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## Catalytic non-thermal plasma reactor for abatement of toluene

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#### ABSTRACT

A non-thermal plasma rector with a catalytic electrode made of sintered metal fibres (SMFs) was tested for the oxidative decomposition of a model VOC toluene. The input energy was varied in the range 160–295 J/l by varying the applied voltage between 12.5 and 22.5 kV at 200 Hz. Influence of various parameters like toluene concentration, SMF modification by Mn and Co oxides, input energy and ozone formation was studied. It has been observed that plasma catalytic approach is very effective for total oxidation of toluene at low input energy, especially at toluene concentration ≤250 ppm and SMF modification by transition metal oxides increased the performance of the reactor significantly.  $MnO_x$  modification appears to be a better choice compared to  $CoO<sub>x</sub>$ , which may be attributed to the *in situ* decomposition of ozone leading to the formation of more reactive oxidants like atomic oxygen.

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#### **1. Introduction**

The emission of volatile organic compounds (VOCs) by various industrial and automobile sources into the atmosphere is a concern as many of VOCs are carcinogens and harmful to living organisms [\[1\].](#page-4-0) For the abatement of dilute VOCs (<1000 ppm), conventional techniques like adsorption, thermal, and thermocatalytic oxidation are not suitable, mainly due to high-energy consumption [\[1–3\].](#page-4-0) Among the alternatives, non-thermal plasma (NTP) generated at atmospheric pressure appears to be the energy saving approach. Non-thermal plasma chemical processing of hazardous air pollutants (HAPs) has been extensively investigated [\[1–6\], a](#page-4-0)nd it has been demonstrated as an efficient technique for the decomposing olefinic HAPs. NTP is a combination of energetic electrons, radicals, ions and excited species as well as radiation. In NTP, the electrical energy is primarily used for the production of energetic electrons without heating the flue gas. In dielectric barrier discharge (DBD) the presence of dielectric distributes the microdischarges throughout the discharge volume. These microdischarges initiate the chemical reactions in the gas phase through electron impact dissociation and ionization of the carrier gas [\[7–9\]. H](#page-4-0)owever, NTP abatement of VOCs shows low selectivity (0.3–0.5) to total oxidation ( $CO<sub>2</sub>$  and  $H<sub>2</sub>O$ ) and may result in the formation of undesired and sometimes toxic by-products [\[3,10\]. I](#page-4-0)n order to improve the efficiency of NTP, often catalyst is combined with plasma technique [\[3–10\]. I](#page-4-0)n catalytic plasma technique, a synergy between plasma

excitation and catalysis has been observed mainly when the catalyst is placed in discharge. During the present study, NTP generated by DBD has been used for the abatement of a model VOC toluene, wherein the inner electrode is either a conventional metallic rod or transitional metal oxides modified sintered metal fibre (SMF). Influence of various parameters like VOC concentration, SMF modification and input energy has been studied.

#### **2. Experimental**

A detailed description of the reactor has been given elsewhere [\[11–13\].](#page-4-0) The dielectric discharge was generated in a cylindrical quartz tube with an inner diameter of 18.5 mm. The silver paste painted on the outer surface of the quartz tube acts as the outer electrode, whereas a sintered metal fibre (SMF) filter was used as the inner electrode. The SMF was modified with 3 wt% of Mn and Co oxides via impregnation of aqueous metal nitrate solutions followed by calcination at 773 K for 4 h. The gas flow rate was maintained at 500 ml/min (STP), whereas the concentration of toluene was varied between 100 and 1000 ppm. The specific input energy (SIE) in the range of 160–295 J/l was applied by varying the AC high voltage (12.5–22.5 kV) at a frequency of 200 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

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

VOC concentration at the outlet of the reactor was measured with an online gas chromatograph (Shimadzu 14 B) equipped with a flame ionization detector and a SP-5 capillary column. The dis-

