Nonthermal plasma assisted photocatalytic oxidation of dilute benzene

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Abstract. Oxidative decomposition of low concentrations (50–1000 ppm) of diluted benzene in air was carried out in a nonthermal plasma (NTP) dielectric barrier discharge (DBD) reactor with the inner electrode made up of stainless steel fibres (SMF) modified with transition metal oxides in such a way to integrate the catalyst in discharge zone. Typical results indicate the better performance of MnO_x and TiO_2/MnO_x modified systems, which may be attributed to the *in situ* decomposition of ozone on the surface of MnO_x that may lead to the formation of atomic oxygen; whereas ultraviolet light induced photocatalytic oxidation may be taking place with TiO_2 modified systems. Water vapour improved the selectivity to total oxidation.

Keywords. Nonthermal plasma; sintered metal fibres; photocatalysis; ozone decomposition; VOC abatement.

1. Introduction

Advanced oxidation processes (AOPs) have been receiving great attention for the removal of various air and water bound pollutants.[1–3] AOPs, in general, mineralize the pollutants through generation of powerful oxidizing agents like atomic oxygen, hydroxyl radical, H_2O_2 etc.[4–6] Photocatalytic oxidation of organic compounds using TiO_2 may present many advantages like the ease of operation, especially during the mineralization of water bound organic pollutants like dyes, etc. and it has been reported to be very efficient for both decolorization and degradation of various pollutants.[7–9] However, all these techniques have limited success during the oxidation of air pollutants. In this context nonthermal plasma (NTP) generated by electrical discharges under ambient conditions have specific advantages in terms of mild operating conditions and may generate strong oxidizing agents like ozone, hydroxyl radical, etc. Hence proper positioning of catalyst is warranted as many of these species are short-lived. NTP-catalytic oxidation has been studied extensively for decomposition of various pollutants, including volatile organic compounds (VOCs).[10–22] It has been reported that with a combination of catalyst, it is possible to overcome the limitations of NTP, especially low selectivity to total oxidation. NTP in air produces ultraviolet (UV) radiation due to excited nitrogen

molecules.[23] However, earlier attempts to promote UV induced oxidation were not promising, probably due to the low intensity of UV light. It is recently reported that by proper modification of the electrodes, it is possible to utilize the UV light for photocatalytic decomposition of chlorinated VOCs.[23]

Benzene, a commonly used industrial solvent, whose abatement under dilute concentrations (<1000 ppm) may not be economical by conventional techniques. The present study was aimed at the total oxidation of dilute benzene in a DBD reactor. The inner electrode of the DBD rector was made of sintered metal fibres (SMF) which were suitably modified with either a photocatalyst TiO_2 and/or MnO_x. In addition, the present study highlights the role of UV light in improving the performance of the combined plasma catalytic technique due to synergy effect.

2. Experimental

The details of DBD reactor and SMF modification with TiO_2, MnO_x and TiO_2/MnO_x was reported elsewhere.[24,25] Briefly, TiO_2/SMF was prepared by the 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.[26] Drying at room temperature followed by calcination in air at 773 K for 5 h resulted metal oxide supported SMF

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catalysts. Finally, SMF filters were shaped into a cylindrical form. Discharge length was 10 cm and discharge gap was 3.5 mm. The desired specific input energy (SIE at 230 or 260 J/l) was applied by varying the AC high voltage. The V-Q Lissajous method was used to determine the discharge power (W) from which SIE was calculated. Benzene (50 to 1000 ppm) diluted in air was fed into the reactor (0.5 l/min STP), whose concentration at the outlet was measured with a gas chromatograph (Varian 450), whereas an infrared CO_x analyzer (AIC, India) was used to monitor the CO and CO_2 formed. Ozone concentration was measured with an UV absorption detector (API-450 NEMA). The catalytic electrodes were characterized as reported earlier.[23] As the influence of ultraviolet light may be expected only if NTP emits radiation with $\lambda \leq$ 370–380 nm, which is equivalent to the band gap of anatase (3.2 eV), emission spectrum of the discharge in the wavelength range 250–500 nm was reported in our earlier publication.[23]

