Catalytic nonthermal plasma reactor for the abatement of low concentrations of benzene

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Abstract Oxidative decomposition of dilute benzene in air was carried out in a dielectric barrier discharge reactor with inner metal fiber electrode that was later modified with transition metal oxides. Typical results indicated the best performance of the designed reactor for the removal of dilute benzene, where conventional techniques may not be efficient. The introduction of transition metal oxides in the discharge zone increased the conversion of benzene and shifted the product distribution to total oxidation. The performance of the reactor was further improved on humidification of air stream. The better performance of MnOx/SMF over CoOx and SMF may be due to in situ decomposition of ozone that may lead to the formation of strong oxidant atomic oxygen, whereas the best performance with TiO2/MnOx/SMF may be assigned due to the synergy between ozone decomposition on MnOx surface and photocatalytic action on TiO2.

Keywords Benzene · Dielectric barrier discharge · Fibers · Nonthermal plasma · Ozone · Sintered metal

Introduction

Benzene (C6H6) is one of the important volatile organic compounds and is widely used as petrifaction material in many industrial applications such as paints, chemical, and printing industries. Benzene is carcinogenic and exposure to it may cause drowsiness, dizziness, and unconsciousness. Moreover, repeated exposure can have adverse impact on human health including anemia, leukemia, blood diseases, and cancer (Weiss and Downs 1920; Lu et al. 2006; Einaga and Futamura 2007; Ye et al. 2008; Einaga and Ogata 2010; Einaga et al. 2011). Many researchers have reported non-thermal plasma (NTP) chemical processing as an effective tool for the removal of volatile organic compounds (VOCs) from gas stream. The abatement of VOCs under dilute concentrations (<1,000 ppm) may not be economical with conventional technologies such as adsorption on activated carbon, catalytic oxidation, and thermal oxidation (Subrahmanyam et al. 2006a; Chorria et al. 2007; Demeestere et al. 2007; Zhu et al. 2008; Li and Gong 2010). NTP generated by electrical discharges under ambient conditions has specific advantages like mild operating conditions and may generate strong oxidizing agents like ozone, hydroxyl radical, H2O2, as well as UV light (Demeestere et al. 2007; Demidyuk and Whitehead 2007; Magureanu et al. 2008; Sugasawa et al. 2010). However, by-products such as CO, CO2, and NOx seem unavoidable under operation of plasma reactors. In order to minimize the toxic products and improve the energy efficiency of the VOCs decomposition process by plasma, combination of heterogeneous catalysts has often been tested (Demidiouk et al. 2003; Subrahmanyam et al. 2006b; Harling et al. 2007; Kim et al. 2007a; Wallis et al. 2007; Quoc An et al. 2011). NTP in air produces ultra violet (UV) radiation due to excited nitrogen molecules; with a suitable combination of photocatalysts, performance of NTP may be further improved. Photocatalytic oxidation has been reported to be an efficient way of removing aqueous organic pollutants like dyes, phenolic compounds, etc. (Shen and Ku 1999; Chen et al. 2006). Earlier attempts combining NTP with a TiO2 photocatalyst to abate VOCs...
indicated the contribution of photocatalysis induced by UV light from the plasma (Kang et al. 2002; Kim et al. 2005b; Subrahmanyam et al. 2007; Huang and Li 2011; Ochiai et al. 2011). Interestingly, Ogata et al. observed an improved efficiency of a photoinactive TiO$_2$-rutile catalyst during the destruction of chlorofluorocarbons, which they attributed to the surface oxygen atoms (Ogata et al. 2004). Several researchers have reported the photocatalytic action of TiO$_2$/rutile during the plasma decomposition of VOCs, (Einaga et al. 2002; Ogata et al. 2003; Lee et al. 2004; Song et al. 2007; Zhu et al. 2008: Huang and Li 2011; Korologos et al. 2011). When the TiO$_2$ anatase is irradiated by UV light with energy greater than the band gap (~3.2 eV, $\lambda$ < 370 nm), excitation of valance-band electrons into the conduction band takes place, resulting in the formation of holes in the valance band. Both the holes and the photoelectrons migrate to the TiO$_2$ surface, where they either recombine or participate in redox reactions with adsorbed species like H$_2$O and O$_2$. The hole oxidizes adsorbed water to hydroxyl radicals, which are the potential oxidants in photocatalysis, whereas the photoelectrons reduce O$_2$ to superoxide. The NTP decomposes benzene into several intermediates, which adsorb on the TiO$_2$ surface. These intermediates may then be oxidized by the hydroxyl radicals (Subrahmanyam et al. 2007a; Zhu et al. 2008; Zhu et al. 2009).

