

Catalytic non-thermal plasma reactor for total oxidation of volatile organic compounds

Ch Subrahmanyam

Department of Chemistry, National Institute of Technology Trichy (NITT),
Trichy 620 015, India

Email: csubbu@nitt.edu, challa168@hotmail.com

Received 11 May 2009; revised and accepted 15 July 2009

A dielectric barrier discharge reactor with inner electrode modified with metal oxides of Ti, Mn and Co has been designed and tested for the oxidation of diluted volatile organic compounds (VOCs) of different nature like toluene, isopropanol and trichloroethylene. It has been observed that at a fixed concentration of VOC, total oxidation of isopropanol is achieved at lower specific input energy compared to toluene and trichloroethylene. Among the catalysts studied, MnO_x/SMF shows the best performance, probably due to the formation of active oxygen species by in situ decomposition of ozone on the catalyst surface. The electrodes modified with MnO_x and TiO_2 catalyst effectively destroy trichloroethylene due to the synergy between plasma excitation of the trichloroethylene molecules and catalytic behaviour. The catalytic process is further enhanced by photocatalysis since TiO_2 absorbs UV light produced by the non-thermal plasma.

Keywords: Catalysis, Photocatalysis, Oxidations, Photooxidation, Non-thermal plasma, Volatile organic compounds

IPC Code: Int. Cl.⁹. B01D53/70; B01D53/86; B01J21/06; B01J23/24; H05H1/24

The emission of volatile organic compounds (VOCs) by various industrial and automobile sources into the atmosphere is an important source of air pollution and social concern as VOCs are precursors of photochemical oxidants and suspended particulate matter (SPM) that have an adverse impact on human health. Therefore, abatement of VOCs is an important issue that has to be handled through highly efficient, low cost processes. For the abatement of dilute VOCs (≤ 1000 ppm), conventional techniques like thermal and thermocatalytic oxidation are not suitable mainly due to high energy demand¹⁻⁵. Among the alternatives, non-thermal plasma (NTP) generated at atmospheric pressure seems to be advantageous. The plasma, also called the fourth state of matter, is characterized by ionization of a gas giving a wide range of species such as energetic electrons, radicals, ions and excited species as well as radiation⁶. 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 a dielectric distributes the microdischarges throughout the discharge volume. These microdischarges initiate chemical reactions in the gas phase through electron impact dissociation and ionization of the carrier gas⁷⁻⁹. However, NTP abatement of VOCs shows low

selectivity (0.3-0.5) to total oxidation (CO_2 and H_2O), resulting in undesired and sometimes toxic byproducts like CO, O_3 , NO_x and partially oxidized hydrocarbons¹⁰. In order to improve the efficiency of NTP, catalytic plasma technique has been proposed where the catalyst can be either placed in discharge zone (in-plasma catalytic reactor or plasma driven catalysis) or downstream to discharge zone (post-plasma catalytic reactor or plasma enhanced catalysis). Even though in-plasma configuration is found to be promising for the abatement of VOCs, deactivation of the catalyst by solid carbon deposits limits the application of this technique. To some extent, deactivation can be minimized by placing the catalyst downstream to plasma zone. A better performance with a post-plasma catalytic treatment has been reported^{1,5,11}. However, contrary to in-plasma technique, where short lived plasma species promote the reaction, during post-plasma catalytic process, oxidation of effluents is mainly due to long-lived species like ozone and oxides of nitrogen¹². Therefore, a synergy between plasma excitation and catalysis is expected only when the catalyst is placed in discharge^{13,14}. Hence, there is a need for a new configuration of plasma catalytic reactors to realize the potential of in-plasma catalytic treatment.

Recently, we have reported a DBD reactor, where the inner electrode made of sintered metal fiber (SMF) filters also acts as the catalyst^{15,16}. The SMF electrode was modified by transition metal oxides in order to improve the efficiency of plasma reaction. In the present study, abatement of model VOCs of different nature like toluene, isopropanol (IPA) and trichloroethylene (TCE) has been tested to evaluate the performance of the catalytic DBD reactor. Influence of applied voltage, frequency, ozone and the ultraviolet light (UV) produced in the discharge on the performance of DBD reactor has also been studied.

