

Catalytic abatement of volatile organic compounds assisted by non-thermal plasma

Part II. Optimized catalytic electrode and operating conditions

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Abstract

Catalytic purification of air containing 250 ppm of toluene assisted by non-thermal plasma was carried out with a novel dielectric barrier discharge (DBD) reactor with an inner electrode made of sintered metal fibers (SMF). The optimization of the reactor performance was carried out by modifying the SMF with Mn and Co oxides, varying the voltage from 12.5 to 22.5 kV and the frequency in the range of 200–450 Hz. Under the experimental conditions used, the MnO_x/SMF showed better activity than CoO_x/SMF and SMF during the total oxidation of toluene. The complete oxidation of 250 ppm of toluene was possible with the MnO_x/SMF catalytic electrode at the specific input energy (SIE) of ~ 1650 J/l. A higher SIE of ~ 2100 J/l was required with CoO_x/SMF for the total oxidation of toluene to CO_2 . The better performance of the MnO_x/SMF compared to other catalytic electrodes seems to be related to the formation of short-lived species by the in situ decomposition of ozone. XPS analysis of the solid deposit formed on the electrode surface shows the formation of carbonaceous species containing oxygen and nitrogen groups.

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Keywords: Volatile organic compound abatement; Non-thermal plasma; Dielectric barrier discharge; Plasma-assisted catalysis; Sintered metal fibers

1. Introduction

The removal of diluted volatile organic compounds (VOC) from exhaust gas streams is an environmental concern. It has to be handled through efficient and lower energy processes. Traditional thermal and thermo-catalytic technologies are energetically efficient only when the VOC concentration is high enough (>1000 ppm) to work in the autothermal regime [1–3]. Therefore, the need to develop alternate technologies for the abatement of diluted VOCs is warranted. In this context, non-thermal plasma (NTP) offers several advantages over the traditional techniques used for the destruction of VOCs [3,4]. In NTP technique, the electric energy is primarily used for the production of high energy electrons, leaving the bulk of the gas at room temperature [5,6]. Dielectric barrier discharge (DBD) reactor has one or two dielectric barriers to distribute microdischarges throughout the reactor volume. This event

initiates the reactions by electron impact dissociation of organic molecules and ionization of the carrier gas [7]. However, the low selectivity towards total oxidation and the presence of toxic by-products (like CO , NO_x , O_3 and aerosols) limit the application of the NTP technique [7–10]. One of the options to improve the selectivity is to combine plasma with a heterogeneous catalyst to promote oxidative decomposition VOCs [11–20]. The catalyst should effectively utilize the oxidants formed in plasma in order to observe a synergy between plasma and catalyst. In this context, plasma combined with MnO_x catalyst has already shown to be able to promote aromatic hydrocarbon oxidation [4]. Also, it was earlier observed that oxides of Co are promising catalysts during the oxidation of VOCs [21]. In practice, the catalyst can be combined with NTP either by introducing the catalyst in the plasma (in-plasma catalytic reactor, IPCR) or placing the catalyst down stream to the plasma zone (post-plasma catalytic reactor, PPCR). However, both techniques suffer from some disadvantages due to the deactivation of the catalyst by the deposition of hydrocarbon based solid.

In our first publication, a detailed description of the novel DBD reactor with catalytic electrode made of sintered metal fibers (SMF) was reported [22]. Its performance during VOC

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abatement in air was tested for the destruction of toluene (100 ppm). Transition metal oxides (Mn and Co) supported on SMF was observed to improve the selectivity towards total oxidation (CO_2 and H_2O). With this background, the present study was aimed at the optimization of the catalytic electrode by varying with suitable metal oxides, the electrode surface composition, the applied voltage and frequency. The objective was to achieve total oxidation of 250 ppm of toluene. The influence of ozone formed in the catalytic DBD reactor on its performance will be discussed.