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charge length was 10 cm and the discharge gap was around 3.5 mm. One end of the SMF electrode was connected to AC high voltage through a copper rod, whereas the other end was connected to the inlet gas stream through a Teflon tube. The gas after passing the discharge zone diffuses through the SMF and was analyzed with a gas chromatograph at the outlet. Conversion of toluene at each applied voltage was measured after 30 min. In a similar way, ozone formed in the plasma reactor was measured at 30 min with an UV absorption ozone monitor (API-450 NEMA). The formation of  $CO<sub>2</sub>$  and CO was simultaneously monitored with a pre calibrated infrared gas analyzer (Siemens Ultramat 22). As the volume changes due to chemical reactions are negligible, selectivity of  $CO<sub>2</sub>$  and  $CO<sub>x</sub>$  may be defined as

$$
S_{CO}(\%) = \frac{[CO]}{7.([VOC]_0 - [VOC])}
$$

$$
S_{CO_2}(\%) = \frac{[CO_2]}{7.([VOC]_0 - [VOC])}
$$

 $S_{CO_x} = S_{CO} + S_{CO_2}$ 

#### **3. Results and discussion**

#### 3.1. Performance of DBD rector during the decomposition of toluene

As mentioned in the introduction, NTP technique is expected to be advantageous when the VOC concentration ≤1000 ppm as it is difficult to maintain adiabatic conditions under dilute concentrations. The activity of the designed reactor was earlier reported during the destruction of 250 ppm of selected VOCs of different natures, including toluene. During the present study, concentration of toluene has been changed between 100 and 1000 ppm in order to understand the influence of VOC concentration on the performance of the reactor. Fig. 1 presents the conversion of 1000 ppm of toluene. The applied voltage was varied between 12.5 and 22.5 kV that corresponds to SIE of 160–295 J/l, respectively. As seen from Fig. 1, conversion of toluene increases with increasing the input energy with all the electrodes including the conventional Cu electrode. Interesting observation is that the SMF electrode showed nearly the same conversion as that of the conventional Cu electrode. Conversion over all the catalysts increased from 40% at 12.5 kV (165 J/l) to 90% at 22.5 kV (295 J/l). Also, as seen from Fig. 1 SMF modification with transition metal oxides has not shown any influence. This may be due to the quick deactivation of the catalyst by polymeric products formed in the reaction.

During the oxidative decomposition of toluene, the desired products are  $CO<sub>2</sub>$  and H<sub>2</sub>O. However, in general NTP may lead to undesired products and hence the selectivity to  $CO<sub>2</sub>$  is not 100%. During the present study, no other hydrocarbon except toluene was observed at the outlet, hence  $CO<sub>x</sub>$  selectivity also represents the carbon balance. Fig. 1b presents the selectivity to  $CO<sub>x</sub>$  (CO +  $CO<sub>2</sub>$ ). As seen from Fig. 1b, the selectivity to  $CO<sub>x</sub>$  was poor with all catalysts and was never close to 100%. The Cu and SMF electrodes showed  $CO<sub>x</sub>$  selectivity of 60 and 90% at 160 and 295 J/l, respectively. Hence, with 1000 ppm of toluene, in the SIE range of the present study, the SMF catalytic electrodes showed poor carbon balance. However, SMF modification with  $CoO<sub>x</sub>$  and  $MnO<sub>x</sub>$  results in higher  $CO<sub>x</sub>$  selectivity. Fig. 1b also presents the  $CO<sub>2</sub>$  selectivity. As seen from Fig. 1b, the selectivity to  $CO<sub>2</sub>$  was not impressive on all the catalysts. SMF and Cu electrode showed around 30% selectivity at 295 J/l, whereas,  $CoO<sub>x</sub>$  and MnO<sub>x</sub> modified SMF electrodes showed slightly higher value of 40%.



**Fig. 1.** (a) Influence of SMF modification and SIE on the conversion of toluene (SIE: 160–295 J/l and 1000 ppm of toluene). (b) Influence of SMF modification and SIE on selectivity to  $CO_x$  and  $CO_2$  (SIE: 160–295 J/l and 1000 ppm of toluene).

As seen earlier during the destruction of 1000 ppm of toluene, conversion, carbon balance and selectivity to  $CO<sub>2</sub>$  were not 100% with all the catalysts, which may be due to high concentration of toluene. In order to understand the influence of VOC concentration, toluene concentration has been varied. [Fig. 2](#page-2-0) presents the performance of the catalytic DBD rector for destruction of 500 ppm of toluene. As seen from [Fig. 2a,](#page-2-0) with decreasing concentration of toluene from 1000 to 500 ppm, conversion increases. Also, as seen from [Fig. 2a](#page-2-0) SMF modification with  $CoO<sub>x</sub>$  and MnO<sub>x</sub> showed higher conversion than unmodified SMF, whereas, at 1000 ppm, all the electrodes showed same activity. Hence, the absence of the catalytic effect at 1000 ppm may be due to the quick deactivation of the catalyst, whereas at lower concentration, the catalysts appear to be active. For 500 of toluene, the activity of the studied catalysts followed the trend  $MnO<sub>x</sub>/SMF > CoO<sub>x</sub>/SMF > Cu \geq SMF$ .

