIE of 10 J L^{-1} . The main findings can be summarized as follows:

- (1) Combining NTP with $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalyst after the discharge zone (CPC) significantly promotes the BTX conversion and improves the corresponding EE; also it enhances the CO_x formation and reduces the O_3 emission.
- (2) Humidity has different effects on the conversion of three BTX compounds: as for benzene, increasing humidity suppresses the conversion by both NTP and CPC; as for toluene, higher humidity slightly promotes the conversion by NTP but suppresses that by CPC; as for *p*-xylene, humidity hardly affects the conversion by both NTP and CPC.
- (3) Increasing humidity enhances the CO_2 yield by NTP but suppresses that by CPC while lower humidity favors the CO_x yield by both NTP and CPC. On the other hand, increasing humidity inhibits the O_3 production in NTP and its catalytic decomposition by CPC.
- (4) The $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalyst suffers from slight deactivation due to the accumulation of organic intermediates over the catalyst

surface. After calcining in air stream for a few hours, the catalyst was completely regenerated.

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