Catalytic Plasma Reactor for Abatement of Dilute Nitrobenzene

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Abstract: Oxidative decomposition of dilute nitrobenzene in air was carried out in a catalytic plasma reactor with an inner electrode made of sintered metal fibres (SMF) that also acted as catalyst. The parameters of the concentration, specific input energy, and gas residence time were optimized. The modification of the SMF inner electrode with transition metal oxides like MnO_x and CoO_x oxides promoted complete oxidation, especially at low input energy. CoO_x/SMF showed higher activity than MnO_x/SMF and SMF, and could oxidise completely 100 ppm of nitrobenzene at 300 J/L.

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Volatile organic compounds (VOCs) are the primary toxic pollutant emitted from chemical industrial and automobile exhausts. Some VOCs are carcinogens and harmful to living organisms [1,2]. Nitrobenzene is widely used in many industrial processes as raw material or solvent and in the manufacture of lubricant oils and dyes. In addition, pesticides and drugs also contain large amounts of nitrobenzene. Excessive exposure to nitrobenzene may affect the reproductive system and also may cause skin cancer [3]. To limit the adverse health effect of nitrobenzene, many countries have emission regulations for it. Many techniques including the use of a nonthermal plasma (NTP) have been tested for the abatement of nitrobenzene. However, many of the techniques are not useful for the removal of nitrobenzene present at low concentrations. Conventional techniques for VOC abatement are thermal oxidation, catalytic oxidation, and carbon adsorption [4,5]. The thermal oxidation and catalytic oxidation methods have the drawback of high operating temperatures. Carbon adsorption is relatively simple but needs a secondary treatment for the removal of adsorbed contaminants. Since the conventional methods are effective only when the VOC concentration is higher than 1000 ppm, there is a need to develop an alternate, efficient, and low energy process. In this regard, the NTP has unique advantages, like ease of operation and presence of highly energetic electrons, over the conventional methods for the removal of VOCs in the gas phase. NTP can generate highly energetic electrons and operate at atmospheric pressure with the background gas at ambient conditions [6–9]. Moreover, when operated in air, NTP produces potentially active spe-

cies like N₂⁺(A³Σ_u⁺), N₂⁺(B³Π_u⁺), O₂⁺(a¹Δ_g), O(¹D), O(³P), and N(⁴S) in addition to ozone [9,10]. Dielectric barrier discharge (DBD), one of the NTP techniques, has the advantages of a uniform distribution of the micro-discharges throughout the discharge. These micro-discharges initiate the chemical reaction by electron impact dissociation of organic molecules as well as ionization of the carrier gas.

The NTP technique has been employed successfully for the destruction of various VOCs like aromatics, aliphatic hydrocarbons [11–14], and inorganic pollutants such as SO₂, H₂S, and NO_x [15–17]. One of the limitations of the NTP technique is low selectivity towards total oxidation. To some extent, the selectivity can be improved by combining NTP with heterogeneous catalysts [18–20]. The action of the catalyst is to utilise the oxidants formed in the plasma to bring about a synergy between plasma and catalytic action [21,22]. In the present study, the design of a DBD reactor for the complete oxidation of nitrobenzene was studied with a modified inner electrode made of sintered metal fibres (SMF). The objective was to achieve the total oxidation of dilute nitrobenzene. Optimization of various parameters like catalyst, input energy, concentration of VOC, and formation of ozone on the performance of the plasma reactor was performed.

1 Experimental

Nitrobenzene was introduced into the reactor by a motor driven syringe pump. It was diluted with air. The gas flow

rate was varied between 250 to 750 ml/min by a mass flow controller (MFC, Alborg). The input concentration of nitrobenzene was varied between 100 to 500 ppm by adjusting the gas flow rate. The reactor outlet was connected to a gas chromatograph (Varian 450) equipped with a FID detector and a GP capillary column (50 m length, 0.25 mm diameter, and 0.5 μm film thickness) to measure the nitrobenzene conversion. The products (CO , CO_2) formed during nitrobenzene oxidation was measured by an infrared analyzer. The selectivities for CO_2 and CO_x used were

$$S_{\text{CO}_2}(\%) = \frac{[\text{CO}_2]}{6([\text{VOC}]_{\text{IN}} - [\text{VOC}]_{\text{OUT}})} \times 100$$

$$S_{\text{CO}_x}(\%) = \frac{[\text{CO}_x]}{6([\text{VOC}]_{\text{IN}} - [\text{VOC}]_{\text{OUT}})} \times 100$$

where $[\text{CO}_x]$ and $[\text{CO}_2]$ are the outlet concentrations of CO_x and CO_2 , respectively, and $[\text{VOC}]_{\text{IN}}$ and $[\text{VOC}]_{\text{OUT}}$ are the initial and final concentrations of nitrobenzene, respectively. Since partially oxidized products were not observed in the present work, the selectivity for CO_x also represented the mass balance. Ozone concentration in the plasma reactor was measured with an UV absorption ozone monitor (API-450 NEMA).