Materials and Methods

Sintered metal fibers (SMF, Southwest Screens & Filters SA, Belgium) made of stainless steel consisting of thin uniform metal fibers of diameter 30 μm , wetness capacity of ~ 30 wt% and porosity of ~ 80 wt% were used in the present study. For the preparation of 3wt% MnO_x and CoO_x , the SMF was oxidized at 873 K for 3 h, followed by impregnation with Co and Mn nitrate aqueous solutions of desired concentration. TiO_2/SMF and $\text{TiO}_2/\text{MnO}_x/\text{SMF}$ were prepared by precipitation of Ti(IV) bis (ammonium lactato) dihydroxide (50 wt%) solution in water. Drying at room temperature followed by calcination in air at 773 K for 5 h resulted in catalytic electrodes of metal oxide supported on SMF. The TiO_2 , CoO_x and MnO_x/SMF contained 3 wt% of the metal oxide, whereas $\text{TiO}_2/\text{MnO}_x/\text{SMF}$ contained 1 and 3 wt% of TiO_2 and MnO_x , respectively. XPS analysis confirmed the formation of metal oxides on SMF, while transmission electron microscopy coupled with diffraction pattern confirmed the formation of titania anatase¹⁷. Finally, SMF filters were subjected to an electrical hot press to shape them into cylindrical form, giving the desired discharge gap.

Plasma reactor

A detailed description of the DBD reactor is reported elsewhere¹⁵. Briefly, 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 acted as the outer electrode, and a modified SMF was used as the inner electrode. The discharge length was 10 cm and discharge gap was fixed at 3.5 mm during the destruction of toluene and IPA, and 1.25 mm for TCE. The specific input energy (SIE) in the range 140-1100 J/l was applied by varying the AC high

voltage (12.5-22.5 kV) and frequency (200-250 Hz). Conversion of VOC at each voltage was measured after 30 min. A voltage (V)-charge (Q) Lissajous method was used to determine the discharge power (W) in the plasma reactor, where the charge Q (i.e. time integrated current) was recorded by measuring the voltage across the capacitor of 220 nF connected to the ground electrode. The voltage was measured with a high voltage probe (Luke 80 K-40 HV). The signals of V and Q were recorded with a digital oscilloscope (Tektronix, TDS 3054) and plotted to get a typical V-Q Lissajous diagram.

Procedure

The experimental set-up consisted of a motor driven syringe pump for the introduction of VOC, which was mixed with air [500 ml/min (STP) for toluene, IPA and 700 ml/min for TCE] and was fed into the plasma reactor with a Teflon tube. VOC concentration at the outlet of the reactor was measured with a gas chromatograph (Shimadzu 14 B) equipped with a flame ionization detector and a SP-5 capillary column. The formation of CO_2 and CO was simultaneously monitored with an infrared gas analyzer (Siemens Ultramat 22), whereas ozone formed in the plasma reactor was measured with UV absorption ozone monitor (API-450 NEMA). The emission spectrum of the discharge at 20 kV was measured with a SM-240 spectrometer (CVI Spectral Products) with a Sony ILX511 CCD linear array detector. As the volume changes due to chemical reactions are negligible, selectivity of CO_2 and CO_x was defined as follows,

$$S_{\text{CO}} (\%) = \frac{[\text{CO}]}{X([\text{VOC}]_0 - [\text{VOC}])} \times 100$$

$$S_{\text{CO}_2} (\%) = \frac{[\text{CO}_2]}{X([\text{VOC}]_0 - [\text{VOC}])} \times 100$$

$$S_{\text{CO}_x} = S_{\text{CO}} + S_{\text{CO}_2}$$

where x = 7, 3 and 2 for toluene, IPA and TCE, respectively.

Results and Discussion

Figure 1 represents a typical V-Q Lissajous plot for 22.5 kV, 17.5 kV and 12.5 kV at a frequency of 250 Hz for a discharge gap of 1.25 mm. The area of the Lissajous plot characterizes the energy dissipated during one period of the voltage. The average power (W) in the discharge was calculated by multiplying the

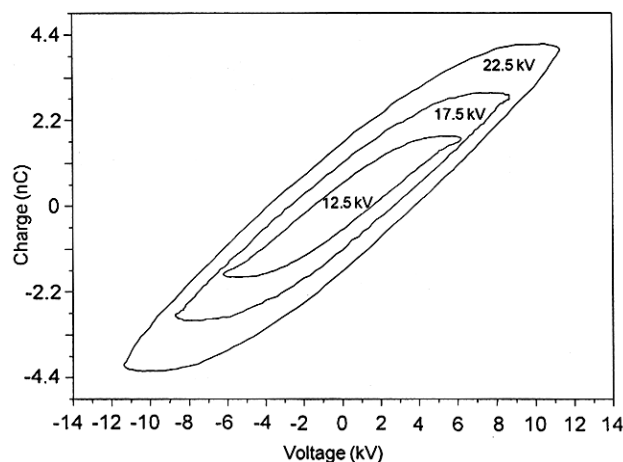


Fig. 1 — V-Q Lissajous plot at different voltages at 250 Hz.

area by the frequency. The specific input energy (SIE) of the discharge was calculated using the relationship, $\text{SIE (J/l)} = \text{power (W)} / \text{gas flow rate (l/s)}$.

