

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 MnO_x/SMF over CoO_x 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 $\text{TiO}_2/\text{MnO}_x/\text{SMF}$ may be assigned due to the synergy between ozone decomposition on MnO_x surface and photocatalytic action on TiO_2 .

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

Introduction

Benzene (C_6H_6) is one of the important volatile organic compounds and is widely used as petrification 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, H_2O_2 , as well as UV light (Demeestere et al. 2007; Demidyuk and Whitehead 2007; Magureanu et al. 2008; Sugawara et al. 2010). However, by-products such as CO , CO_2 , and NO_x 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 TiO_2 photocatalyst to abate VOCs

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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 TiO₂-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 TiO₂-anatase 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 TiO₂ 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 TiO₂ surface, where they either recombine or participate in redox reactions with adsorbed species like H₂O and O₂. The hole oxidizes adsorbed water to hydroxyl radicals, which are the potential oxidants in photocatalysis, whereas the photoelectrons reduce O₂ to superoxide. The NTP decomposes benzene into several intermediates, which adsorb on the TiO₂ 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 TiO₂ 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 (Guitella et al. 2008; Kim et al. 2004; Kim et al. 2007b).

Materials and methods

The details of DBD reactor and SMF modification with TiO₂, MnO_x, and TiO₂/MnO_x have been given in elsewhere (Subrahmanyam et al. 2006b, 2007). Briefly, TiO₂/SMF and TiO₂/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:

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

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 CO₂ formed. As the volume changes during the reaction are negligible, the selectivity to CO₂ and CO_x has been defined as

$$\begin{aligned} S_{\text{CO}_2}(\%) &= \frac{[\text{CO}_2]}{6.([\text{VOC}]_0 - [\text{VOC}])} \times 100 \\ S_{\text{CO}_x}(\%) &= \frac{[\text{CO}_x]}{6.([\text{VOC}]_0 - [\text{VOC}])} \times 100, \end{aligned}$$

where [CO] and [CO₂] are outlet concentrations of CO and CO₂, 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 TiO₂ (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, CO_x selectivity also represents the carbon balance. Figure 1b presents the selectivity to CO_x (CO + CO₂). As seen from Fig. 1b, the selectivity to CO_x was poor with all catalysts and was never close to 100 %. The SMF and TiO₂ electrodes showed CO_x 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 MnO_x and TiO₂/MnO_x results in higher CO_x 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 MnO_x and TiO₂/MnO_x 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 presents 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/MnO_x and MnO_x showed higher conversion than unmodified SMF, whereas

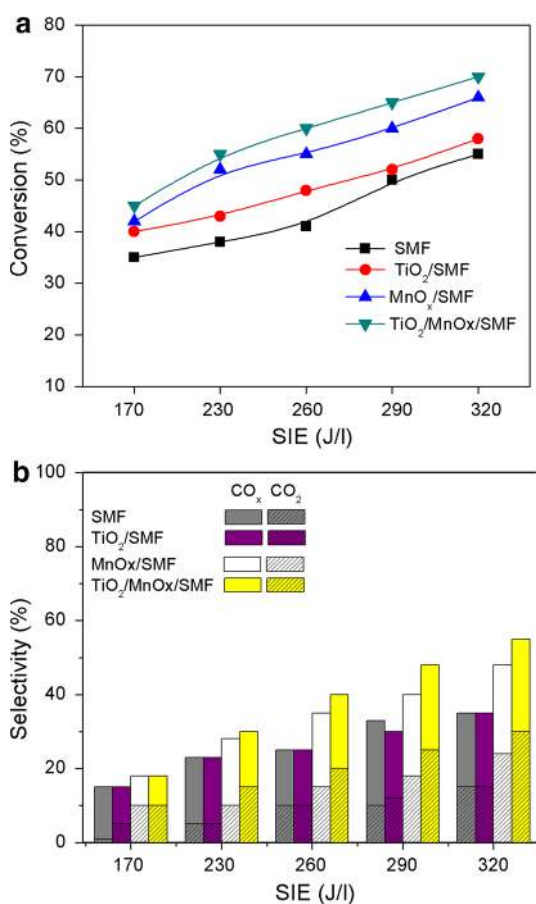


Fig. 1 a Influence of SMF modification and SIE on the conversion of benzene (SIE 170–320 J/l and 1,000 ppm of benzene) b Influence of SMF modification and SIE on selectivity to CO_x and CO₂ (SIE 170–320 J/l and 1,000 ppm of benzene)