2. Experimental

Details of the novel dielectric barrier discharge reactor with catalytic electrode were given in Part-I of the related manuscript [22]. The dielectric discharge was generated in a cylindrical quartz tube with an inner diameter of 18.5 mm. A silver paste painted on the outer surface of the quartz tube acts as the outer electrode, whereas, a modified stainless steel filter SMF was used as the inner electrode. The SMF was modified by Mn and Co oxides via impregnation of SMF by aqueous solutions of metal nitrates followed by calcination at 773 K for 4 h. Typical discharge length was 10 cm and discharge gap 3.5 mm. Throughout the course of the present study, the concentration of toluene and the gas flow rate were maintained at 250 ppm and 500 ml/min (STP), respectively. The specific input energy (SIE) was used in the range of 160–2100 J/l varying the ac high voltage (12.5–22.5 kV) and frequency (200–450 Hz). The V–Q Lissajous method was used to determine the discharge power (W) in the plasma reactor, whereas, the SIE of the discharge was calculated using the relation:

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

In order to examine the influence of the applied voltage and frequency, the toluene destruction was used as a probe reaction by varying the voltage in the range of 12.5–22.5 kV at the fixed frequency of 200, 300 and 350 Hz. In further experiments, the frequency was varied in the range of 200–450 Hz at a fixed voltage of 17.5 kV.

3. Results and discussion

3.1. Influence of the catalytic electrode modification by Mn and Co oxides on the efficiency of the DBD reactor

Fig. 1 shows the dependence of the metal oxide modified SMF electrodes on the performance of the plasma DBD reactor during the abatement of 250 ppm of toluene at a SIE 160 J/l (12.5 kV and 200 Hz). The non-modified SMF showed a conversion of only $\sim 60\%$, whereas the conversion of $\sim 70\%$ was achieved with CoO_x and MnO_x/SMF . A selectivity of $>55\%$ to CO_x was observed for the CoO_x and MnO_x modified electrodes, as compared to 40% only for the SMF. The selectivity towards CO_2 followed the same trend. The highest selectivity of $\sim 30\%$ was observed for MnO_x/SMF as compared to the non-modified SMF electrode, which showed 15%

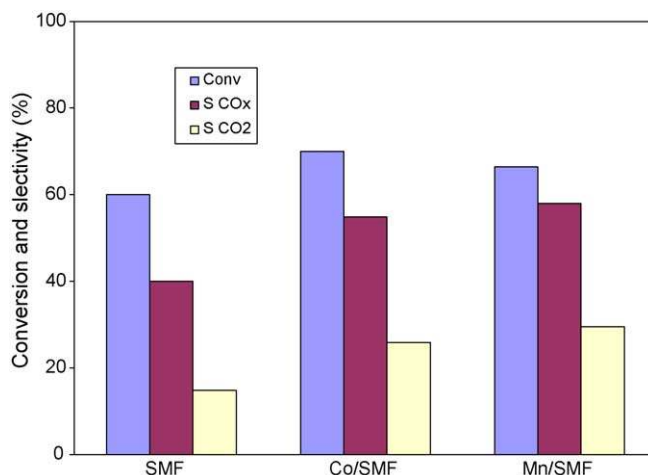


Fig. 1. Influence of the catalytic electrode modification on the toluene conversion and product formation at SIE 160 J/l (250 ppm toluene, 12.5 kV, 200 Hz).

selectivity. As the metal oxide modified SMF electrodes improved the efficiency of the DBD reactor, further studies were focused on the optimization of various operating parameters like voltage and frequency to further improve the total oxidation of toluene (250 ppm).

3.2. Influence of voltage on the efficiency of plasma reactor during destruction of 250 ppm of toluene

Figs. 2 and 3 show the dependency of the applied voltage on the toluene (250 ppm) conversion and selectivity over the catalytic electrodes at a frequency 200 Hz. Using SMF catalyst at 12.5 kV, the observed conversion was $\sim 60\%$ and increased to $\sim 100\%$ at 22.5 kV. A similar behavior was also observed with CoO_x and MnO_x/SMF electrodes, where a 100% conversion of toluene was obtained at the highest applied voltage of 22.5 kV.