As seen from Fig. 1, with increasing applied voltage, power increases and thereby SIE. At 200 Hz for a discharge gap of 3.5 mm, the SIE increased from 160 J/l (12.5 kV) to 295 J/l (22.5 kV).

It is known that NTP reactors operated in air produce ultraviolet light due to the excited nitrogen molecules. Earlier attempts to combine NTP with a TiO_2 photocatalyst to abate VOCs indicate that the contribution of photocatalysis induced by UV light from the plasma was not significant¹⁸. In addition, the improvement in the activity was attributed only to surface activation of TiO_2 by discharge plasma. Nevertheless, the position of the photocatalyst should be optimized to utilize the UV light emitted by NTP. During the destruction of TCE with TiO_2/SMF electrodes, the effect of the UV light can be expected only if NTP emits radiation in the range $\lambda \leq 370\text{--}380$ nm, which is equivalent to the band gap of anatase (3.2 eV). The emission spectrum of the discharge in the wavelength range 250–500 nm confirms the presence of UV light originating from excited nitrogen molecules (N_2^*). Therefore, the emission from excited nitrogen molecules (N_2^*) is in the range of the band gap of TiO_2 catalyst^{17,19,20}.

Abatement of toluene

Conversion of toluene (100 ppm) diluted by air was followed by varying the applied voltage between 12.5–22.5 kV at a constant frequency of 200 Hz, corresponding to the SIE values of 160 and 295 J/l, respectively. The inner electrode was either a conventional Cu electrode, or the catalytic SMF electrode. As seen from the Fig. 2, SMF electrode

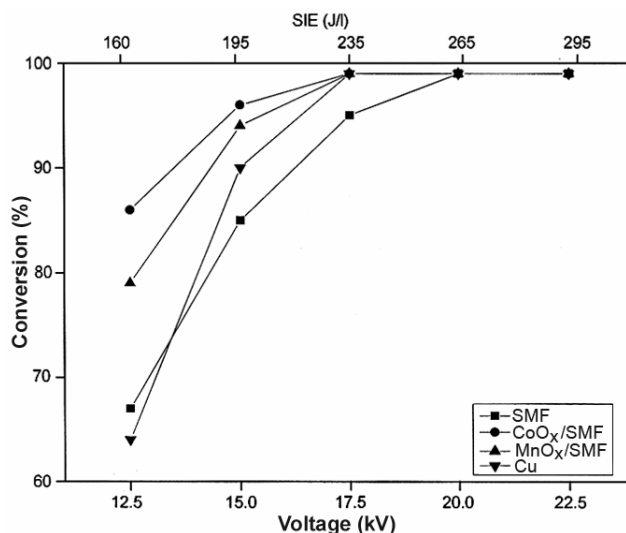


Fig. 2 — Influence of specific input energy and SMF modification during the destruction of toluene at 200 Hz. [Toluene: 100 ppm; voltage: 12.5–22.5 kV].

shows the same activity as that of Cu electrode. With SMF electrode, conversion increases with increasing applied voltage reaching ~100% at 20 kV (265 J/l). Interestingly, with CoO_x and MnO_x/SMF catalytic electrodes, ~100% conversion of toluene was achieved even at 17.5 kV that corresponds to SIE of 235 J/l.

Selectivity to CO_x during destruction of 100 ppm of toluene was also studied (Fig. 3a). Selectivity to CO_x increases with increasing voltage and reaches 100% (no carbon deposit) on all the catalysts when the voltage was higher than 17.5 kV, the SIE of 235 J/l. The selectivity to CO_2 is shown in Fig. 3b. SMF shows only ~50% selectivity to CO_2 at 295 J/l, whereas MnO_x/SMF shows better performance, for which the selectivity to CO_2 was ~80% even at 235 J/l (17.5 kV). It is worth mentioning that with MnO_x/SMF catalyst, at 17.5 kV the conversion was ~100% (Fig. 2) and there was no polymeric carbon deposit (Fig. 3a). Hence, the DBD reactor with catalytic SMF electrode shows remarkable activity during the destruction of toluene. The better performance of CoO_x and MnO_x/SMF may be due to the formation of atomic oxygen by in situ decomposition of ozone on the surface of the catalytic electrode¹⁵.