In the present study, we assembled three types of dielectric barrier discharge (DBD) plasma reactors coupled with oxide catalysts and evaluated the contributions of photocatalytic and catalytic effects on the decomposition of benzene. The study aimed to suggest the effectiveness of DBD-catalytic hybrid system for the decomposition of benzene in air. The inner electrode of the DBD reactor was made of sintered metal fibers (SMF) which was suitably modified with either a photocatalyst TiO$_2$ and/or with MnO$_x$ and CoO$_x$. However, earlier attempts to promote UV-induced oxidation were not very promising, probably due to the low intensity of UV light generated in plasma. Hence, the present study highlights the role of UV light in improving the performance of the combined plasma catalytic technique, possibly due to synergy effect as reported earlier (Guaitella et al. 2008; Kim et al. 2004; Kim et al. 2007b).

Materials and methods

The details of DBD reactor and SMF modification with TiO$_2$, MnO$_x$, and TiO$_2$/MnO$_x$ have been given in elsewhere (Subrahmanyam et al. 2006b, 2007). Briefly, TiO$_2$/SMF and TiO$_2$/MnO$_x$/SMF were prepared by precipitation of Ti(IV) bis(ammonium lactato) dihydroxide, 50 wt.% solution in water at 333 K for 3 h, whereas MnO$_x$ was deposited by impregnation followed by drying and calcination. Finally, SMF filters were shaped into a cylindrical form. Discharge length was 10 cm and discharge gap was 3.5 mm. Voltage charge ($V$-$Q$) Lissajous method was used to calculate the discharge power ($W$) and specific input energy (SIE) of the discharge was calculated by following relation:

$$\text{SIE} \left( \frac{J}{l} \right) = \frac{\text{Power} \left( W \right)}{\text{gas flow rate} \left( l/s \right)}$$

During the present study SIE was varied between 170 and 320 (J/l) by varying the voltage between 14 and 22 kV at 50 Hz. Benzene was introduced with a motor-driven syringe pump and was diluted with 0.5 l/min (STP) of air, and the mixture was introduced into the plasma reactor with a Teflon tube. Flow rate of benzene was varied to get desired benzene concentration between 50 to 1,000 ppm. A gas chromatograph (Varian 450) equipped with a FID detector and a capillary column (50 m length, 0.25 mm diameter, and 0.5 µm film thickness) was used to estimate the conversion of benzene, whereas an infrared CO$_x$ analyzer (AIC, India) was used to monitor the CO and CO$_2$ formed. As the volume changes during the reaction are negligible, the selectivity to CO$_2$ and CO$_x$ has been defined as

$$\text{S}_{\text{CO}_2} (\%) = \frac{[\text{CO}_2]}{6([\text{VOC}]_0 - [\text{VOC}])} \times 100 \text{ S}_{\text{CO}_2} (\%) \times 100,$$

where [CO] and [CO$_2$] are outlet concentrations of CO and CO$_2$, respectively, and [VOC]$_0$ and [VOC] the initial and final concentration of benzene. Ozone concentration was measured with an UV absorption detector (API-450 NEMA). The emission spectrum of the discharge confirmed the formation of ultraviolet light with wavelength below 370 nm, which is equivalent to the band gap of anatase TiO$_2$ (3.2 eV) (Subrahmanyam et al. 2007).

