Abatement of mixture of volatile organic compounds (VOCs) in a catalytic non-thermal plasma reactor

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HIGHLIGHTS

► Oxidation of mixture of VOCs in a catalytic dielectric barrier discharge reactor.
► Synergy effect on integration of catalyst to plasma.
► Positive effect of water vapor during removal of mixture of VOCs.
► Best activity of AgO_x/MnO_x under humid conditions.

GRAPHICAL ABSTRACT
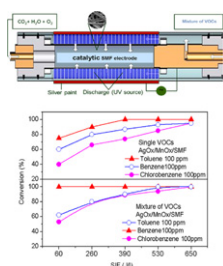
ABSTRACT

Total oxidation of mixture of dilute volatile organic compounds was carried out in a dielectric barrier discharge reactor with various transition metal oxide catalysts integrated in-plasma. The experimental results indicated the best removal efficiencies in the presence of metal oxide catalysts, especially MnO_x, whose activity was further improved with AgO_x deposition. It was confirmed water vapor improves the efficiency of the plasma reactor, probably due to the formation of hydroxyl species, whereas, in situ decomposition of ozone on the catalyst surface may lead to nascent oxygen. It may be concluded that non-thermal plasma approach is beneficial for the removal of mixture of volatile organic compounds than individual VOCs, probably due to the formation of reactive intermediates like aldehydes, peroxides, etc.

1. Introduction

Volatile organic compounds (VOCs) are one of the major contributors to the atmospheric pollution and may have adverse effects on human health [1]. Technical VOC mixtures of different chemical character such as aromatic hydrocarbons, alkanes, alcohols, acetates and ketones are utilized for commercial and industrial applications such as paints, chemical plants, and printing industries. Exposure to VOCs has implications in a number of human diseases, including cancer, cardiovascular and several insusceptible diseases [2]. As some of the VOCs are carcinogenic more rigorous environmental regulations have to be followed in order to reduce the VOCs emission [1–3]. There are many conventional methods for VOCs reduction including adsorption, absorption, catalytic oxidation and thermal incineration. These techniques are not effective, especially for dilute concentrations (<1000 ppmv), where non-thermal plasma (NTP) generated at atmospheric pressure may be energy saving due to fast ignition response and generation of highly energetic electrons that may contribute to plasma chemistry reactions [2–6]. Further, a synergy

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between NTP and catalytic action is expected with suitable catalyst integration with plasma in order to overcome the low selectivity problems of NTP [4–6]. As the typical industrial emissions comprise a blend of VOCs, an effective technology for the oxidative decomposition of VOCs is desirable [7,8]. Catalytic NTP technique has often been tested for the removal of various single component VOCs, but reports on VOCs mixture are limited [9,10]. During the present study, a mixture of VOCs of different nature was tested with NTP combined with MnO_x and AgO_x/MnO_x catalysts and results were compared with NTP alone. Influence of various parameters like design of the reactor, catalyst, presence of water vapor, concentration of VOCs, nature of the by-products formed and ozone formation inside the NTP reactor has been studied.

2. Experimental set-up

2.1. Materials

Toluene (TOL), benzene (BZ) chlorobenzene (CB), manganese acetate tetrahydrate and silver nitrate were also purchased from

$$\text{Conversion of CB } (\%) = \frac{[CB]_{in} - [CB]_{out}}{[CB]_{in}} \times 100\%$$

$$\text{Conversion of TOL } (\%) = \frac{[TOL]_{in} - [TOL]_{out}}{[TOL]_{in}} \times 100\%$$

$$\text{Conversion of BZ } (\%) = \frac{[BZ]_{in} - [BZ]_{out}}{[BZ]_{in}} \times 100\%$$

$$\text{Global selectivity of CO } S_{CO} = \frac{[CO]_{out}}{6 \times ([BZ]_{in} - [BZ]_{out}) + 7 \times ([TOL]_{in} - [TOL]_{out}) + 6 \times ([CB]_{in} - [CB]_{out})} \times 100\%$$

$$\text{Global selectivity of } CO_2 \ S_{CO_2} = \frac{[CO_2]_{out}}{6 \times ([BZ]_{in} - [BZ]_{out}) + 7 \times ([TOL]_{in} - [TOL]_{out}) + 6 \times ([CB]_{in} - [CB]_{out})} \times 100\%$$

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

Merck (Germany). All the solutions were prepared with deionized water. Sintered metal fiber (SMF) filters made of stainless steel consisting of thin uniform metal fibers of diameter 30 μm, wetness capacity of ~30 wt% and porosity of ~80% were acquired, Southwest Screens and Filters SA, Belgium.