3. Results and discussion

Activity of the modified catalytic SMF electrodes was tested at a specific input energy (SIE) of 230 J/l as a function of benzene concentration varied between 50 and 1000 ppm and the results are presented in figure 1a. As seen from the figure 1a, conversion of benzene increases with decreasing benzene concentration and among the catalysts studied, unmodified SMF showed the lowest activity, probably due to the lack of catalyst component. This is further supported by better conversion over transition metal modified SMF electrodes. For example, for 1000 ppm of benzene, TiO_2/SMF showed slightly higher conversion to that of SMF and TiO_2/MnO_x/SMF showed the best conversion of 65% compared to 50% on SMF electrode. It is worth mentioning that TiO_2/MnO_x/SMF demands energy 1.6 × 10^5 J/mol. However, decreasing benzene concentration increased the conversion over the entire range of catalysts including unmodified SMF. This increase is significant when SMF is modified with MnO_x, which may be due to the formation of a strong oxidizing agent, atomic oxygen by *in situ* decomposition of ozone, as reported earlier.[26] Interesting observation is that SMF modified with both MnO_x and TiO_2 showed highest activity for any concentration. For example, for 50 ppm of benzene the activity of the catalytic electrodes followed the order SMF<TiO_2/SMF<MnO_x/SMF<TiO_2/MnO_x/SMF and TiO_2/MnO_x/SMF showed ∼100% conversion at 230 J/l. It is worth mentioning that the conventional methods for the removal of VOCs may not be effective under such lower concentrations due to the non-adiabatic conditions.[20,23,24]
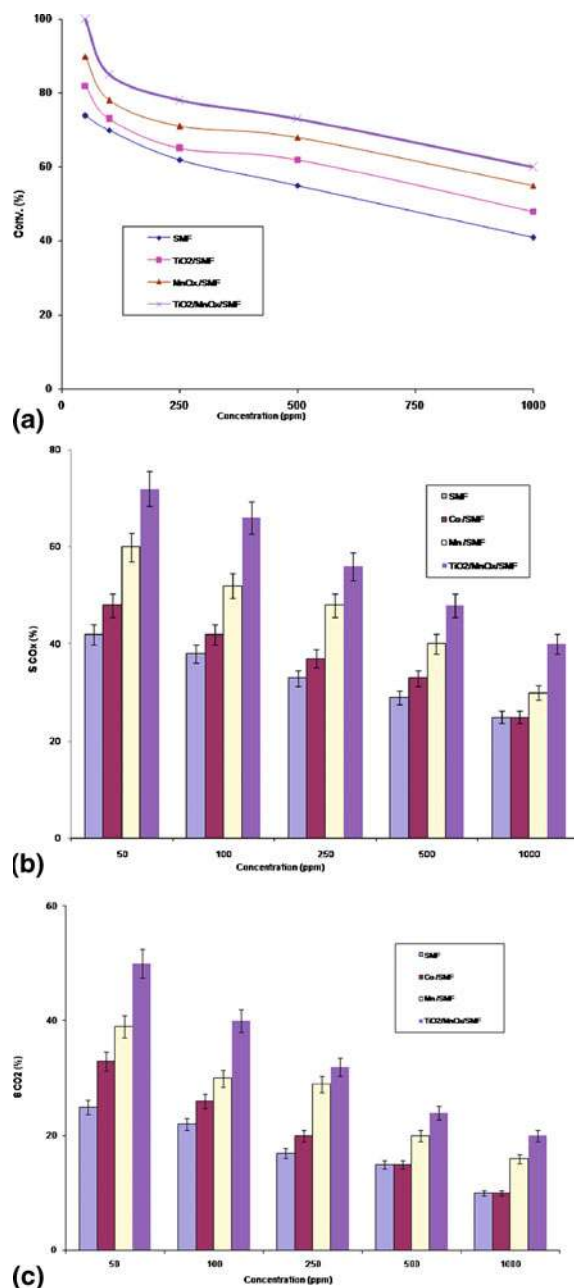

Figure 1. Influene of SMF modification and benzene concentration on (**a**) conversion, (**b**) selectivity to CO_x and (**c**) selectivity to CO_2 at 230 J/l.