Results and discussion

Performance of the DBD reactor on benzene decomposition

As mentioned in the introduction, NTP technique has advantages, especially for VOC concentration $\leq$ 1,000 ppm, where the traditional thermocatalytic techniques are not energetically favorable. During the present study, concentration of benzene has been varied between 50 and 1,000 ppm to understand the influence of VOC concentration on the performance of the reactor. Figure 1a presents the conversion of 1,000 ppm of benzene for the SIE variation between 170 and 320 J/l. As seen from Fig. 1a, benzene conversion increases with increasing input energy with
all the electrodes and among the catalysts studied, TiO₂/SMF showed better conversion than SMF. Similar observation was made with other transition metal oxides. Conversion with all the catalysts increased from 30% at SIE 170 (J/l) to 70% at 320 (J/l). However, the catalyst modification marginally improved the conversion. This may be due to the quick deactivation of the catalyst by polymeric products formed in the reaction and also due to high concentration of benzene. During the oxidative decomposition of benzene, the desired products are CO₂ and H₂O. In general, NTP may lead to undesired products and hence the selectivity to total oxidation is not 100%. During the present study, as no other hydrocarbon except benzene was observed at the outlet, COₓ selectivity also represents the carbon balance. Figure 1b presents the selectivity to COₓ (CO + CO₂). As seen from Fig. 1b, the selectivity to COₓ was poor with all catalysts and was never close to 100%. The SMF and TiO₂ electrodes showed CO₂ selectivity of 15 and 30% at 170 and 320 J/l, respectively. Hence, with 1000 ppm of benzene, in the SIE range of the present study, the SMF catalytic electrodes showed poor carbon balance. However, SMF modification with MnOₓ and TiO₂/MnOₓ results in higher COₓ selectivity as presented in Fig. 1b. The selectivity to CO₂ was also not very appreciable on all the catalysts. SMF and TiO₂/SMF electrodes showed around 30% selectivity at 320 J/l, whereas MnOₓ and TiO₂/MnOₓ modified SMF electrodes showed slightly higher value of 40%. As seen during the destruction of 1000 ppm of benzene, conversion, carbon balance, and selectivity to CO₂ were not 100% with all the catalysts, which may be due to high concentration of benzene. To understand the influence of the concentration of benzene on the performance of the reactor, initial concentration was varied between 50 and 1,000 ppm.

Figure 2a represents the performance of the catalytic DBD reactor for destruction of 500 ppm of benzene. As seen from Fig. 2a, with decreasing concentration of benzene from 1.000 to 500 ppm, conversion increases. Also, as seen in Fig. 2a, SMF modification with TiO₂/MnOₓ and MnOₓ showed higher conversion than unmodified SMF, whereas
at 1000 ppm, all the electrodes showed nearly same activity. Hence, the absence of catalytic effect at 1,000 ppm may be due to the quick deactivation of the catalyst, whereas at lower concentrations, the catalysts appear to be active. For 500 of benzene, the activity of the studied catalysts followed the trend TiO$_2$/MnO$_x$/SMF > MnO$_x$/SMF > TiO$_2$/SMF ≥ SMF. Figure 2b, presents the carbon balance during the oxidation of 500 ppm of benzene. The general observation is that carbon balance improves with decreasing concentration of benzene. Also, $S_{COx}$ increases with increasing the SIE with all the electrodes. At 170 J/l, SMF and TiO$_2$/SMF electrodes showed nearly same carbon balance ~20 %. With increasing SIE, TiO$_2$/MnO$_x$ and MnO$_x$ modified electrodes showed better selectivity than unmodified systems. As seen from the Fig. 2 TiO$_2$/MnO$_x$/SMF showed carbon balance close to 60 % at SIE 320 J/l, whereas at the same SIE for TiO$_2$/MnO$_x$/SMF and MnO$_x$/SMF it was only 50 %. It is also worth mentioning that for 1000 ppm, metal oxide modification did not increase the carbon balance significantly, whereas with decreasing concentration to 500 ppm, polymeric deposits were reduced significantly. A similar observation has been also made of the CO$_2$ selectivity as given in Fig. 2b. SMF and TiO$_2$/SMF showed poor CO$_2$ selectivity of 10 % at 170 J/l that increased to only 20 % at SIE 320 J/l, whereas under the same conditions MnO$_x$ and TiO$_2$/MnO$_x$ showed CO$_2$ selectivity close to 40 %. Figure 3a and b, presents the influence of SIE on the conversion of 250 ppm of benzene. SMF electrode at 170 J/l shows conversions close to 40 % that increases to ~80 % at 320 J/l. A similar behavior was also observed with TiO$_2$/SMF, MnO$_x$/SMF, and TiO$_2$/MnO$_x$/SMF electrodes, where ~90 % conversion of benzene was observed at 290 J/l. As seen from Fig. 3b, for 250 ppm of benzene CO$_x$ selectivity ~70 % was observed at 320 J/l, whereas under the same conditions, for 500 ppm of benzene, CO$_2$ selectivity was not more than 50 %. Hence, during the destruction of 250 ppm of benzene, SIE close to 290 J/l is required to avoid carbon deposit. Figure 3b also represents CO$_2$ selectivity, where with increasing SIE the CO$_2$ selectivity also increases for the catalytic electrodes. At 170 J/l, the best selectivity to CO$_2$ was only 20 % that reached 70 % at 320 J/l. A similar trend was observed with all the catalytic electrodes. Hence at lower VOC concentrations, SMF modification by MnO$_x$ and TiO$_2$/MnO$_x$ showed improved performance towards total oxidation. A similar observation was made during the destruction of 100 ppm of benzene. Generally, NTP reactor shows better performance with decreasing VOC concentration. In order to ensure this observation, benzene concentration was further decreased to 50 ppm. As seen from Fig. 4a, with SMF electrode, conversion increases with increasing SIE and reaches ~90 % at 320 J/l, whereas, MnO$_x$/SMF and TiO$_2$/MnO$_x$/SMF showed close to 100 % conversion at SIE higher than 260 J/l. It is worth mentioning that 260 J/l is nearly equal to heating a liter of gas to ~523 K and at this temperature, none of these catalysts show activity, especially for concentration less than 1,000 ppm. Figure 4b represents the selectivity to CO$_x$ during destruction of 50 ppm of benzene. Selectivity to CO$_x$ increases with increasing SIE and reached 80–90 % on TiO$_2$/MnO$_x$ and MnO$_x$ ~320 J/l, whereas it was ~65 % over unmodified SMF. Figure 4b also presents CO$_2$ selectivity over various catalysts during destruction of 50 ppm of benzene. As seen from Fig. 4b, SMF showed only ~35 % selectivity to CO$_2$ at 320 J/l, whereas 70 % selectivity to CO$_2$ was observed over TiO$_2$/MnO$_x$/SMF at 320 J/l. With TiO$_2$/MnO$_x$/SMF catalyst, at 260 J/l, the conversion was ~100 % (Fig. 4a) and there was no polymeric carbon deposit (Fig. 4b). Hence, the DBD reactor with catalytic SMF electrode showed remarkable activity during the destruction of 50 ppm of benzene.