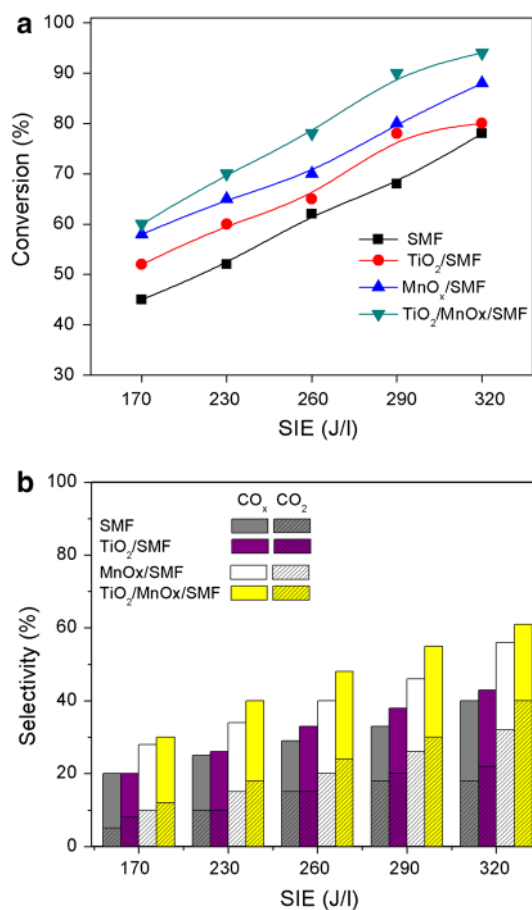


Fig. 2 a Influence of SMF modification and SIE on the conversion of benzene (SIE 170–320 J/l and 500 ppm of benzene) b Influence of SMF modification and SIE on selectivity to CO_x and CO₂ (SIE 170–320 J/l and 500 ppm of benzene)

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 ppm of benzene, the activity of the studied catalysts followed the trend $\text{TiO}_2/\text{MnO}_x/\text{SMF} > \text{MnO}_x/\text{SMF} > \text{TiO}_2/\text{SMF} \geq \text{SMF}$. 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_{CO_x} increases with increasing the SIE with all the electrodes. At 170 J/l, SMF and TiO_2/SMF electrodes showed nearly same carbon balance $\sim 20\%$. With increasing SIE, $\text{TiO}_2/\text{MnO}_x$ and MnO_x modified electrodes showed better selectivity than unmodified systems. As seen from the Fig. 2 $\text{TiO}_2/\text{MnO}_x/\text{SMF}$ showed carbon balance close to 60 % at SIE 320 J/l, whereas at the same SIE for $\text{TiO}_2/\text{MnO}_x/\text{SMF}$ 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 $\text{TiO}_2/\text{MnO}_x$ 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 $\sim 80\%$ at 320 J/l. A similar behavior was also observed with TiO_2/SMF , MnO_x/SMF , and $\text{TiO}_2/\text{MnO}_x/\text{SMF}$ electrodes, where $\sim 90\%$ conversion of benzene was observed at 290 J/l. As seen from Fig. 3b, for 250 ppm of benzene CO_x selectivity $\sim 70\%$ 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 $\text{TiO}_2/\text{MnO}_x$ 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 $\sim 90\%$ at 320 J/l, whereas, MnO_x/SMF and $\text{TiO}_2/\text{MnO}_x/\text{SMF}$