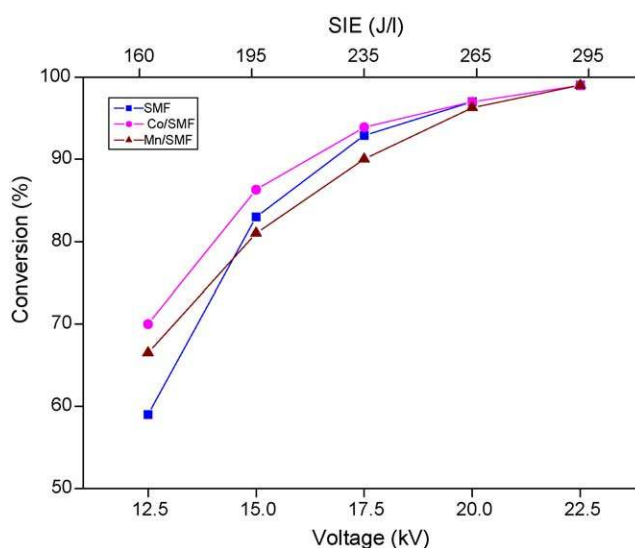


Fig. 2. Influence of applied voltage on the destruction of toluene (250 ppm toluene, 200 Hz).

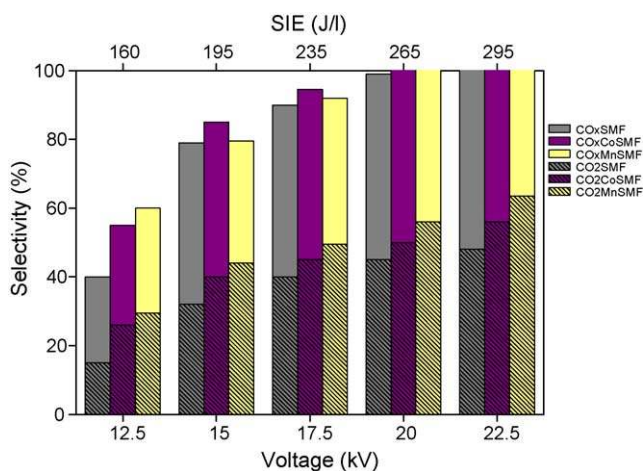


Fig. 3. Influence of applied voltage on the selectivity to CO_x and CO₂ (250 ppm toluene, 200 Hz).

Selectivity to the gaseous products (CO_x) is shown in Fig. 3. Unlike what happens during the destruction of 100 ppm of toluene (Fig. shown in Part-I), where ~100% selectivity to CO_x was observed at 17.5 kV (235 J/l), for 250 ppm of toluene ~100% selectivity to CO_x was achieved only at 20 kV (265 J/l). Hence, a higher SIE (265 J/l) is required to avoid carbon deposit. Fig. 3 also represents the selectivity to CO₂. Interestingly, with increasing SIE, the CO₂ selectivity increases for all electrodes. For example, with MnO_x/SMF, 12.5 kV (160 J/l) the selectivity to CO₂ was around 30%, and reached 65% at 22.5 kV (295 J/l). A similar trend was observed with other catalytic electrodes. The selectivity towards total oxidation of toluene increases on the metal oxide supported SMF electrodes at constant SIE. The MnO_x/SMF showed the best performance towards total oxidation of toluene to CO₂.

3.3. Influence of the applied voltage and frequency on the performance of plasma reactor with MnO_x/SMF electrode

From the previous studies, it follows that changing the voltage between 12.5 and 22.5 kV at 200 Hz frequency (SIE 160–295 J/l) leads to an increase in toluene conversion and CO₂ selectivity. Toluene destruction was studied on MnO_x/SMF electrode changing SIE between 160 and 1650 J/l, by varying the voltage between 12.5 and 22.5 kV and the frequency in the range of 200–350 Hz. Fig. 4 presents the conversion of toluene as a function of voltage and frequency, whereas, Fig. 5 reports the selectivity profiles of MnO_x/SMF to CO_x and CO₂, respectively. As seen from the Fig. 4, irrespective of the applied frequency, conversion >90% was attained at voltage higher than 17.5 kV. Better results were obtained with 200 Hz frequency as a conversion of ~100% was achieved at 295 J/l. A SIE of 450 and 700 J/l was required to achieve ~100% conversion with frequencies of 300 and 350 Hz, respectively. With increasing frequency from 200 to 350 Hz, higher SIE were necessary to attain the total conversion. It is suggested that at low voltage and high frequency, conditions are close to the ignition threshold, where the discharge may not be uniform throughout the reactor volume.