As seen from the data presented above, SMF modified with both TiO$_2$ and MnO$_x$ showed highest activity. Over
the surface of this bimodal catalyst TiO$_2$/MnO$_x$/SMF, TiO$_2$ and MnO$_x$ exhibit different activities, namely ozone decomposition, photocatalysis, and plasma activation of oxygen atoms on catalyst surface. The synergy between plasma excitation of the VOC molecules and their catalytic oxidation may be further enhanced by photocatalysis, since TiO$_2$ absorbs the UV light produced by the NTP. The improved performance of TiO$_2$ modified systems may be either due to surface activation of TiO$_2$ by thermal activation, ozone decomposition, and/or UV initiated photocatalytic action (Thevenet et al. 2007; Xie et al. 2010; Zhu et al. 2011).

Ozone formation inside the NTP reactor is a known fact and it has been reported that with suitable catalyst integration to NTP, the selectivity to total oxidation can be improved (Karuppiah et al. 2010). During the present study, at 230 J/l, 350 ppm of ozone was observed, whereas at the same input energy MnO$_2$ and TiO$_2$/MnO$_2$/SMF showed complete destruction of ozone. Decomposition of ozone on MnO$_x$ may lead to the formation of atomic oxygen that may improve the performance of the NTP reactor (Futamura and Gurusamy 2005; Harling et al. 2009; Karuppiah et al. 2010). However, TiO$_2$ may not show any appreciable activity for ozone decomposition. As the outlet temperature is not more than 300 K, thermal activation of TiO$_2$ may also be ruled out. Hence, the best activity of TiO$_2$/MnOx/SMF may be due to synergy between photocatalytic activity of TiO$_2$ and ozone decomposition ability of MnO$_x$. (Van Durme et al. 2007, 2009; Vandenbroucke et al. 2010, 2011; Subrahmanyam et al. 2007).