Abatement of isopropanol

Isopropanol (IPA) is one of the common solvents used in the electronic industry for cleaning the printed circuit boards and LCD monitors. IPA from industrial effluent can be recovered by adsorption into water using wet scrubbers followed by distillation or pervaporation. Thermal oxidation of

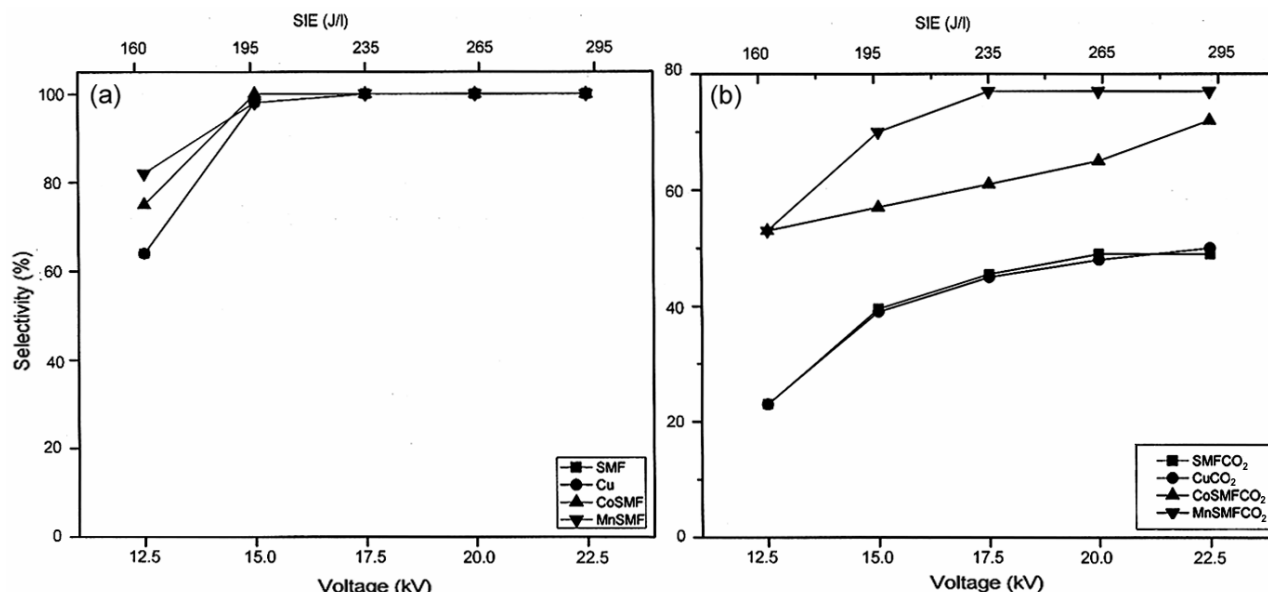


Fig. 3 — Influence of specific input energy and SMF modification during the destruction of toluene at 200 Hz. [Toluene: 100 ppm; voltage: 12.5–22.5 kV. (a) selectivity to CO_x ; (b) selectivity to CO_2].

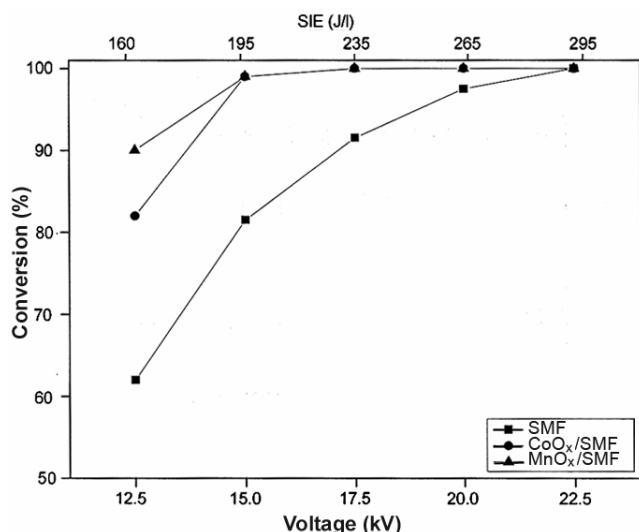


Fig. 4 — Influence of specific input energy and SMF modification during the destruction of isopropanol.