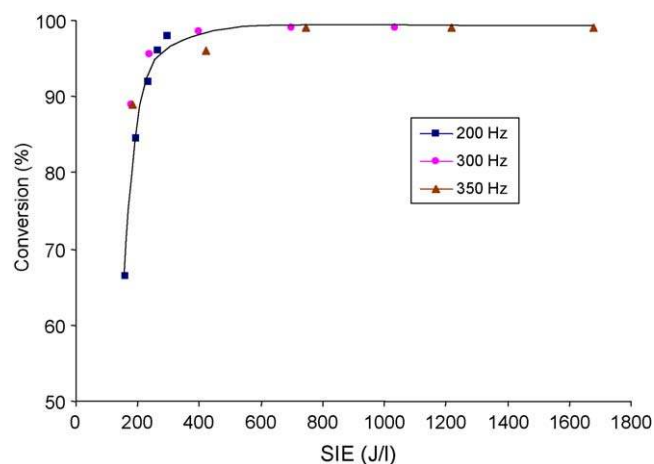


Fig. 4. Influence of SIE on the destruction of toluene with the MnO_x/SMF catalytic electrode (250 ppm toluene, voltage 12.5–22.5 kV).

The selectivity profiles also followed a similar trend. Fig. 5 reports the selectivity to gaseous products formed during the destruction of toluene as a function of SIE. As explained earlier, the observed decrease in CO_x selectivity with increasing frequency at constant SIE may be due to the non-uniform distribution of discharge. The selectivity of solid deposits can be estimated as: $(100 - S_{CO_x})\%$. Increasing both voltage and frequency leads to a higher selectivity to CO_x and also increases SIE. For example, at 180 J/l (12.5 kV and 300 Hz), nearly 40% of the converted toluene was in the form of the surface deposit, whereas, it was ~10% at SIE 400 J/l. By further increasing the SIE to 700 J/l (20 kV and 300 Hz), it was possible to selectively destroy the toluene to CO_x gases without observing carbon based deposits in the DBD reactor with catalytic electrode.

Fig. 5 also shows the CO₂ selectivity profile of MnO_x/SMF electrode as a function of SIE during the destruction of 250 ppm of toluene. The selectivity to CO₂ also follows the same trend as the conversion and selectivity to CO_x (Figs. 4 and 5). At lower SIE (~200 J/l), the CO₂ selectivity was <40%. When SIE was varied in the range of 160–295 J/l (i.e. frequency 200 Hz), the

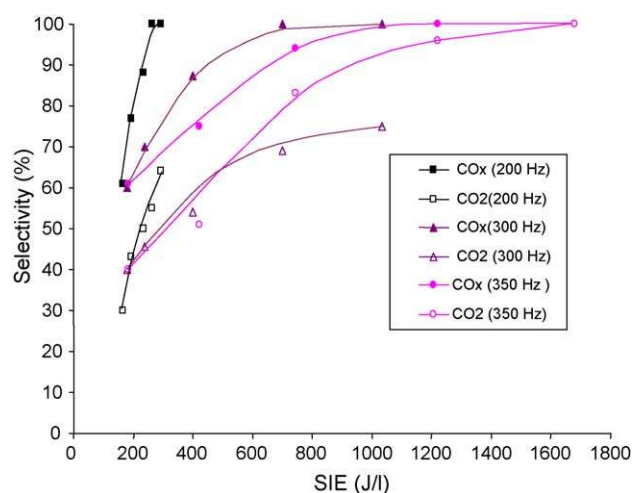


Fig. 5. Influence of SIE on the selectivity to CO_x and CO₂ with the MnO_x/SMF electrode (250 ppm toluene, voltage 12.5–22.5 kV).

maximum selectivity to CO₂ was around 65% at 295 J/l. However, with increasing SIE up to 740 J/l (17.5 kV, 350 Hz) the CO₂ selectivity reached ~80%. Moreover, at the same SIE value both conversion and selectivity to CO_x was ~90%. Hence, at this SIE, the selectivity to CO and to carbon deposit was around 10%. Close to 100% selectivity to CO₂ can be obtained by further increasing SIE. With SIE 1100 J/l, CO₂ selectivity was >95% and reaches 100% at 1650 J/l. During this study, by maintaining the SIE around 740 J/l (17.5 kV and 350 Hz), a better performance of the plasma reactor was achieved. It can be concluded that for an initial toluene concentration of 250 ppm, by operating at a threshold SIE value of 740 J/l, a high selectivity (>80%) towards CO₂ can be achieved.