2.2. Catalyst supported SMF preparation

Manganese oxide and silver supported manganese oxide on SMF were prepared by wet chemical route. The SMF was first oxidized at 873 K for 3 h, followed by impregnation with manganese acetate aqueous solutions of desired concentration. Then it was dried at room temperature followed by calcination in air at 773 K for 5 h to obtain MnO_x/SMF, whereas, $AgO_x/MnO_x/SMF$ were prepared by deposition of $AgNO_3$ and drying at room temperature followed by calcination at 773 K for 5 h. Finally, SMF filters were subjected to an electrical hot press to shape them into cylindrical form giving the desired discharge gap of 2.5 mm.

2.3. Experimental procedure

A detailed description of the reactor has been given elsewhere [11]. Briefly, the dielectric discharge was generated in a cylindrical quartz tube with an inner diameter of 18.5 mm. One end of the SMF electrode was connected through a stainless steel rod to AC high voltage, 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. The discharge length was 10 cm and

discharge gap was fixed at 2.5 mm during the destruction of VOCs. V-Q Lissajous method was used to determine the discharge power (W) from which specific input energy (SIE) was calculated by dividing power (W) with flow rate (l/s). SIE in the present study was varied in between 60 and 650 J/l by changing the amplitude of AC high voltage (14–22 kV/50 Hz). The VOCs BZ, CB and TOL were introduced with a motor driven syringe pump and were mixed with air at a flow rate of 250 ml/min at standard temperature and pressure and were fed into the plasma reactor with a Teflon tube. Conversion at each voltage was measured after 30 min. The concentration of VOCs at the outlet of reactor was measured with a gas chromatograph (Varian 450) equipped with a flame ionization detector and a VF1 capillary column (50 m length, 0.25 mm thickness), whereas an on-line GC–MS (Thermo Fisher Scientific) was used to identify the by-products formed. The formation of CO_2 and CO was simultaneously monitored with an online infrared gas analyser (Analyser Instruments Company, India), whereas ozone formed in the plasma reactor was measured with UV absorption ozone monitor (API-450 NEMA). As the volume change due to chemical reactions is negligible, global selectivity of CO_2 and CO_x was defined as follows:

where all concentrations are in ppmv.

3. Results and discussion

The present study has been aimed at the removal of mixture of VOCs of different nature. However, in order to understand the oxidation behavior of VOCs in a mixture, initial experiments were carried out with single component VOCs over MnO_x/SMF, $AgO_x/MnO_x/SMF$ and SMF and the results are presented in Fig. 1. As seen in Fig. 1a, SMF showed least conversion compared to modified catalysts. At 60 J/l, MnO_x/SMF showed conversion of 30, 50 and 60%, respectively for CB, BZ and TOL and with increasing SIE to 650 J/l, conversion increased up to 90, 90 and 100%, respectively. Interestingly, $AgO_x/MnO_x/SMF$ catalyst showed higher conversion compared to MnO_x/SMF in the entire SIE range. Even at 60 J/l, $AgO_x/MnO_x/SMF$ showed 45, 60 and 75% for CB, BZ and TOL. Even though, during the decomposition of VOCs total oxidation is desired, in general, NTP leads to the formation of undesired products and the selectivity to CO_2 may not be 100%. As seen in Fig. 1b, selectivity to CO_x (CO + CO_2) was never 100%, indicating the formation of by products along with carbonaceous deposits on the walls of the reactor. For the VOCs tested in the present study, the selectivity to CO_2 followed the order SMF < MnO_x < $AgO_x/MnO_x/SMF$.

3.1. Plasma-catalytic oxidation of mixture of VOCs

The performance of various catalytic electrodes during the destruction of 200 ppm of mixture of VOCs (50 ppm CB, 100 ppm BZ and 50 ppm TOL) in the SIE range of 60–650 J/l was tested. As seen in Fig. 2a, SMF without any modification showed ~100% conversion