alcohols needs temperature in the range of 873–973K, whereas thermocatalytic oxidation takes place in the temperature range of 523–673K. However, these techniques are not suitable for the abatement of diluted alcohols. The NTP technique has already been tested for the destruction of IPA. However, formation of acetone as a stable secondary product was observed. Abatement of acetone demands a high energy (~ 1000 J/l), which is not energetically favorable. During the present study, oxidation of 100 ppm of IPA over catalytic SMF electrodes has been investigated. As in the case

of toluene, at any SIE, metal oxide supported SMF electrodes shows better activity compared to SMF non-modified electrode (Fig. 4). With the SMF electrode, the IPA conversion reaches $\sim 100\%$ only at 22.5 kV (295 J/l), whereas with Co and Mn oxides supported SMF electrodes, it was achieved at 15 kV, which corresponds to SIE of 195 J/l. Figure 5a shows the selectivity to CO_x during the destruction of 100 ppm of IPA in the range of SIE 160–295 J/l. As seen with SMF electrode, selectivity to CO_x reaches $\sim 100\%$ at voltage higher than 20 kV (265 J/l), whereas with CoO_x and MnO_x/SMF electrodes this was achieved at 235 J/l. The selectivity to CO_2 (Fig. 5b) also follows the same trend. MnO_x/SMF shows $\sim 100\%$ CO_2 selectivity at 265 J/l, whereas under the same experimental conditions, non-modified SMF shows only $\sim 50\%$ selectivity. As explained above, formation of atomic oxygen by in situ decomposition of ozone on the surface of catalytic MnO_x/SMF electrode shifts the product distribution towards total oxidation. Hence, with the DBD reactor with the catalytic MnO_x/SMF electrode, total oxidation of alcohol (100 ppm IPA in air) was achieved at 265 J/l.

Abatement of trichloroethylene

Chlorinated organic compounds, especially trichloroethylene (TCE) are effective washing agents to remove hydrophobic contaminants². Photocatalytic

decomposition of chlorinated hydrocarbons has been traditionally used for its abatement. However, catalytic and photocatalytic methods for the abatement of TCE produce toxic byproducts like phosgene. Attempts were made to combine NTP with a photocatalyst, TiO_2 , for the destruction of VOCs^{14,18,20}. However, results indicate that the contribution of photocatalysis induced by UV light from plasma was not significant. In addition, the improvement in the activity was attributed to the

surface activation of TiO_2 by discharge plasma^{18,20}. In the present study, abatement of diluted TCE (250 ppm in air) was tested by using the DBD reactor with catalytic SMF electrode modified with TiO_2 , MnO_x and $\text{TiO}_2/\text{MnO}_x$. Since the formation of ultraviolet light in the wavelength range 200-500 nm has been confirmed, the SMF modified with TiO_2 anatase has been used to study the influence of UV light on the performance of the DBD reactor.