[Fig. 2b](#page-2-0) presents the carbon balance during the decomposition off 500 ppm of toluene. The carbon balance increases with increasing the SIE with all the electrodes. At 160 J/l, all the electrodes showed the same carbon balance  $\sim$  65%. With increasing SIE, CoO<sub>x</sub> and  $MnO<sub>x</sub>$  modified electrodes showed better selectivity than unmodified systems. As seen from the figure,  $CoO<sub>x</sub>/SMF$  showed carbon balance close to 100% at SIE 295 J/l, whereas at the same SIE for Cu and SMF the value is only 90%. It is also worth mentioning that for 1000 ppm, metal oxide modification did not increase the car-

<span id="page-2-0"></span>

**Fig. 2.** (a) Influence of SMF modification and SIE on the conversion of toluene (SIE: 160–295 J/l and 500 ppm of toluene). (b) Influence of SMF modification and SIE on selectivity to  $CO<sub>x</sub>$  and  $CO<sub>2</sub>(SIE: 160–295$  ]/l and 500 ppm of toluene).

bon balance, whereas with decreasing concentration by two times, polymeric deposits were reduced significantly. A similar observation has been also made from the  $CO<sub>2</sub>$  selectivity profile given in Fig. 2b. As seen from Fig. 2b, Cu and SMF showed poor  $CO<sub>2</sub>$  selectivity of 10% at 160 J/l that increased to 40% at SIE 295 J/l, whereas under the same conditions,  $CoO<sub>x</sub>$  and  $MnO<sub>x</sub>$  showed  $CO<sub>2</sub>$  selectivity close to 50%.

Fig. 3a and b presents the influence of the applied voltage on the conversion of 250 ppm of toluene. SMF catalyst at 160 J/l shows conversions close to 60% that increases to 100% at 265 J/l. A similar behavior was also observed with  $CoO<sub>x</sub>$  and  $MnO<sub>x</sub>/SMF$  electrodes, where ∼100% conversion of toluene was observed at 235 J/l. As seen from Fig. 3b, for 250 ppm of toluene  $CO<sub>x</sub>$  selectivity ~100% was achieved only at 265 J/l, whereas under the same conditions, for 500 and 1000 ppm of toluene,  $CO<sub>2</sub>$  selectivity was <90%. Hence, during the destruction of 250 ppm of toluene, SIE close to 265 J/l is required in order to avoid carbon deposit. Fig. 3b also represents  $CO<sub>2</sub>$  selectivity, where with increasing SIE, the  $CO<sub>2</sub>$  selectivity also increases for the catalytic electrodes.  $MnO<sub>x</sub>/SMF$ , at 160 J/l the maximum selectivity to  $CO<sub>2</sub>$  was around 30% which reached 65% at 295 J/l. A similar trend was observed with other catalytic electrodes. Hence at lower VOC concentrations, SMF modification by  $MnO<sub>x</sub>$  and  $CoO<sub>x</sub>$  showed improved performance towards total oxidation.



**Fig. 3.** (a) Influence of SMF modification and SIE on the conversion of toluene (SIE: 160–295 J/l and 250 ppm of toluene). (b) Influence of SMF modification and SIE on selectivity to  $CO<sub>x</sub>$  and  $CO<sub>2</sub>(SIE: 160–295$  J/l and 250 ppm of toluene).

In order to ensure the influence of VOC concentration, conversion of 100 ppm of toluene was followed in the same SIE range and the results are presented in [Fig. 4. A](#page-3-0)s seen from [Fig. 4](#page-3-0) with SMF electrode conversion reaches∼100% at 20 kV (265 J/l). Interestingly, with  $CoO<sub>x</sub>$  and MnO<sub>x</sub>/SMF catalytic electrodes, ~100% conversion of toluene was achieved even at 17.5 kV that corresponds to SIE of 235 J/l.