During the destruction of VOCs, the desired is total oxidation, i.e., CO_2 and H_2O, however, NTP destruction of VOCs is non-selective and may lead to the undesired polymeric deposit in addition to CO and CO_2, and hence elimination of carbonaceous deposit is warranted. Figure 1b presents the selectivity to gaseous products (CO and CO_2). As these are the only gaseous products observed, S_{CO_x} may also present the carbon

balance of the present reaction. Interesting observation is that at 230 J/l, decreasing concentration of benzene increased the selectivity to gaseous products. As seen from figure 1b, SMF electrode at 50 ppm showed 40% S_{COx} against 25% for 1000 ppm. SMF modification with transition metal oxides also increased the selectivity. TiO_2/SMF showed slightly higher selectivity than unmodified SMF, whereas MnO_x and TiO_2/MnO_x/SMF showed still higher activity. For 50 ppm of benzene, TiO_2/MnO_x/SMF showed around 80% S_{COx} against 40% on SMF. CO_2 selectivity also followed the same trend where TiO_2 modified electrodes showed better activity as presented in figure 1c. For 50 ppm of benzene, SMF showed ∼25% selectivity to CO_2 against 50% with TiO_2/MnO_x/SMF. For any electrode, S_{CO2} decreased significantly with increasing concentration. For example, during the oxidation of 1000 ppm of benzene, TiO_2/MnO_x/SMF showed only 25% selectivity.

The better 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 photo catalytic oxidation. In order to ensure the role of TiO_2, ozone concentration at the outlet of the reactor was measured. At 260 J/l, with SMF and TiO_2/SMF, formation of 350 ppm of ozone was observed, whereas, MnO_x and TiO_2/MnO_x/SMF produced ∼0 ppm. It clearly indicates that the improvement observed with MnO_x/SMF may be due to *in situ* decomposition of ozone that may lead to the formation of strong oxidant atomic oxygen, whereas, TiO_2 modified electrodes are not effective for decomposition of ozone. Thermal activation of TiO_2 catalyst in general requires a temperature in the range 573 to 673 K, whereas, during the present study, the outlet gas temperature never exceeded ∼ 303 K. Hence, it may be concluded that the DBD reactor with catalytic electrode showed higher activity due to synergy between ozone decomposition and photocatalytic action.

In order to ensure the observation that TiO_2 modified electrodes increased the performance of the DBD plasma reactor, benzene conversion was followed at 260 J/l in the concentration range 50–1000 ppm and data was presented in figure 2. As seen from the figure 2a, SMF electrodes followed the same trend as observed earlier.

As the time scales of the reactions taking place in plasma are very small and catalyst may also deactivate due to the solid carbonaceous deposits on the walls of the reactor, long-term performance of the DBD reactor is much warranted. Figure 3, presents the performance of the DBD reactor over a period of time at SIE of 260 J/l during the destruction of 1000 ppm of benzene. As seen from the figure 3, all the catalytic
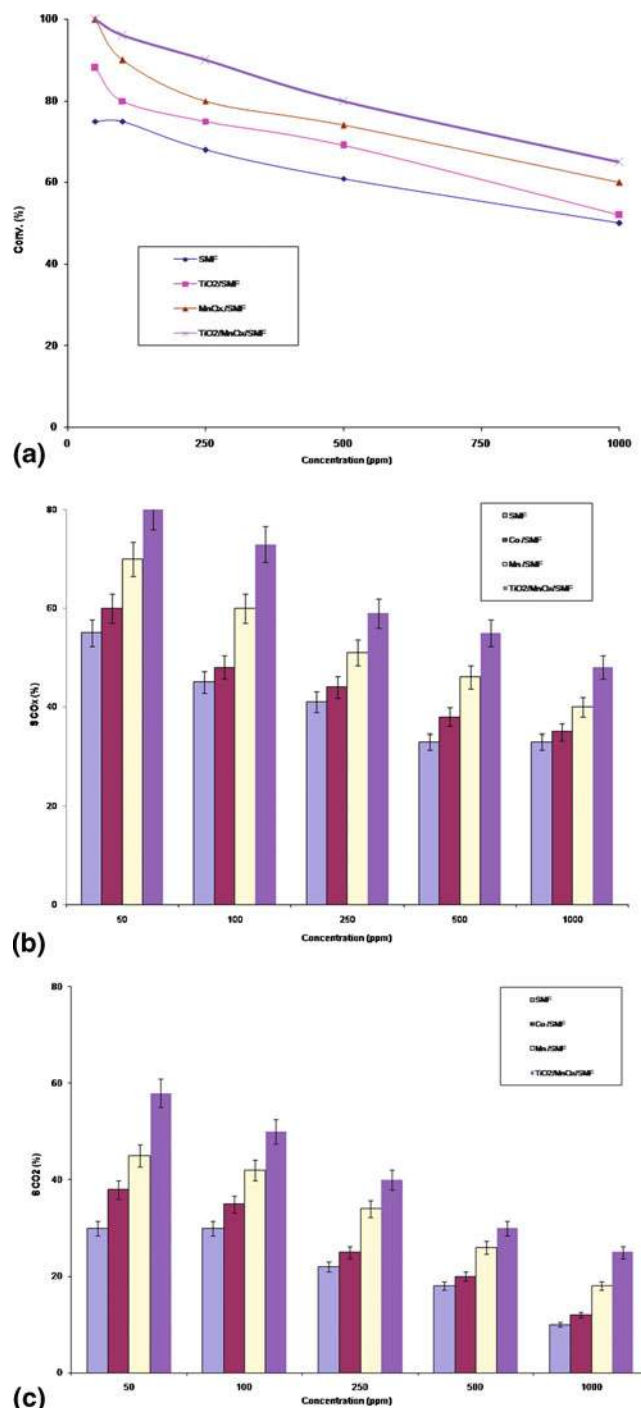