3.4. Influence of frequency at a constant voltage on the performance of the DBD catalytic plasma reactor

As noticed above, toluene destruction was followed either by changing the voltage and/or the frequency. It was observed that with the MnO_x/SMF electrode it is possible to achieve total oxidation of toluene at 1650 J/l (22.5 kV and 350 Hz). The performance of plasma reactor during the destruction of 250 ppm toluene was tested by varying the frequency in the range of 200–450 Hz at a constant voltage 17.5 kV with SMF, MnO_x/SMF and CoO_x/SMF catalytic electrodes and reported in Figs. 6 and 7. It is seen from Fig. 6, with the lowest frequency of 200 Hz all electrodes showed conversion ~90%, which increases with increasing frequency. When the applied frequency was more than 300 Hz, nearly 100% conversion was achieved. This is also consistent with the observation in Fig. 4, where at 17.5 kV and 300 Hz frequency, a conversion of ~100% was attained.

Fig. 7 demonstrates the selectivity to CO_x and CO₂ as a function of frequency over SMF, CoO_x and MnO_x/SMF electrodes at 17.5 kV. At the lowest frequency for the electrodes

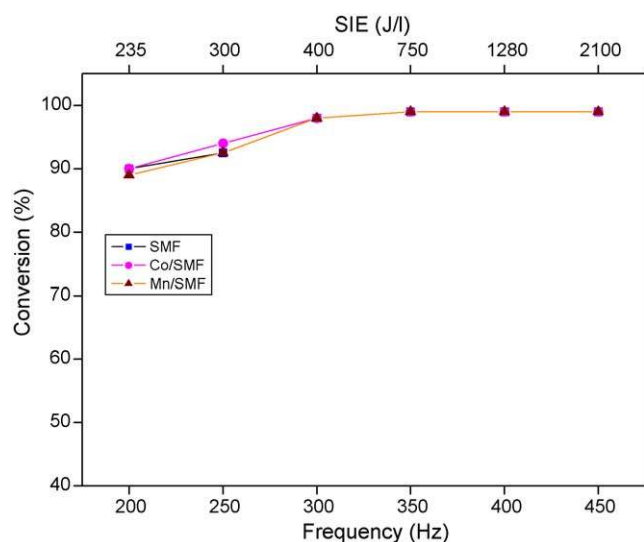


Fig. 6. Influence of frequency on the destruction of toluene (250 ppm toluene, 17.5 kV).

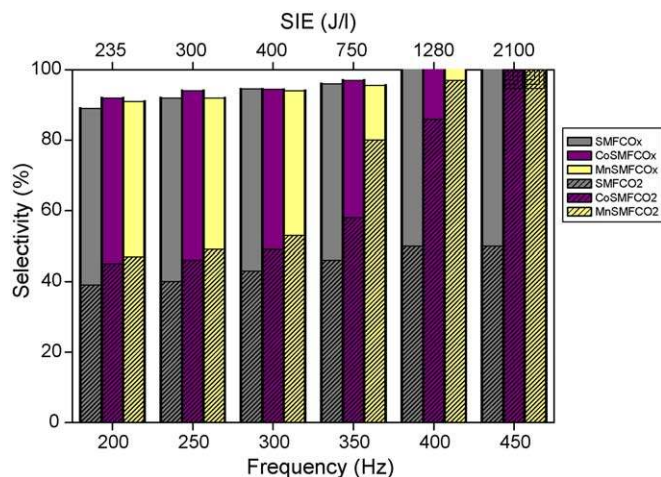


Fig. 7. Influence of frequency on the selectivity to the gaseous products (CO_x and CO₂) (250 ppm toluene, 17.5 kV).

under the study, ~90% selectivity to CO_x and 10% to carbon solid deposit was observed. However, with increased frequency >350 Hz, ~100% selectivity to CO_x was achieved with these electrodes.