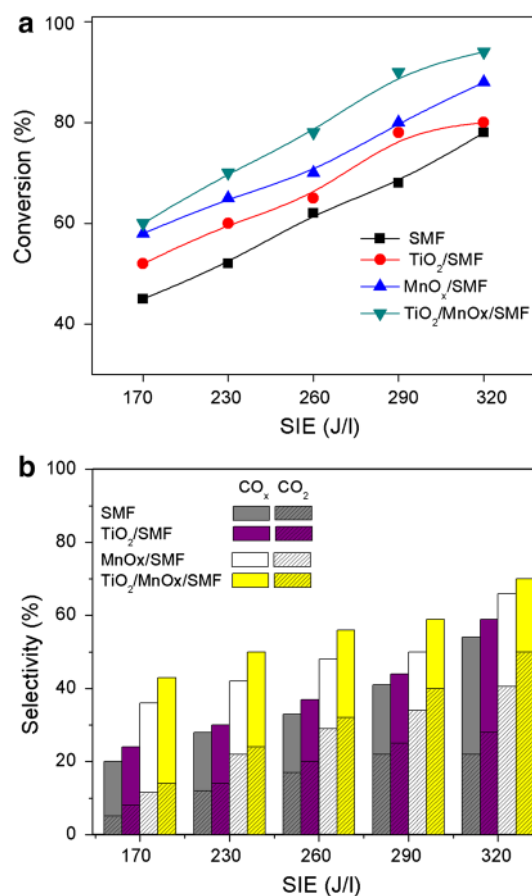


Fig. 3 a Influence of SMF modification and SIE on the conversion of benzene (SIE 170–320 J/l and 250 ppm of benzene) b Influence of SMF modification and SIE on selectivity to CO_x and CO_2 (SIE 170–320 J/l and 250 ppm of benzene)

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 $\sim 523\text{ K}$ 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 $\text{TiO}_2/\text{MnO}_x$ and MnO_x $\sim 320\text{ J/l}$, whereas it was $\sim 65\%$ 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 $\sim 35\%$ selectivity to CO_2 at 320 J/l, whereas 70 % selectivity to CO_2 was observed over $\text{TiO}_2/\text{MnO}_x/\text{SMF}$ at 320 J/l. With $\text{TiO}_2/\text{MnO}_x/\text{SMF}$ catalyst, at 260 J/l, the conversion was $\sim 100\%$ (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

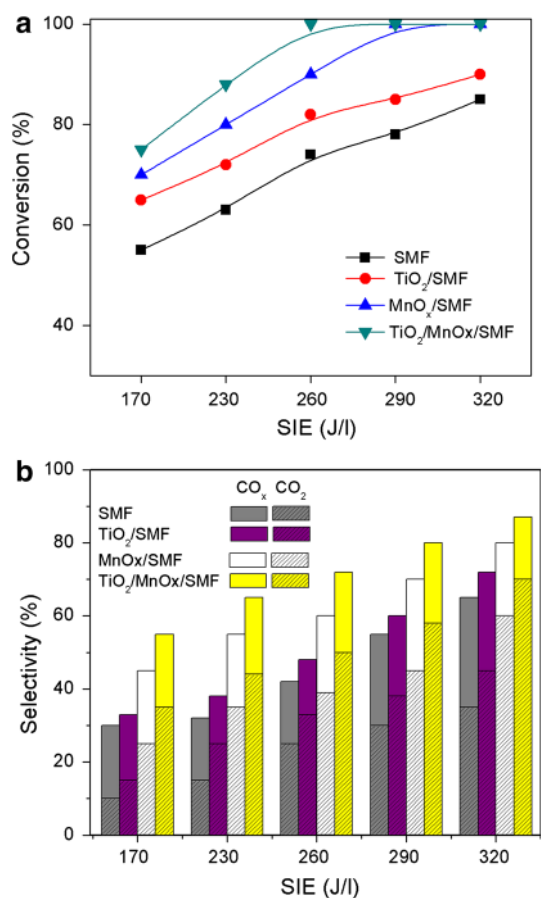


Fig. 4 **a** Influence of SMF modification and SIE on the conversion of benzene (SIE 170–320 J/l and 50 ppm of benzene) **b** Influence of SMF modification and SIE on selectivity to CO_x and CO₂ (SIE 170–320 J/l and 50 ppm of benzene)

the surface of this bimodal catalyst TiO₂/MnO_x/SMF, TiO₂ 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 TiO₂ absorbs the UV light produced by the NTP. The improved performance of TiO₂ modified systems may be either due to surface activation of TiO₂ 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 (Karuppiyah et al. 2010). During the present study, at 230 J/l, 350 ppm of ozone was observed, whereas at the same input energy MnO₂ and TiO₂/MnO_x/SMF showed complete destruction of ozone. Decomposition of ozone on MnOx 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; Karuppiyah et al. 2010). However, TiO₂ may not show any appreciable activity for ozone decomposition. As the outlet temperature is not more than 300 K, thermal activation of TiO₂ may also be ruled out. Hence, the best activity of TiO₂/MnOx/SMF may be due to synergy between photocatalytic activity of TiO₂ and ozone decomposition ability of MnOx. (Van Durme et al. 2007, 2009; Vandembroucke et al. 2010, 2011; Subrahmanyam et al. 2007).