Figure 2. Influene of SMF modification and benzene concentration on (**a**) conversion, (**b**) selectivity to CO_x and (**c**) selectivity to CO_2 at 260 J/l.

electrodes maintain nearly the same activity throughout the course of the reaction. This may be due to the fact that in the present study, as the SMF electrode was used the high voltage electrode, where the microdischarges originate and reach the ground electrode, the carbonaceous deposit may be taking place only on the ground
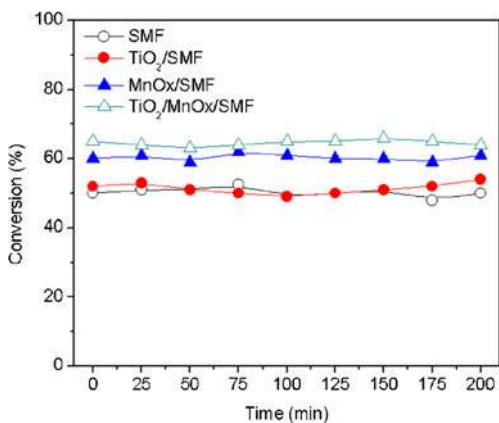
Figure 3. Conversion of 1000 ppm of benzene as a function of time at 230 J/l.

electrode, hence activity of SMF electrodes remains nearly the same.

3.1 *Influence of specific input energy (SIE) on the destruction of 100 ppm of benzene over catalytic SMF electrodes*

Conversion of 100 ppm of benzene was studied as a function of SIE variation between 170 and 320 J/l and the results are presented in figure 4a. As seen in figure 4a, the benzene conversion increases with the increasing SIE. However, at a particular SIE, metal oxide supported SMF electrodes showed higher conversion compared to SMF unmodified electrode. For example, at 320 J/l, SMF electrode showed 80% conversion of benzene, whereas $TiO_2/MnO_x/SMF$ and MnO_x/SMF showed ~90% conversion even at 290 J/l. The better performance of MnO_x/SMF and $TiO_2/MnO_x/SMF$ may

be due to the formation of active oxygen species on metal oxide surface by the *in situ* decomposition of ozone. Figure 4b presents the selectivity to CO_x and CO_2 formed in the above reaction. As seen, metal oxide supported SMF showed ~75% CO_x selectivity at SIE of 290 J/l, whereas, with SMF this was achieved only at 320 J/l. Figure 4b also represents the selectivity to CO_2, which also followed the same trend as conversion and CO_x selectivity. At any SIE, $TiO_2/MnO_x/SMF$ electrode showed higher CO_2 selectivity than MnO_x/SMF, TiO_2/SMF and unmodified SMF. During the present study, at SIE of 320 J/l, ~65% CO_2 selectivity was achieved with $TiO_2/MnO_x/SMF$.

3.2 *Influence of water vapour and catalyst on the decomposition of benzene*

The effect of humidity is of great interest for practical applications in industry since process gas consists of ambient air that usually contains water vapour at fluctuating concentration. Water vapour plays an important role in the plasma chemistry since it may lead to the formation of OH radicals.[27,28] The oxidation power of OH is higher than other oxidants like oxygen atoms and peroxyl radicals generated in NTP. For that purpose, air containing benzene stream was bubbled through water maintained at a constant temperature (298 K) that corresponds to ~3% of water vapour.

