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Improved performance of non-thermal plasma reactor during decomposition of trichloroethylene: Optimization of the reactor geometry and introduction of catalytic electrode

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Abstract

The decomposition of trichloroethylene (TCE) by non-thermal plasma was investigated in a dielectric barrier discharge (DBD) reactor with a copper rod inner electrode and compared with a plasma-catalytic reactor. The particularity of the plasma-catalytic reactor is the inner electrode made of sintered metal fibers (SMF) coated by transition metal oxides. In order to optimize the geometry of the plasma reactor, the efficiency of TCE removal was compared for different discharge gap lengths in the range of 1–5 mm. Shorter gap lengths (1–3 mm) appear to be more advantageous with respect to TCE conversion. In this case TCE conversion varies between 67% and 100% for input energy densities in the range of 80–480 J/l, while for the 5 mm discharge gap the conversion was lower (53–97%) for similar values of the input energy. As a result of TCE oxidation carbon monoxide and carbon dioxide were detected in the effluent gas. Their selectivity was rather low, in the range 14–24% for CO_2 and 11–23% for CO, and was not influenced by the gap length. Several other chlorinated organic compounds were detected as reaction products.

When using MnOx/SMF catalysts as the inner electrode of the DBD reactor, the TCE conversion was significantly enhanced, reaching ~95% at 150 J/l input energy. The selectivity to CO_2 showed a major increase as compared to the case without catalysts, reaching 58% for input energies above 550 J/l.

Keywords: Non-thermal plasma; Dielectric barrier discharge; Chlorinated volatile organic compounds; Trichloroethylene; Plasma-catalysis

1. Introduction

Air pollution by volatile organic compounds (VOC) is an issue of major concern due to both environmental and medical reasons. Non-thermal plasma generated in electrical discharges is attractive for VOC removal from contaminated air streams, since it can be operated at room temperature and atmospheric pressure, over a wide range of gas flow rates and concentrations [1–5]. The energy dissipated in the plasma is mostly used to accelerate the electrons and not spent on heating the entire gas stream, as in thermal or thermo-catalytic processes. The energetic electrons in the plasma are highly efficient in producing radicals and oxidizing agents, which can react with the VOC molecules decomposing them.

Various types of electrical discharges have been investigated for the oxidation of chlorinated hydrocarbons: pulsed corona discharges [5–9], atmospheric pressure glow discharges [10], dielectric barrier discharges [8,9,11–16], dielectric packed-bed discharges [3,4,8,12,15,17], surface discharges [13,14,18]. In a recent review of the physics and applications of dielectric barrier discharges (DBD) [2], Kogelschatz addresses also the treatment of VOC, mentioning as main advantages of DBDs their simplicity and scalability.

In this work trichloroethylene (C_2HCl_3, TCE) was chosen as a model VOC compound. The plasma was generated in a dielectric barrier discharge (DBD) operated in ac mode at

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50 Hz frequency. In order to optimize the geometry of the discharge reactor, the effect of the discharge gap length on TCE conversion and on the selectivity to CO_2 and CO was investigated. With increasing the discharge gap, the residence time of the gas in the plasma region increases, which was found to be beneficial for pollutants removal [19,20]. On the other hand, the electrical characteristics of the discharge also change with the gap length, which may also influence TCE oxidation.

Manganese oxides and manganese phosphates placed either inside the electrical discharge or downstream of the discharge reactor were found useful for the oxidation of benzene and toluene [12,19,21–23]. In these works it was suggested that Mn-based catalysts have the ability to decompose ozone, forming strong oxidizing species which react with the VOC molecules on the catalyst surface. When the catalysts are placed directly inside the discharge region other active species generated in the plasma can contribute as well to VOC decomposition. Therefore, the TCE decomposition was also performed in a novel plasma catalytic reactor described in Refs. [22–25]. The particularity of this novel reactor is the inner electrode made of sintered metal fibers (SMF) coated by transition metal oxides serving in the same time as electrode and as catalyst. In this work manganese oxide catalysts were deposited on SMF as a washcoat and tested for TCE decomposition.

2. Experimental set-up

The experimental set-up is illustrated in Fig. 1.