[Fig. 4b](#page-3-0) represents the selectivity to  $CO<sub>x</sub>$  during destruction of 100 ppm of toluene. Selectivity to  $CO<sub>x</sub>$  also increases with increasing voltage and reaches 100% (no carbon deposit) on all catalysts when SIE more than 235 J/l. [Fig. 4b](#page-3-0) represents the selectivity to CO<sub>2</sub> for various catalysts during destruction of 100 ppm of toluene. As seen from [Fig. 4b,](#page-3-0) SMF showed only  $\sim$ 50% selectivity to CO<sub>2</sub> at 295 J/l, whereas  $MnO<sub>x</sub>/SMF$  shows better performance, where the selectivity to CO<sub>2</sub> was ~80% even at 235 J/l (17.5 kV). It is worth mentioning that with  $MnO<sub>x</sub>/SMF$  catalyst, at 17.5 kV, the conversion was ∼100% ([Fig. 4a\)](#page-3-0) and there was no polymeric carbon deposit [\(Fig. 4b](#page-3-0)). Hence, the DBD reactor with catalytic SMF electrode showed remarkable activity during the destruction of 100 ppm of toluene.

As the time scales of the reactions taking place in plasma are very small, decrease in the performance is often observed over a period

<span id="page-3-0"></span>

**Fig. 4.** (a) Influence of SMF modification and SIE on the conversion of toluene (SIE: 160–295 J/l and 100 ppm of toluene). (b) Influence of SMF modification and SIE on selectivity to  $CO_x$  and  $CO_2(SIE: 160-295$  J/l and 100 ppm of toluene).

of time, hence long-term performance of the DBD reactor is much warranted. Fig. 5 presents the performance of the DBD reactor over a period of time at a constant SIE of 235 J/l during the destruction of 1000 ppm of toluene. As seen from the figure, all the catalytic electrodes maintain the same activity throughout the course of the reaction. A similar behavior was observed at different concentrations. This confirms the long-term stability of the electrodes during the destruction of VOC.

#### 3.2. Discussion

As seen from the data presented above, the NTP reactor with catalytic electrodes show better performance compared to the plasma reactor using conventional Cu or SMF electrode. Modification of SMF by  $MnO<sub>x</sub>$  and  $CoO<sub>x</sub>$  increased the product selectivity towards total oxidation (CO<sub>2</sub> and H<sub>2</sub>O). The better performance of CoO<sub>x</sub> and  $MnO<sub>x</sub>/$  SMF may be due to the formation of atomic oxygen by "in situ" decomposition of ozone on the surface of the catalytic electrode [\[11–17\].](#page-4-0) Various attempts were reported earlier combining catalyst with plasma, often referred as 'hybrid reactors'. These hybrid reactors may be classified either as in-plasma or postplasma catalytic reactor, also referred as one-stage and two-stage plasma reactors. This hybrid plasma-catalysis has been extensively investigated and it has been established that the performance of



**Fig. 5.** Conversion of 1000 ppm of toluene as a function of time at 235 J/l.

NTP technique for removal of VOCs can be improved significantly by the addition of catalyst [\[1,7–12,16–24\].](#page-4-0) Advantages of using plasma-catalysis systems over NTP include increase in conversion of VOC at low input energy, higher selectivity to total oxidation and decrease in undesired by-products. A synergistic effect has also been reported during catalytic plasma technique, especially when the catalyst was placed in the discharge zone [\[11–13\].](#page-4-0) Another advantage is that the VOCs can be decomposed at ambient temperatures, where in general, the catalyst will not be active. The main oxidizing species formed by NTP when produced in air is ozone, even though other oxidizing species like hydroxyl radicals and ultraviolet light were reported [\[13\].](#page-4-0) Influence of ozone has been reported in two ways: either during direct interaction with the VOCs or may lead to the formation atomic oxygen on the catalyst surface. The former process increases the conversion, whereas the latter process may increase the  $CO<sub>2</sub>$  selectivity.