Efficiency of the modified catalytic SMF electrodes

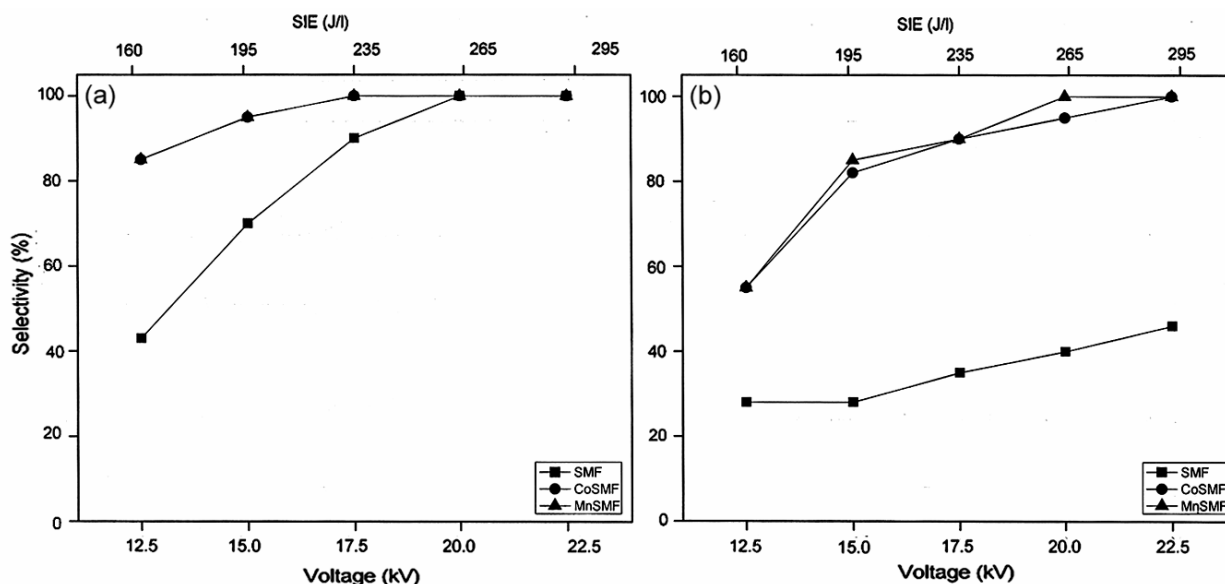


Fig. 5 — Influence of specific input energy and SMF modification during the destruction of isopropanol at 200 Hz. [Toluene: 100 ppm; voltage: 12.5–22.5 kV. (a) selectivity to CO_x ; (b) selectivity to CO_2].

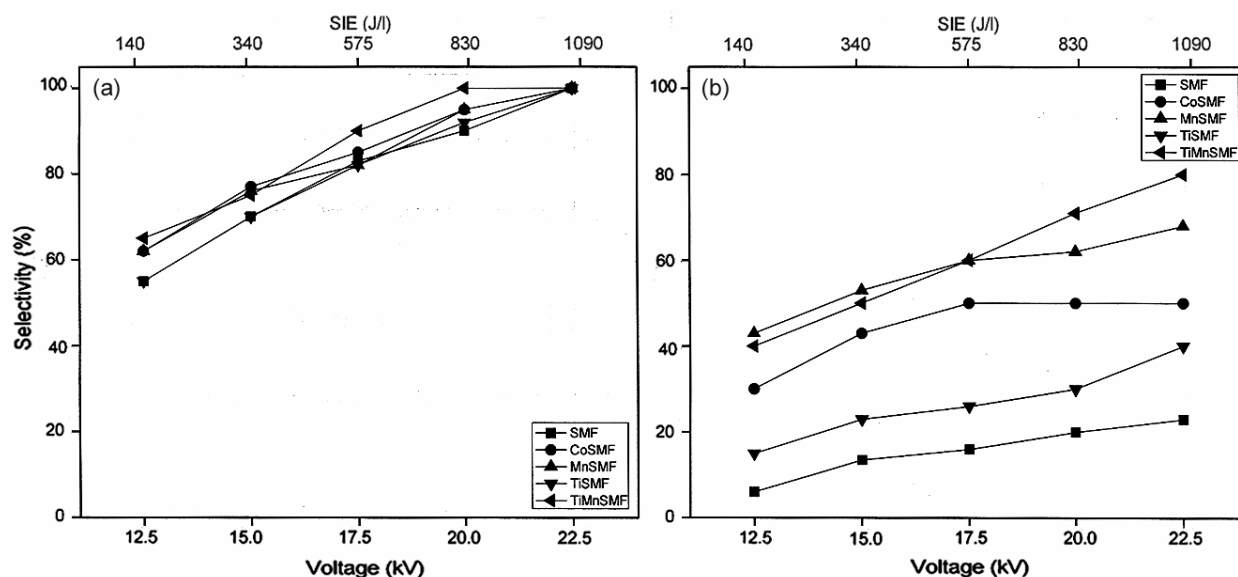


Fig. 6 — Influence of specific input energy and SMF modification during the destruction of trichloroethylene at 200 Hz. [Toluene: 100 ppm; voltage: 12.5–22.5 kV. (a) selectivity to CO_x ; (b) selectivity to CO_2].

was tested during the destruction of 250 ppm of TCE for a discharge gap of 1.25 mm as a function of SIE, which was varied in the range 140-1100 J/l by changing the voltage (12.5-22.5 kV) at 250 Hz. The results are presented in Fig. 6. Throughout the range of the SIE applied, starting from 140 J/l, ~ 100% conversion of TCE was achieved. However, during the abatement of VOCs, total oxidation is desired without the formation of undesired products like CO and polymeric carbon deposit that deactivate the catalyst. With non-modified SMF electrode at 140 J/l (12.5 kV and 250 Hz), the selectivity to CO_x is only ~ 55% and 45% towards unidentified polymeric carbon deposit (Fig. 6a). However, formation of phosgene was not observed. The selectivity to CO_x increases to ~ 100% with increasing SIE to ~ 1100 J/l.