Water vapor plays an important role in the plasma catalysis since it may decompose into OH and H radicals in NTP. The oxidation potential of OH is higher (2.8 V) than other oxidants such as ozone (2.2 V) and peroxyl radicals (1.8 V). The effect of humidity has been tested for several VOCs and it has been reported that water vapor strongly influences the product selectivity (Aubry and Cormier 2009; Kogoma et al. 2006; Lee and Chang 2003). However, the product selectivity also depends on the water content in addition to VOC chemical structure. Some studies reported the optimal water vapor content for achieving the best VOC removal efficiency (Ricketts et al. 2004; Sugasawa et al. 2010; Karuppiah et al. 2012). The effect of water vapor has been mostly studied with packed-bed DBD reactors for removal of benzene (Ogata et al. 2000; Cal and Schluep 2001; Futamura et al. 2002). The influence on the removal process seems to be suppression or a negative effect. During this study, water effect was studied for 50 ppm of benzene. For this purpose, air flow was passed through a water bubbler maintained at a constant temperature (298 K), and the humid air stream contains ~3 % of water content. Experiments were carried out in both dry and humid condition at SIE 170 J/l over MnO$_x$/SMF and TiO$_2$/SMF electrodes. Typical results indicated the better conversion with humid air on MnO$_x$/SMF when compared with dry conditions. With MnO$_x$/SMF and TiO$_2$/SMF under dry conditions, conversion was only 70 % at 170 J/l whereas, on humidifying the gas stream, conversion increased to 95 % for MnO$_x$/SMF, whereas no change in the conversion was observed with TiO$_2$/SMF. Another interesting observation is that MnO$_x$/SMF under dry condition showed only 45 % selectivity to CO$_x$, which was improved up to 70 % on humidification. The selectivity to CO$_2$ also followed the same trend as humid conditions showed better results than dry condition. Such a difference between dry and wet air condition may be due to increase in the concentration of OH radicals as shown in (Eq. 4) in the humid conditions. It may be concluded that the water vapor improves benzene oxidation with MnO$_x$/SMF. But in the case of TiO$_2$/SMF

![Fig. 4](https://example.com/fig4.png)
electrode, significant improvement in the activity was not observed. The possible reaction pathways of active species production in NTP may be written as follows:

\[
\begin{align*}
H_2O + e^- &\rightarrow H + OH^- \\
H^- + O_3 &\rightarrow HO^- + O_2 \\
HO^- + O_3 &\rightarrow HO_2^+ + O_2 \\
HO_2 + O_3 &\rightarrow HO_2^- + 2O_2
\end{align*}
\]

During the present study, the effect of water vapor on destruction of ozone has been examined by for SMF modified with MnO_x and TiO_2. Ozone concentration was 300 and 320 ppm at SIE of 170 J/l in dry air and decreased to 80 ppm in humid air for MnO_x/SMF and there was no change in TiO_2/SMF electrode. It has also been shown that water vapor decreases the formation of CO and enhances the selectivity towards CO_2 (Song et al. 2007; Zhu et al. 2008; Karuppiah et al. 2012). In DBD reactor, catalytic ozonation will play a minor role due to the inhibition of ozone formation by water vapor. Second, the catalyst surface can be covered with layers of H_2O preventing the adsorption of ozone there by limiting the VOC’s reaction with the catalyst (Einaga et al. 2001; Van Durme et al. 2009).

**Comparison with other plasmas**

To evaluate the plasma technology for pollutant treatment, removal efficiency and energy efficiency were widely used. Energy efficiency has expression with specific energy density SIE (J/l). In this context, we attempted to get a performance comparison between the present work and literature data. Table 1 summarizes the decomposition efficiency for benzene removal with various nonthermal plasma technologies (Vandenbroucke et al. 2011). As shown in Table 1, the order of removal efficiency of dilute benzene followed the trends of Surface discharge (Kim et al. 2008), DBD (Hyun-Ha et al. 2005) > DBD (Zhu et al. 2009) > Multistage corona (Chavadej et al. 2007) > DBD (Park et al. 2002) > Present study > Surface discharge (Kim et al. 2005a) > packed-bed DBD (Kim et al. 2003) > BaTiO_3-packed-bed DBD (Harling et al. 2008) > DBD glow discharge (Lee et al. 2004) > DBD (Chae et al. 2004) > DBD (Lu et al. 2006). SIE increases in the order of BaTiO_3-packed bed (Harling et al. 2008) < Surface discharge (Kim et al. 2008) < DBD (Ag 2wt.%)/TiO_2 (Hyun-Ha et al. 2005) < DBD glow discharge (Lee et al. 2004) < Present study < DBD-TiO_2 (Lu et al. 2006) < DBD (TiO_2–silica) (Chae et al. 2004) < DBD-TiO_2