Influence of water vapor on plasma catalytic decomposition of benzene

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 peroxy 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; Sugawara et al. 2010; Karuppiyah 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 TiO₂/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 TiO₂/SMF under dry conditions, conversion was only 70 % at 170 J/l whereas, on humidifying the gas stream, conversion increased to 95 % for MnOx/SMF, whereas no change in the conversion was observed with TiO₂/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 CO₂ 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 MnOx/SMF. But in the case of TiO₂/SMF



electrode, significant improvement in the activity was not observed. The possible reaction pathways of active species production in NTP may be written as follows:



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 1 Comparison of benzene removal efficiencies with various nonthermal plasma technologies

Plasma type	Catalyst	Position	T_{CAT} (K)	Conc. ppm	Maximum removal efficiency (%)	Energy efficiency	References
DBD	TiO_2	IPC	–	100	60	900	(Chae et al. 2004)
	TiO_2 -silica			105	50	320	
DBD	TiO_2	IPC	293	300–380	12	170	(Lu et al. 2006)
DBD	TiO_2	IPC	–	200	90	3,150	(Park et al. 2002)
	Pt (1wt.%)/ TiO_2				>99		
	V_2O_5 (1wt.%)/ TiO_2				>99		
DBD	Ag (2 wt.%)/ TiO_2	IPC	373	110	>99	125	(Hyun-Ha et al. 2005)
DBD	TiO_2	IPC	293	188	98	–	(Zhu et al. 2009)
DBD glow discharge	TiO_2 - Al_2O_3	IPC	–	100	50	140	(Lee et al. 2004)
Multistage corona	TiO_2	IPC	293	1,500	92.17 91.7	–	(Chavadej et al. 2007)
	Sol-gel TiO_2				>99		
	Pt/Sol-gel TiO_2				>99		
Surface discharge	Ag(1wt.%)/ TiO_2	IPC	373	200–210	89	383	(Kim et al. 2005a)
Packed-bed	TiO_2	IPC	373	203–210	82	388	(Kim et al. 2003)
DBD	Pt(1 wt.%)/ TiO_2				80	391	
	V_2O_5 (1 wt.%)/ TiO_2				90	383	
	TiO_2	IPC	292	500	66	60	(Harling et al. 2008)
BaTiO_3 packed-bed	Ag(0.5 wt.%)/ TiO_2				60		
	TiO_2 Ag(0.5 wt.%)/ TiO_2				49		
	TiO_2				46		
Surface discharge	Ag (4 wt.%)/ TiO_2	IPC	373	200	>99	89–194	(Kim et al. 2008)
	Ni (2 wt.%)/ TiO_2				>99		
DBD	TiO_x /MnO $_x$ /SMF	IPC	–	50–1,000	>75–90	170–320	Present study

(Park et al. 2002). Accordingly, the concentration of benzene (ppm): Multistage corona (Chavadej et al. 2007) > Present study > BaTiO₃ Packed bed (Harling et al. 2008) > DBD-TiO₂ (Lu et al. 2006) > Packed-bed-DBD (Kim et al. 2003) > Surface discharge (Kim et al. 2005a) > Surface discharge (Kim et al. 2008), DBD (Park et al. 2002) > DBD-TiO₂ (Chae et al. 2004), DBD glow discharge (Lee et al. 2004). 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/MnO_x/SMF. This best activity may be attributed due to the formation of atomic oxygen on the surface of MnO_x 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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References