Figure 6b presents the selectivity to CO₂, showing the effect of the metal oxide modification. As seen from Fig. 6b, at 140 J/l (12.5 kV) the SMF electrode shows only ~5% selectivity to CO₂, which increases only up to ~ 20% at 1100 J/l (22.5 kV). The selectivity to CO₂ follows the order: TiO₂/MnO_x/SMF (80%) > MnO_x/SMF (65%) > TiO_x/SMF (40%) > SMF (25%). Interestingly, TiO₂ modified SMF also shows higher CO₂ selectivity as compared to SMF electrode. Even at 140 J/l, the TiO₂/SMF shows ~ 15% selectivity to CO₂ against ~ 5% on the SMF. On increasing SIE to 1100 J/l (22.5 kV), the selectivity to CO₂ increases up to ~ 40%, whereas, under these experimental conditions the SMF shows only 20% selectivity. The better performance of TiO₂ over SMF could be either due to in situ decomposition of ozone or due to the influence of UV light formed in the discharge on the anatase photocatalyst.

In order to study the possible mechanism of TCE destruction, ozone concentration at the outlet of the reactor was measured. At 575 J/l (17.5 kV), with SMF and TiO₂/SMF, the formation of 750 and 800 ppm of ozone was observed, respectively. When MnO_x and TiO₂/MnO_x/SMF electrodes were used, the ozone concentration decreased to ~ 0 ppm, clearly indicating that the improvement observed with MnO_x modified electrodes may be due to in situ decomposition of ozone that leads to the formation of strong oxidant (atomic oxygen). Likewise, the thermal activation of TiO₂ catalyst requires a temperature in the range 573-673 K, whereas, during the present study, the outlet gas temperature never exceeded ~ 310 K. Hence, the better performance of TiO₂/SMF over SMF cannot be attributed to the thermal activation of TiO₂. The

improvement in the activity may be due to the influence of UV light coming from NTP. In order to confirm this observation, MnO_x/SMF was modified with TiO₂, and the resulting catalytic electrode increased the CO₂ selectivity to ~ 80% against ~65 % with MnO_x/SMF (Fig. 6b). This improvement is probably due to the synergy between plasma excitation of the molecules and their catalytic oxidation. The latter is further enhanced by photocatalysis, since TiO₂ absorbs the UV light produced by NTP.

As seen from the data presented, plasma alone can oxidize the VOC leading to a maximum of 50% CO₂. On combining with a heterogeneous catalyst, increment in both conversion and selectivity to CO₂ was observed. The increase in the conversion is due to in situ decomposition of ozone on the catalyst surface, leading to the formation of atomic oxygen, which is a strong oxidizing agent. In the case of TiO₂/MnO₂/SMF, it is similar to a bimodal system, where TiO₂ may act as a photocatalyst and MnO₂ facilitates the formation of atomic oxygen. When both TiO₂ and MnO₂ were combined, an increase in performance was observed, which was attributed to the synergy between plasma excitation and photocatalytic behaviour of TiO₂.

The significance of the DBD reactor presented in this study is the use of catalytic SMF electrode as the inner electrode. From the data presented above, it may be noted that the main advantage of using catalytic SMF electrode is high selectivity to CO₂ at low input energy and the minimization of undesired C-solid deposit. During the destruction of VOCs, the better performance of MnO_x/SMF over other electrodes may be due to in situ decomposition of ozone leading to the formation of active oxygen atoms (O^{*}) on the catalyst surface^{13,16}. It has earlier been reported that on MnO_x surface, a part of the atomic oxygen O^{*} is present in the form of O (³P) (ref. 13). The formation and stabilization of O (³P) species on the MnO_x/SMF may be responsible for the improved performance of the plasma reactor. The reported DBD reactor with the catalytic electrode also minimizes the carbon deposit diminishing the deactivation. During the destruction of TCE, TiO₂ modified SMF electrodes improved the selectivity to total oxidation due to the influence of UV light formed in the discharge. When the TiO₂ anatase semiconductor is irradiated with UV light with energy higher than the band gap (~ 3.2 eV, λ ≤ 380 nm), excitation of a valance band electron into the conduction band takes place leaving a hole in

the valance band. Both the hole and the photoelectron migrate to the TiO_2 surface, where either they recombine or participate in redox reactions with adsorbed species like H_2O and O_2 . The hole oxidizes adsorbed water to hydroxyl radical, while the photoelectron reduces O_2 to superoxide. With the catalytic TiO_2 electrodes, NTP decomposes TCE into several intermediates, which is adsorbed on the TiO_2 surface. These intermediates are oxidized by the hydroxyl radical and superoxide. During the destruction of TCE, $\text{TiO}_2/\text{MnO}_x/\text{SMF}$ showed the best performance which may be due to the synergy between plasma excitation of the TCE molecules and their catalytic oxidation. This is further enhanced by photocatalysis, since TiO_2 absorbs the UV light produced by the NTP. Hence, it may be concluded that during the NTP abatement of VOCs, performance of catalytic plasma reactor can be improved with suitable modification of catalytic SMF electrode.