<table>
<thead>
<tr>
<th>Plasma type</th>
<th>Catalyst</th>
<th>Position</th>
<th>T_CAT (K)</th>
<th>Conc. ppm</th>
<th>Maximum removal efficiency (%)</th>
<th>Energy efficiency</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>DBD</td>
<td>TiO_2</td>
<td>IPC –</td>
<td>100</td>
<td>60</td>
<td></td>
<td>900</td>
<td>(Chae et al. 2004)</td>
</tr>
<tr>
<td></td>
<td>TiO_2–silica</td>
<td>IPC –</td>
<td>105</td>
<td>50</td>
<td></td>
<td>320</td>
<td>(Lu et al. 2006)</td>
</tr>
<tr>
<td>DBD</td>
<td>TiO_2</td>
<td>293</td>
<td>300–380</td>
<td>12</td>
<td></td>
<td>170</td>
<td>(Park et al. 2002)</td>
</tr>
<tr>
<td></td>
<td>Pt (1wt.%)/TiO_2</td>
<td>IPC –</td>
<td>200</td>
<td>90</td>
<td></td>
<td>3,150</td>
<td>(Park et al. 2002)</td>
</tr>
<tr>
<td></td>
<td>V_2O_5(1wt.%)/TiO_2</td>
<td></td>
<td></td>
<td>&gt;99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DBD</td>
<td>Ag (2 wt.%)/TiO_2</td>
<td>IPC 373</td>
<td>110</td>
<td>&gt;99</td>
<td></td>
<td>125</td>
<td>(Hyun-Ha et al. 2005)</td>
</tr>
<tr>
<td>DBD</td>
<td>TiO_2</td>
<td>IPC 293</td>
<td>188</td>
<td>98</td>
<td></td>
<td>–</td>
<td>(Zhu et al. 2009)</td>
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<tr>
<td>DBD glow discharge</td>
<td>TiO_2–Al_2O_3</td>
<td>IPC –</td>
<td>100</td>
<td>50</td>
<td></td>
<td>140</td>
<td>(Lee et al. 2004)</td>
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<tr>
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<td>TiO_2</td>
<td>IPC 293</td>
<td>1,500</td>
<td>92,17</td>
<td>91.7</td>
<td>&gt;99</td>
<td>(Chavadej et al. 2007)</td>
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<td></td>
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<tr>
<td>Surface discharge</td>
<td>Ag(1wt.%)/TiO_2</td>
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<td>200–210</td>
<td>89</td>
<td></td>
<td>383</td>
<td>(Kim et al. 2005a)</td>
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<tr>
<td>Packed-bed</td>
<td>TiO_2</td>
<td>IPC 373</td>
<td>203–210</td>
<td>82</td>
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<td>388</td>
<td>(Kim et al. 2003)</td>
</tr>
<tr>
<td>DBD</td>
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<td>203–210</td>
<td>80</td>
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<td>391</td>
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<td></td>
<td>V_2O_5(1 wt.%)/TiO_2</td>
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<td>90</td>
<td></td>
<td>383</td>
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<tr>
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<td>TiO_2</td>
<td>IPC 292</td>
<td>500</td>
<td>66</td>
<td></td>
<td>60</td>
<td>(Harling et al. 2008)</td>
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<tr>
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<td>200</td>
<td>&gt;99</td>
<td></td>
<td>89–194</td>
<td>(Kim et al. 2008)</td>
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<tr>
<td></td>
<td>Ag(0.5 wt.%)/TiO_2</td>
<td>IPC 373</td>
<td>200</td>
<td>&gt;99</td>
<td></td>
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<td>(Kim et al. 2008)</td>
</tr>
<tr>
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<td>TiO_x/MnO_x/SMF</td>
<td>IPC –</td>
<td>50–1,000</td>
<td>&gt;75–90</td>
<td></td>
<td>170–320</td>
<td>Present study</td>
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The abovementioned results indicate that the importance of energy density and inlet concentration are the governing factors for removal of benzene. Even though conditions differ in each of the systems, the present study complements the observations made earlier for the removal of dilute benzene.

**Conclusion**

Oxidative decomposition of low concentration of benzene was studied in a DBD plasma reactor, where the inner electrode was modified with transition metal oxides. The experimental results indicated that the benzene removal efficiency enhanced significantly in the presence of metal oxide catalysts, especially TiO₂/MnOₓ/SMF. The activity may be attributed due to the formation of atomic oxygen on the surface of MnOₓ by in situ decomposition of ozone; whereas photocatalytic oxidation on TiO₂ surface may further increase the efficiency of the process. The presence of water vapor showed improved conversion and selectivity to total oxidation of benzene, which may be due to the formation of a strong oxidant hydroxyl radical.

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