Oxidation of 100 ppm of benzene in both dry and humid condition at SIE 260 J/l over MnO_x/SMF electrode was tested. It has been observed that conversion improved in humid air when compared to dry conditions. With MnO_x/SMF under dry conditions conversion was only 85% whereas, on humidifying the gas
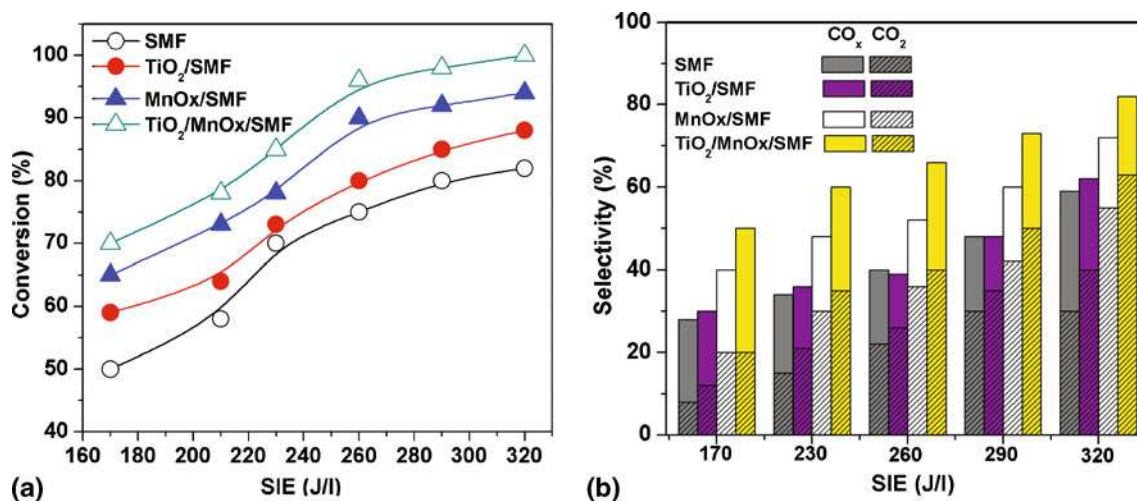

Figure 4. Influence of specific input energy on (**a**) conversion and (**b**) selectivity to the gas products (100 ppm of benzene).

stream, conversion increased to 100%. Another interesting observation is that MnO$_x$/SMF under dry condition showed only 60% selectivity to CO$_x$, which was improved up to 90% under humid condition. The selectivity to CO$_2$ also followed the same trend. Such a difference between dry and wet air condition may be explained by formation of OH radicals in the humid conditions that may lead to high selectivity to total oxidation.[27,28]

However, the presence of water vapour decreases the ozone concentration. During the present study, with MnO$_x$/SMF, in dry air 350 ppm of ozone was observed at 260 J/l that decreased to 75 ppm on humidification. However, water vapour decreased the formation of CO and enhanced the selectivity towards CO$_2$.[29,30] Therefore, it may be reasonable to assume the presence of humidity even though decreases the ozone formation; it improves the selectivity to total oxidation.

As seen from the data presented above, SMF modified with both TiO$_2$ and MnO$_x$ showed improved 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. In the absence of thermal activation, the catalytic activity of TiO$_2$ in NTP may be due to the photocatalysis due to UV light generated in plasma. The synergy between plasma excitation of the VOC molecules and their catalytic oxidation was further enhanced by photocatalysis, since TiO$_2$ absorbs the UV light produced by the NTP. As seen from the figures 1 and 2, the SMF modified with MnO$_2$ and TiO$_2$ is able to oxidize dilute benzene, which is otherwise difficult with the conventional thermo-catalytic techniques.

4. Conclusions

Abatement of low concentration of benzene was studied in a DBD plasma reactor, where the inner SMF electrode was modified with transition metal oxides. Typical results highlighted the better performance of TiO$_2$/MnO$_x$ supported SMF, which may be assigned due to the formation of atomic oxygen on the surface of MnO$_x$ by *in situ* decomposition of ozone; whereas ultraviolet light induced photocatalytic oxidation on TiO$_2$ surface may further promote the oxidation.

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