Conclusions

A catalytic non-thermal plasma reactor with a metallic SMF electrode which also functions as a catalyst has been tested for the destruction of VOCs of different nature. It demonstrates high efficiency at low specific input energy. During the destruction of toluene and isopropanol, MnO_x/SMF showed the best performance, which is attributed to the formation of atomic oxygen by in situ decomposition of ozone on the catalyst surface. The selectivity to CO_2 during TCE destruction at a discharge gap of 1.25 mm is improved up to ~ 80 % at 1100 J/l by modifying MnO_x/SMF with TiO_2 . This improvement may be due to the synergy between plasma excitation of the TCE molecules and their catalytic oxidation. This is further enhanced by photocatalysis as TiO_2 absorbs the UV light produced by the NTP. Hence, the NTP catalytic reactor is an efficient system for the abatement of VOCs at low consumption of energy compared to thermocatalytic method. However, the reactor still needs to be optimized for achieving the total oxidation at low SIE.

Acknowledgement

The author thanks Prof. Albert Renken and Dr. Kiwi-Minsker for postdoctoral fellowship.

References

- 1 Magureanu M, Mandache N B, Eloy P, Gaigneaux E M & Parvulescu, V I, *Appl Catal B Environ*, 61 (2005) 13.
- 2 Urashima K & Chang J S, *IEEE Trans Ind Appl*, 7 (2000) 602.
- 3 Francke K P, Miessner H & Rudolph R, *Plasma Chem Plasma Process*, 20 (2000) 393.
- 4 Roland U, Holzer F & Kopinke F D, *Appl Catal B Environ*, 58 (2005) 217.
- 5 Ayrault C, Barrault J, Blin-Simiand N, Jorand F, Pasquiers S, Rousseau A & Tatibouet J M, *Catal Today*, 89 (2004) 75.
- 6 Kogelschatz U, *Plasma Chem Plasma Process*, 23 (2003) 1.
- 7 Yamamoto T, Mizuno K, Tamori I, Ogata A, Nifuku M, Michalska M & Prieto G, *IEEE Trans Ind Appl*, 32 (1996) 100.
- 8 Penetratnte B, Hsiao M C, Bardsley J N, Merrit B T, Vogtlin G E, Kuthi A, Burkhart C P & Bayless J R, *Plasma Sources Sci Technol*, 6 (1997) 251.
- 9 Eliasson B & Kogelschatz U, *IEEE Trans Plasma Sci*, 19 (1991) 1063.
- 10 Roland U, Holzer F & Kopinke F D, *Catal Today*, 73 (2002) 315.
- 11 Roland U, Holzer F & Kopinke F D, *Appl Catal B Environ*, 58 (2005) 227.
- 12 Ogata A, Mizuno K, Kushiyama S & Yamamoto T, *Plasma Chem Plasma Process*, 19 (1999) 383.
- 13 Futamura S, Einaga H, Kabashima H & Jwan L Y, *Catal Today*, 89 (2004) 89.
- 14 Kim H H, Oh S M, Ogata A & Futamura S, *Appl Catal B Environ*, 56, (2005) 213.
- 15 Subrahmanyam Ch, Magureanu M, Renken A & Kiwi-Minsker L, *Appl Catal B Environ*, 65 (2006) 150.
- 16 Subrahmanyam Ch, Renken A & Kiwi-Minsker L, *Appl Catal B Environ*, 65 (2006) 157.
- 17 Subrahmanyam Ch, Magureanu M, Laub D, Renken A & Kiwi-Minsker L, *J Phys Chem C*, 111 (2007) 4315.
- 18 Ogata A, Kim H H, Futamura S, Kushiyama S & Mizuno K, *Appl Catal B Environ*, 53 (2004) 175.
- 19 Spyrou N & Manassis C, *J Phys D Appl Phys*, 22 (1989) 120.
- 20 Kim H H, Lee Y H, Ogata A & Futamura S, *Catal Commun*, 4 (2003) 347.