TCE vapor was introduced by passing a flow of air through a vessel containing liquid TCE. The concentration was varied by adding a flow of ambient air, and adjusting both flow rates by mass flow controllers (MFC-1 and -2). The total gas flow rate was 500 sccm. The plasma was generated in a DBD reactor kept at atmospheric pressure and ambient temperature. In some experiments manganese oxide catalysts were used; they were placed inside the plasma reactor, as described below. The effluent gas was analyzed by gas chromatography coupled with mass spectrometry (GC–MS) and also using an infrared gas analyzer for CO and CO_2.

2.1. Dielectric barrier discharge reactor

A dielectric barrier discharge in coaxial configuration was used. The discharge reactor is shown in Fig. 2a, while Fig. 2b shows the structure of the catalytic inner electrode used in some experiments, which will be described later in more detail.

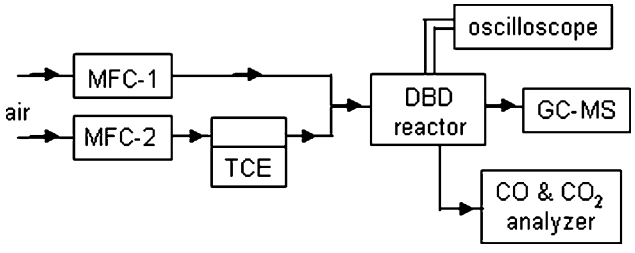

Fig. 1. Experimental set-up.

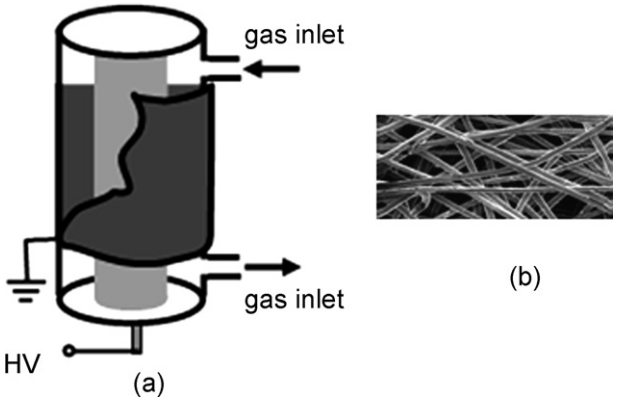

Fig. 2. (a) DBD reactor and (b) SMF catalytic electrode.

The DBD was generated in a cylindrical reactor made of quartz, with the outer diameter of 22 mm and 1.5 mm wall thickness. The inner electrode was a metallic rod placed on the axis of the reactor. Rods with diameters of 17, 13 and 9 mm were used, therefore the discharge gap was 1, 3 and 5 mm, respectively. The outer electrode was painted with silver paste on the outer surface of the quartz tube, and had a length of 10 cm. The volume of the discharge was 5.7, 15.1 and 22 cm^3 for the gap lengths of 1, 3 and 5 mm, respectively, and the corresponding residence times of the gas in the plasma zone were 0.7, 1.8 and 2.6 s, respectively.

2.2. Electrical measurements

The electrical circuit is shown in Fig. 3.

A high voltage transformer with a transformation ratio $T_R = 300$ providing sinusoidal voltage at 50 Hz frequency was used. The voltage of 10–23 kV amplitude was applied to the inner electrode, while the outer electrode was grounded. The discharge voltage was measured by a high voltage probe (Tektronix P6015A) with a resistance $R_{HV_p} = 100\,M\Omega$ connected in parallel with the discharge. The current was determined from the voltage drop across a shunt resistor ($R_C = 3\ \Omega$) connected in series with the grounded electrode. The total charge was measured with a non-inductive capacitor ($C = 1\ \mu F$), placed instead of the shunt resistor. The voltage, charge and current waveforms were monitored by a digital oscilloscope (Tektronix TDS 320). The average power dissipated in the discharge was measured by the Lissajous method [26].

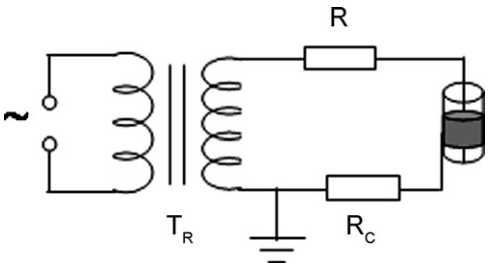

Fig. 3. Electrical circuit (transformation ratio: $T_R = 300$, $R = 800\,k\Omega$ and $R_C = 3\ \Omega$).