Fig. 7 also represents the selectivity to CO₂ over the catalytic electrodes. As seen from the Fig. 7, Mn and Co oxide supported SMF showed higher CO₂ selectivity than unmodified SMF electrode. A significant difference in the selectivity of CO₂ was not observed up to 300 Hz, but at 350 Hz, MnO_x/SMF electrode showed 80% selectivity against ~60% on CoO_x/SMF. An increase in frequency at a constant voltage also increases the SIE: at 350 Hz and SIE of 740 J/l, MnO_x catalyst showed nearly 95% CO_x selectivity with 5% towards carbon deposit. Also important is that CO₂ selectivity was >80%. However, under the same experimental conditions, CoO_x/SMF showed only ~60% CO₂ selectivity. Selectivity to CO₂ increased to >95% at 400 Hz, but at the expense of high input energy ~1300 J/l. It is also possible to achieve 100% selectivity to CO₂ with CoO_x/SMF at SIE of 2100 J/l (450 Hz), but this high input of energy seems not to be realistic from the economic point of view.

3.5. Ozone formation in the DBD plasma reactor

It is known that non-thermal plasma produces ozone from air by the ionization of oxygen molecules [5,7,10,14,15]. There is no direct correlation between the amount of O₃ formed and the observed conversion of VOC during its oxidation by plasma. The decomposition of VOC in the NTP reaction is due to the dissociation under electron impact and also due to the reaction of organic species with ozone and other oxidizing species formed in plasma. In the absence of toluene, the increased SIE increases ozone formation reaching a maximum of 1100 ppm at 195 J/l. Further increase in SIE decreases the ozone concentration and eventually reaches zero at 295 J/l. The decrease in the ozone formation with increase in SIE values may be due to the formation of other reactive species like nitrogen oxides destroying ozone [23,24]. At the same time, the increase of

the in situ temperature of the bulk gas in the plasma reactor at high SIE also cannot be ruled out, as ozone is not thermally stable above 100 °C. However, during the present study, even at a high SIE of 1650 J/l, the maximum outlet gas temperature was <35 °C. Hence, thermal decomposition of ozone in-plasma reactor can be neglected. It is also interesting to note that on the SMF electrode, at SIE of 195 J/l, the presence of toluene diminished ozone formation down to 800 ppm, which further decreased to 500 ppm when metal oxide was supported on SMF electrode. From the data presented above, a higher performance of the plasma reactor was achieved with the MnO_x/SMF catalytic electrode. It is also known that some transition metal oxides decompose ozone, but only at high temperatures. During the present study, the electrodes modified by transition metal oxide changed the product distribution towards total oxidation, whereas, the conversion remains nearly the same. However, the decrease in the ozone concentration at higher SIE suggests in situ decomposition of ozone leading to the formation of reactive oxygen species (atoms) on the oxide surface. These reactive oxygen species are the possible oxidants in this reaction. Similar observation was made earlier during the destruction of benzene when MnO₂ catalyst was placed in the plasma reactor [4].

3.6. XPS study of the carbon deposited on the catalytic electrodes

For both in-plasma and post-plasma catalytic reactors, the deactivation of the catalyst has been reported mainly due to the deposition of carbonaceous species. In order to understand the nature of the deposit formed on the catalytic electrode, the MnO_x/SMF electrode was subjected to a XPS study before and after its use for the destruction of 250 ppm toluene. The XP spectrum of pure MnO_x/SMF shows only peaks corresponding to Mn and oxygen in addition to the peaks corresponding to SMF, but not to the carbon peak. After toluene decomposition, the survey spectrum (not shown) mainly consisted of C and O in addition to a small quantity of nitrogen. Fig. 8 represents the XP spectrum of the MnO_x/SMF electrode in C 1s region after

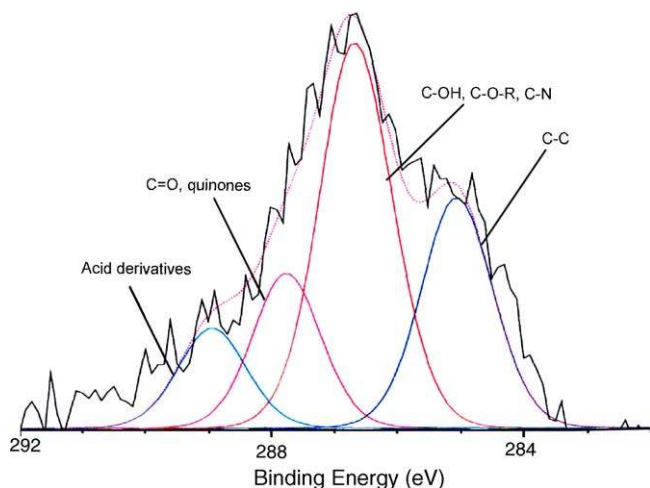


Fig. 8. XP spectrum of the solid carbon deposit (C 1s region).