1.1 Catalyst preparation

SMF filters made of stainless steel with 0.29 mm thickness, 80% porosity, and 675 g/m^2 surface area were used as the inner electrodes. Their modified counterparts with a deposited catalyst (MnO_x/SMF and CoO_x/SMF) were also used. For the deposition of 5 wt% MnO_x and CoO_x , the SMF was first oxidised at 873 K for 3 h, followed by impregnation with Co or Mn nitrate solution. Drying at room temperature and calcination at 773 K for 5 h gave a metal oxide catalytic film deposited on SMF. Finally, the SMFs were shaped into a cylindrical form with a diameter of 12.5 mm.

1.2 Plasma reactor and discharge characterization

The details of the DBD reactor have been given elsewhere. It is shown in Fig. 1 [22]. The discharge was generated in a cylindrical glass tube with an inner diameter of 18.5 mm and a wall thickness of 1.5 mm. Silver pasting on

Fig. 1. Schematic of the DBD plasma reactor [22].

the outer surface of the glass tube acted as the outer electrode. The modified SMF cylinder was the inner electrode. The discharge length was 10 cm and discharge gap was fixed at 2.5 mm. One end of the SMF electrode was connected by a stainless steel rod to an alternating current (AC) high voltage source. The other end was connected by a teflon tube to the gas chromatograph. The discharge was generated by applying an AC high voltage in the range of 14–22.0 kV (peak to peak), which was generated by a high voltage source (Jayanthi Transformer) at 50 Hz. The reacting gas passing through the discharge zone diffused through the SMF electrode. The conversion of nitrobenzene was recorded after 30 min.

The electrical circuit is shown in Fig. 2. The voltage-charge (V-Q) Liassajous method was used to determine the discharge power generated in the reactor. Figure 3 shows a typical V-Q Lissajous figure for 22 kV at a frequency of 50 Hz. The area of the V-Q figure is the energy dissipated. The discharge power was calculated by multi-

Fig. 3. V-Q Lissajous figure of the DBD reactor at 300 J/L.

Fig. 2. Electrical circuit of the reactor used.

plying the area of the V-Q figure with the frequency. The specific input energy (SIE) of the discharge was calculated using $\text{SIE (J/L)} = \text{Power (W)} / \text{gas flow rate (L/s)}$. Increasing the applied voltage increased the power and SIE. For example, at 50 Hz and 500 ml/min, SIE was increased from 60 (14 kV) to 310 J/L (22.0 kV).

2 Results and discussion

2.1 Effect of applied voltage on the destruction of nitrobenzene

The conversion of 100 ppm of nitrobenzene was followed as a function of the SIE. The conversion increased with increasing SIE. Figure 4(a) shows the activity of different catalytic electrodes during the conversion of 100 ppm of nitrobenzene for applied voltages of 14 to 22.0 kV, which corresponded to SIE of 60 and 310 J/L, respectively. With the SMF electrode, the nitrobenzene conversion reached 67% at 310 J/L. CoO_x/SMF and MnO_x/SMF electrodes under the same conditions showed 80% and 90% conversion, respectively. The improved performance with CoO_x/SMF and MnO_x/SMF electrodes may be due to the formation of active oxygen species on the metal oxide surface by in situ decomposition of ozone. One of the major problems in plasma catalytic techniques is the deposition of polymerized products on the electrode. But in the present study, no carbon deposit was observed in the DBD reactor with any of the catalytic electrodes (~100% selectivity for CO_x). Figure 4(b) shows the selectivity for CO_2 of the different catalysts in the destruction of 100 ppm of nitrobenzene. Nitrobenzene was completely oxidised. As compared with SMF and MnO_x/SMF , the CoO_x/SMF electrode had the highest activity. Even at 100 J/L, MnO_x/SMF gave a conversion of 70%, which reached 90% at 310 J/L, but the CoO_x/SMF electrode showed still better performance.

Fig. 4. Influence of SIE on nitrobenzene conversion (a) and CO_2 selectivity (b) with different catalytic electrodes.

Fig. 5. Influence of SIE and flow rate on nitrobenzene conversion (a) and CO_2 selectivity (b) for 500 ppm of nitrobenzene.