- Aubry O, Cormier JM (2009) Improvement of the diluted propane efficiency treatment using a non-thermal plasma. *Plasma Chem Plasma Process* 29(1):13–25
- Cal MP, Schluep M (2001) Destruction of benzene with non-thermal plasma in dielectric barrier discharge reactors. *Environ Prog* 20(3):151–156
- Chae JO, Demidiouk V, Yeulash M, Choi IC, Jung TG (2004) Experimental study for indoor air control by plasma-catalyst hybrid system. *IEEE trans plasma Sci* 32(2 I):493–497
- Chavadej S, Kiatubolpaiboon W, Rangsunvigit P, Sreethawong T (2007) A combined multistage corona discharge and catalytic system for gaseous benzene removal. *J Mol Catal A Chem* 263:128–136
- Chen WR, Sharpless CM, Linden KG, Suffet H (2006) Treatment of volatile organic chemicals on the EPA contaminant candidate list using ozonation and the O₃/H₂O₂ advanced oxidation process. *Environ Sci Technol* 40(8):2734–2739
- Chorria J, Jaroniec M, Kloske M (2007) Ordered siliceous and carbonaceous nanomaterials in environmental protection. *Ochroona Srodowiska* 29:3–12
- Demeestere K, Dewulf J, Van Langenhove H (2007) Heterogeneous photocatalysis as an advanced oxidation process for the abatement of chlorinated, monocyclic aromatic and sulfurous volatile organic compounds in air: state of the art. *Crit Rev Environ Sci Technol* 37(6):489–538
- Demidiouk V, Moon SI, Chae JO, Lee DY (2003) Application of a plasma-catalytic system for decomposition of volatile organic compounds. *J Korean Phys Soc* 42(2):S966–S970
- Demidiouk V, Whitehead JC (2007) Influence of temperature on gas-phase toluene decomposition in plasma-catalytic system. *Plasma Chem Plasma Process* 27:85–94
- Einaga H, Futamura S (2007) Catalytic oxidation of benzene with ozone over Mn ion-exchanged zeolites. *Catal Commun* 8(3):557–560
- Einaga H, Ogata A (2010) Catalytic oxidation of benzene in the gas phase over alumina-supported silver catalysts. *Environ Sci Technol* 44(7):2612–2617
- Einaga H, Ibusuki T, Futamura S (2001) Performance evaluation of a hybrid system comprising silent discharge plasma and manganese oxide catalysts for benzene decomposition. *IEEE Trans Ind Appl* 37(5):1476–1482
- Einaga H, Futamura S, Ibusuki T (2002) Heterogeneous photocatalytic oxidation of benzene, toluene, cyclohexene and cyclohexane in humidified air: comparison of decomposition behavior on photoirradiated TiO₂ catalyst. *Appl Catal B* 38(3): 215–225
- Einaga H, Teraoka Y, Ogata A (2011) Benzene oxidation with ozone over manganese oxide supported on zeolite catalysts. *Catal Today* 164:571–574
- Futamura S, Gurusamy A (2005) Synergy of nonthermal plasma and catalysts in the decomposition of fluorinated hydrocarbons. *J Electrostatics* 63(6–10):949–954
- Futamura S, Zhang A, Einaga H, Kabashima H (2002) Involvement of catalyst materials in nonthermal plasma chemical processing of hazardous air pollutants. *Catal Today* 72(3–4):259–265
- Guaitella O, Thevenet F, Puzenet E, Guillard C, Rousseau A (2008) C₂H₂ oxidation by plasma/TiO₂ combination: Influence of the porosity, and photocatalytic mechanisms under plasma exposure. *Appl Catal B* 80(3–4):296–305
- Harling AM, Wallis AE, Whitehead JC (2007) The effect of temperature on the removal of DCM using non-thermal, atmospheric-pressure plasma-assisted catalysis. *Plasma Processes Polym* 4:463–470
- Harling AM, Demidiouk V, Fischer SJ, Whitehead JC (2008) Plasma-catalysis destruction of aromatics for environmental clean-up: Effect of temperature and configuration. *Appl Catal B* 82(34): 180–189
- Harling AM, Glover DJ, Whitehead JC, Zhang K (2009) The role of ozone in the plasma-catalytic destruction of environmental pollutants. *Appl Catal B Environ* 90:157–161
- Huang H, Li W (2011) Destruction of toluene by ozone-enhanced photocatalysis: performance and mechanism. *Appl Catal B* 102:449–453
- Hyun-Ha K, Atsushi O, Shigeru F (2005) Atmospheric plasma-driven catalysis for the low temperature decomposition of dilute aromatic compounds. *J Phys D Appl Phys* 38(8):1292
- Kang M, Kim BJ, Cho SM, Chung CH, Kim BW, Han GY, Yoon KJ (2002) Decomposition of toluene using an atmospheric pressure plasma/TiO₂ catalytic system. *J Mol Catal A Chem* 180(1–2): 125–132
- Karuppiyah J, Sivachandiran L, Karvembu R, Subrahmanyam C (2010) Catalytic nonthermal plasma reactor for the abatement of low concentrations of isopropanol. *Chem Eng J* 165(1): 194–199
- Karuppiyah J, Karvembu R, Subrahmanyam C (2012) The catalytic effect of MnO_x and CoO_x on the decomposition of nitrobenzene in a non-thermal plasma reactor. *Chem Eng J* 180:39–45