toluene destruction. Deconvolution of C 1s peak confirms the presence of C–C peak centered at 285 eV. In addition, it also contains a peak between 286 and 287 eV that can be assigned to the presence of C–OH, C–O–R and also to C–N species [25]. Likewise, the peak around 288 eV has been assigned to the presence of carbonyl and quinone groups, whereas, the peak centered on 289 eV confirms the presence of acid derivatives. Since the presence of nitrogen has been confirmed, we assume that a nitrogen containing polymer is formed on the surface of the catalytic electrode.

4. Discussion

The NTP reactor with catalytic electrode shows better performance compared to the plasma reactor using conventional Cu electrode. MnO_x and CoO_x deposited on the SMF electrode significantly increased the product selectivity towards total oxidation (CO₂ and H₂O) especially at high specific input energy (SIE >700 J/l).

There is a need to differentiate the configuration of this reactor with respect to the former developments. Performance of the plasma reactor was observed to increase when the catalyst was placed down stream. This seems to be due to the oxidizing properties of long-lived species mainly ozone and oxides of nitrogen. Other short-lived oxidizing species such as oxygen radical anion O_n^{−1} and activated O₂^{*} can not reach the catalyst surface in down stream configuration [4,7,10,14,15]. In order to utilize them effectively, a high flow rate of the gas should be maintained. But maintaining a high flow rate leads to solid deposits on the catalyst surface.

The second configuration used is in-plasma catalytic reactor, where the catalyst is placed in the discharge zone. The better performance of in-plasma over post-plasma catalytic treatment may be due to a better reaction with the short-lived oxidizing species. However, the main disadvantage with this configuration is the faster deactivation of the catalyst as a result of the carbonaceous deposit.

The novelty of the configuration presented in this study is the use of catalytic SMF as the inner electrode. From the data presented above, the main advantage of using MnO_x(CoO_x)/SMF can be seen from two points: a higher selectivity to CO₂ at low input energy and the minimization of undesired C-solid deposit. During the destruction of 100 ppm toluene, with as low as 160 J/l SIE, a high selectivity up to 80% to CO_x was achieved with the MnO_x/SMF electrode. With a slight increase in the SIE to ~235 J/l, selectivity to CO₂ also increased to 80%. The better performance of MnO_x/SMF compared to others may be due to in situ decomposition of ozone leading to the formation of active oxygen atoms O^{*} on the catalyst surface [4]. One of the plausible explanations for the observed higher activity is that the MnO_x/SMF catalytic electrode facilitates the formation of short-lived oxidizing species that interact with partially oxidized species of toluene. It was earlier reported that on MnO_x surface, a part of the atomic oxygen O^{*} is present in the form of O(³P) [4,26]. The formation and stabilization of O(³P) species on the MnO_x/SMF may be responsible for the better performance of the plasma reactor. The reported DBD reactor

with the catalytic electrode also minimizes the carbon deposit diminishing the deactivation. It has been demonstrated that $\sim 100\%$ selectivity to CO_x and CO_2 can be achieved depending on the voltage and/or frequency used.

5. Conclusions

1. A novel dielectric barrier discharge reactor with a catalytic electrode made of sintered metal fibers (SMF) was designed and optimized for the best performance during the destruction of toluene in air.
2. During the destruction of toluene, CO and CO_2 are the only gaseous products formed in addition to a small amount of solid carbon deposited on the electrodes at a low specific input energy (SIE).
3. Deposition of transition metal oxides (Mn and Co) on SMF shifts the product distribution towards complete oxidation, especially at low SIE. This is important since the combination of catalyst and non-thermal plasma allowed for more efficient air purification at lower energy consumption.
4. At constant SIE, a decreasing frequency increases the selectivity to CO_x and CO_2 .
5. During the destruction of 250 ppm of toluene with SIE ~ 1650 J/l, selectivity $\sim 100\%$ towards total oxidation (CO_2 and H_2O) was achieved with the MnO_x /SMF catalytic electrode.
6. The better performance of MnO_x /SMF compared to other catalytic electrodes may be due to its efficiency in the production of short-lived oxidizing species due to the in situ decomposition of ozone.

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