2.2 Influence of residence time on the reactor performance

The influence of flow rate and concentration at a fixed discharge gap on nitrobenzene decomposition was studied. The flow rates were 250, 500, and 750 ml/min, which corresponded to gas residence times of 3.1, 1.5, and 1.03 s, respectively. The initial concentration was 500 ppm. Figure 5(a) shows the conversion of nitrobenzene as a function of SIE. Nitrobenzene conversion increased with increasing SIE and decreasing flow rate. For 3.1 s residence time, nitro-

benzene conversion reached 100% at a SIE of 684 J/L, which decreased to 95% and 85% for 1.5 and 1.03 s that corresponded to the SIE of 324 and 216 J/L, respectively. Figure 5(b) shows the selectivity for CO_2 as a function of SIE. From the Fig. 5(b), a longer residence time of the gas gave a better performance.

The influence of initial concentration was studied. Typical results are presented in Fig. 6(a). The conversion of nitrobenzene at different concentrations as a function of SIE and initial concentration varied between 400 and 800 ppm. The conversion of nitrobenzene decreased with increasing inlet concentration of nitrobenzene. The removal efficiency for 400 ppm of nitrobenzene at SIE of 324 J/L was ~95%, which decreased to ~85% for 600 and 800 ppm. Figure 6(b) presents the selectivity for CO_2 as a function of SIE. For 400 ppm of nitrobenzene, the selectivity for CO_2 was ~90% at a SIE of 324 J/L, which decreased to 75% for 800 ppm.

Fig. 6. Influence of SIE and concentration of nitrobenzene on nitrobenzene conversion (a) and CO_2 selectivity (b) for different concentrations.

2.3 Influence of initial concentration of nitrobenzene on the reactor performance

To understand the influence of the concentration of nitrobenzene on the performance of the reactor, the initial concentration was varied between 100 and 500 ppm at a SIE of 190 J/L. The results are presented in Fig. 7(a). The conversion decreased with increasing concentration of nitrobenzene from 100 to 500 ppm. With the SMF electrode at a SIE of 190 J/L, for 100 ppm of nitrobenzene, the conversion

was ~60%, which decreased to 30% for 500 ppm. A similar trend was observed for the DBD reactor with the CoO_x/SMF and MnO_x/SMF electrodes. Of the two catalysts, CoO_x/SMF showed the better activity.

Figure 7(b) presents the selectivity for CO_x ($\text{CO}_2 + \text{CO}$) as a function of concentration of nitrobenzene, which was varied between 100 and 500 ppm. As partially oxygenated products were not detected at the outlet of the reactor, CO_x selectivity also was the carbon balance of the reaction. For 100 ppm of nitrobenzene, with the SMF electrode, there was ~90% selectivity for CO_x , whereas for 500 ppm, it was only 60% and the remaining 40% was in the form of undesired solid deposits. Interestingly, the selectivity for CO_x was high with the modified SMF electrodes, where for 100 ppm, ~100% selectivity for CO_x was observed. Figure 7(c) presents the selectivity for CO_2 , which decreased significantly with increasing nitrobenzene concentration. For 100 ppm, the SMF electrode showed 70% selectivity for CO_2 , which dropped to 40% for 500 ppm. It is worth pointing out that

Fig. 7. Influence of the initial concentration of nitrobenzene on nitrobenzene conversion (a), CO_2 selectivity (b), and CO_x ($\text{CO} + \text{O}_2$) selectivity (c) at SIE of 190 J/L.

the modified SMF electrodes showed a higher selectivity for CO_2 , especially for the nitrobenzene concentration of 100 ppm.

2.4 Ozone formation in the DBD reactor

It is known that NTP produce ozone from air by the ionization of oxygen molecules [23,24]. In the catalytic plasma approach, the role of the catalyst is to facilitate in situ decomposition of ozone to produce the highly active atomic oxygen oxidant [19,25–28]. Figure 8 shows the influence of the catalytic electrodes on in situ ozone decomposition. At 100 J/L, ozone formation was 720 ppm with the SMF, which decreased to 450 and 280 with the CoO_x/SMF and MnO_x/SMF electrodes, respectively. The interaction of ozone with the metal oxide catalyst probably increased the formation of reactive atomic oxygen, which resulted in improved performance. CoO_x/SMF showed a higher activity than MnO_x/SMF . Further studies are in progress to understand the higher activity of CoO_x over MnO_x .

Fig. 8. Activity of the SMF electrodes during ozone decomposition. Applied voltage = 16 kV.

3 Conclusions

The oxidative decomposition of low concentrations of nitrobenzene was carried out in a catalytic plasma reactor with a modified inner electrode, and the reactor was optimized for a better performance. The modification of the SMF inner electrode with transition metal oxides like MnO_x and CoO_x promoted total oxidation, especially at low concentrations. In the removal of 100 ppm of nitrobenzene, the selectivity to CO_2 was ~100% at 300 J/L with the CoO_x/SMF catalytic electrode, which gave a higher activity than MnO_x/SMF .

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