- Kim HH, Lee YH, Ogata A, Futamura S (2003) Plasma-driven catalyst processing packed with photocatalyst for gas-phase benzene decomposition. *Catal Commun* 4(7):347–351
- Kim HH, Oh SM, Ogata A, Futamura S (2004) Decomposition of benzene using Ag/TiO₂ packed plasma-driven catalyst reactor: influence of electrode configuration and Ag-loading amount. *Catal Lett* 96(3–4):189–194
- Kim HH, Kobara H, Ogata A, Futamura S (2005a) Comparative assessment of different nonthermal plasma reactors on energy efficiency and aerosol formation from the decomposition of gas-phase benzene. *IEEE Trans Ind Appl* 41(1):206–214
- Kim HH, Oh SM, Ogata A, Futamura S (2005b) Decomposition of gas-phase benzene using plasma-driven catalyst (PDC) reactor packed with Ag/TiO₂ catalyst. *Appl Catal B* 56(3):213–220
- Kim HH, Tsubota S, Daté M, Ogata A, Futamura S (2007a) Catalyst regeneration and activity enhancement of Au/TiO₂ by atmospheric pressure nonthermal plasma. *Appl Catal A* 329:93–98
- Kim HH, Tsubota S, Daté M, Ogata A, Futamura S (2007b) Catalyst regeneration and activity enhancement of Au/TiO₂ by atmospheric pressure nonthermal plasma. *Appl Catal A* 329:93–98
- Kim HH, Ogata A, Futamura S (2008) Oxygen partial pressure-dependent behavior of various catalysts for the total oxidation of VOCs using cycled system of adsorption and oxygen plasma. *Appl Catal B* 79(4):356–367
- Kogoma M, Miki Y, Tanaka K, Takahashi K (2006) Highly efficient VOC decomposition using a complex system (OH radical, ozone-UV, and TiO₂). *Plasma Process Polym* 3(9):727–733
- Korologos CA, Philippopoulos CJ, Pouloupoulos SG (2011) The effect of water presence on the photocatalytic oxidation of benzene, toluene, ethylbenzene and m-xylene in the gas-phase. *Atmos Environ* 45:7089–7095
- Lee HM, Chang MB (2003) Abatement of gas-phase p-Xylene via dielectric barrier discharges. *Plasma Chem Plasma Process* 23(3):541–558
- Lee BY, Park SH, Lee SC, Kang M, Choung SJ (2004) Decomposition of benzene by using a discharge plasma-photocatalyst hybrid system. *Catal Today* 93–95:769–776
- Li WB, Gong H (2010) Recent progress in the removal of volatile organic compounds by catalytic combustion. *Wuli Huaxue Xuebao/Acta Physico Chimica Sinica* 26(4):885–894
- Lu B, Zhang X, Yu X, Feng T, Yao S (2006) Catalytic oxidation of benzene using DBD corona discharges. *J Hazard Mater* 137(1):633–637
- Magureanu M, Piroi D, Mandache NB, Parvulescu V (2008). Decomposition of methylene blue in water using a dielectric barrier discharge: Optimization of the operating parameters. *J Appl Phys* 104. doi:10.3306/103306-103306/103307
- Ochiai T, Nakata K, Murakami T, Morito Y, Hosokawa S, Fujishima A (2011) Development of an air-purification unit using a photocatalysis-plasma hybrid reactor. *Electrochemistry* 79:838–841
- Ogata A, Shintani N, Yamanouchi K, Yamanouchi K, Mizuno K, Kushiyama S, Yamamoto T (2000) Effect of water vapor on benzene decomposition using a nonthermal-discharge plasma reactor. *Plasma Chem Plasma Process* 20(4):453–467
- Ogata A, Einaga H, Kabashima H, Futamura S, Kushiyama S, Kim HH (2003) Effective combination of nonthermal plasma and catalysts for decomposition of benzene in air. *Appl Catal B* 46(1):87–95
- Ogata A, Kim HH, Futamura S, Kushiyama S, Mizuno K (2004) Effects of catalysts and additives on fluorocarbon removal with surface discharge plasma. *Appl Catal B* 53(3):175–180
- Park DW, Yoon SH, Kim GJ, Sekiguchi H (2002) The effect of catalyst on the decomposition of dilute benzene using dielectric barrier discharge. *J Ind Eng Chem* 8(4):393–398