In-plasma catalytic rector, where the catalyst is placed in the discharge zone shows better performance over post-plasma catalytic treatment, probably due to a better reaction condition like ready availability of other short-lived oxidizing species and ozone. Synergy was thought to be limited to when the catalyst is placed inside the discharge region. In one-stage configuration, the synergistic effect may be due to the increase in concentration of short-lived excited species on the surface of the catalyst and the effect of photons and electrons generated in the plasma. It was earlier shown that the presence of ultraviolet light also increases the efficiency of the NTP reactor [\[13\]. I](#page-4-0)n addition plasma catalytic systems have been shown to follow zero-order kinetics during VOC decomposition, indicating the importance of surface reactions, hence this configuration is expected to show promising results [\[23\].](#page-5-0) However, the main disadvantage with this configuration is the faster deactivation of the catalyst as a result of the carbonaceous deposit.

A higher performance of the NTP technique has also been reported when the catalyst was placed down stream to discharge zone in post-plasma reactor. 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<sub>n</sub><sup>-1</sup> and activated O<sub>2</sub><sup>\*</sup> cannot reach the catalyst surface in downstream configuration [\[12\]. I](#page-4-0)n 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 [\[12\].](#page-4-0)

The reactor studied in the present case is a modified single stage reactor, where the catalyst component was integrated on SMF

<span id="page-4-0"></span>



electrode. The specific advantage, as seen from the data presented above, is the high selectivity to total oxidation at any SIE as opposed to nearly the same conversion. Direct catalytic oxidation of VOCs may be neglected due to the low quantity of the catalyst (3 wt%) and also the time scales of plasma activation of VOCs and direct catalytic action are different. In order to understand the role of the ozone, its concentration with and without SMF modification was studied. There is no direct correlation between the amount of  $O<sub>3</sub>$  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. It is known that reaction between ozone and toluene in the gas phase is very slow (1.2 × 10<sup>-20</sup> cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>)[\[22\]](#page-5-0) compared to the reaction of toluene with atomic oxygen (5.7  $\times$  10<sup>-12</sup> cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) indicating that without catalyst ozone may not show any gas phase reactivity with toluene [\[22\].](#page-5-0) As reported recently, in onestage configuration, electron-induced processes, surface discharges and short-lived radicals are potential active species as opposed to long-lived species like ozone and oxides of nitrogen in a twostage configuration. Although decomposition of ozone to oxygen is a thermodynamically favored process, temperature higher than 373 K is required. At lower temperatures, a catalyst is necessary for ozone decomposition, producing active species on the catalyst surface that may induce secondary oxidation reactions [\[23\]. D](#page-5-0)ue to its long lifetime ozone is of importance in both one and two-stage plasma systems. In the two-stage configuration, ozone may still be present in significant concentrations and partial oxidation of the VOCs may take place with ozone in the gas phase. It is believed that the conversion of VOCs is mainly due to ozone acting either directly or indirectly via adsorption or decomposition on catalyst surfaces, leading to the formation of strongly oxidizing species, such as atomic oxygen [\[23\]. T](#page-5-0)o understand the role of ozone, its concentration was measured in the present study.

In the absence of toluene, with increasing SIE, ozone formation increases and reaches to a maximum of 1100 ppm at 195 J/l and reaches zero at 295 J/l. The decrease in the ozone formation with increase in SIE may be due to the formation of other reactive species like nitrogen oxides destroying ozone [\[21\]. A](#page-5-0)t 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 373 K. As seen from Fig. 6, in the presence of toluene, at 195 J/l, ozone formation decreased to 800 ppm, which was further decreased to 500 ppm when SMF was modified with  $MnO<sub>x</sub>$ and  $CoO<sub>x</sub>$ . From the data presented above, a higher performance of the plasma reactor was achieved with the  $MnO<sub>x</sub>/SMF$  catalytic electrode. SMF modification by metal oxide mainly resulted in high selectivity rather conversion. This may be due to in situ decomposition of ozone leading to the formation of reactive oxygen species (atoms) on the catalyst surface. These reactive oxygen species are the possible oxidants in this reaction. Similar observation was made earlier during the destruction of benzene when  $MnO<sub>2</sub>$  catalyst was placed in the plasma reactor [\[22\].](#page-5-0)

#### **4. Conclusions**

A catalytic plasma reactor with the inner electrode made of sintered metal fibre was designed and tested for the oxidative decomposition of toluene. It has been observed that modification of SMF with transition metal oxides not only increased the conversion of toluene at low consumption of VOC, but also increased the total oxidation selectivity. Better results were obtained at low concentration of VOC, especially for 100 ppm of toluene.

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