- Quoc An HT, Pham Huu T, Van Le T, Cormier JM, Khacef A (2011) Application of atmospheric non thermal plasma-catalysis hybrid system for air pollution control: toluene removal. *Catal Today* 176(1):474–477
- Ricketts CL, Wallis AE, Whitehead JC, Zhang K (2004) A Mechanism for the Destruction of CFC-12 in a Nonthermal, Atmospheric Pressure Plasma. *J Phys Chem A* 108(40):8341–8345
- Shen Y-S, Ku Y (1999) Treatment of gas-phase volatile organic compounds (VOCs) by the UVO3 process. *Chemosphere* 38(8):1855–1866
- Song H, Bai S, Han S, Li J, Wang B, Shi X (2007) Decomposition of benzene by integrated action of non-thermal plasma and photocatalyst. *Shiyu Huagong* 36:397–401
- Subrahmanyam C, Magureanu M, Renken A, Kiwi-Minsker L (2006a) Catalytic abatement of volatile organic compounds assisted by non-thermal plasma. Part I. A novel dielectric barrier discharge reactor containing catalytic electrode. *Appl Catal B* 65:150–156
- Subrahmanyam C, Renken A, Kiwi-Minsker L (2006b) Catalytic abatement of volatile organic compounds assisted by non-thermal plasma: Part II. Optimized catalytic electrode and operating conditions. *Appl Catal B* 65(1–2):157–162
- Subrahmanyam C, Magureanu M, Laub D, Renken A, Kiwi-Minsker L (2007) Nonthermal plasma abatement of trichloroethylene enhanced by photocatalysis. *J Phys Chem C* 111(11):4315–4318
- Sugasawa M, Terasawa T, Futamura S (2010) Additive effect of water on the decomposition of VOCs in nonthermal plasma. *IEEE Trans Ind Appl* 46:1692–1698
- Thevenet F, Guaitella O, Puzenat E, Herrmann JM, Rousseau A, Guillard C (2007) Oxidation of acetylene by photocatalysis coupled with dielectric barrier discharge. *Catal Today* 122:186–194
- Van Durme J, Dewulf J, Sysmans W, Leys C, Van Langenhove H (2007) Efficient toluene abatement in indoor air by a plasma catalytic hybrid system. *Appl Catal B* 74(1–2):161–169
- Van Durme J, Dewulf J, Demeestere K, Leys C, Van Langenhove H (2009) Post-plasma catalytic technology for the removal of toluene from indoor air: Effect of humidity. *Appl Catal B* 87(1–2):78–83
- Vandenbroucke A, Morent R, De Geyter N, Nguyen Dinh MT, Giraudon JM, Lamonier JF, Leys C (2010) Plasma-catalytic decomposition of TCE. *Int J plasma environ sci technol* 4:135–138
- Vandenbroucke AM, Morent R, De Geyter N, Leys C (2011) Non-thermal plasmas for non-catalytic and catalytic VOC abatement. *J Hazard Mater* 195:30–54
- Wallis AE, Whitehead JC, Zhang K (2007) Plasma-assisted catalysis for the destruction of CFC-12 in atmospheric pressure gas streams using TiO₂. *Catal Lett* 113:29–33
- Weiss JM, Downs CR (1920) Catalytic oxidation. I—Benzene. *J Ind Eng Chem* 12(3):228–232
- Xie Z, Chen L, Sun F, Ye Q (2010) VOC decomposition in airflow by pulsed discharge. *Environ Eng Manage J* 9:897–902
- Ye Z, Zhang Y, Li P, Yang L, Zhang R, Hou H (2008) Feasibility of destruction of gaseous benzene with dielectric barrier discharge. *J Hazard Mater* 156(1–3):356–364
- Zhu T, Li J, Jin Y, Liang Y, Ma G (2008) Decomposition of benzene by non-thermal plasma processing: photocatalyst and ozone effect. *Int J Environ Sci* 5(3):375–384
- Zhu T, Li J, Jin YQ, Liang YH, Ma GD (2009) Gaseous phase benzene decomposition by non-thermal plasma coupled with nano titania catalyst. *Int J Environ Sci* 6(1):141–148
- Zhu T, Wan Y, Zhang C, Sun M, He X, Xu D, Shu X (2011) VOCs decomposition using multiple catalysis in non-thermal plasma processing. *Adv Mater Res* 152–153:973–977