USING CERIUM OXIDES AS CATALYSTS FOR THE ABATAMENT OF TRICHLOROETHYLENE BY PLASMA-CATALYSIS ROUTE

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In this study, the abatement of trichloroethylene was examined with a negative DC corona/glow discharge with CeO₂ catalyst downstream. The abatement with the plasma alone system showed a poor COₓ selectivity. However, by combining the plasma source with CeO₂ catalyst the COₓ selectivity was greatly improved, proving that this plasma-catalysis route shows great potential as air pollution control technology for low concentrated VOC air streams.

1 Introduction

In recent years, many countries have imposed new and more severe regulations to improve air quality [1]. These measures are necessary because an increasing number of people are dealing with health issues such as respiratory problems [2], cardiovascular damage [3] and carcinogenic effects [4]. In order to reduce the emission of air pollutants such as volatile organic compounds (VOCs) new and innovative air control technologies are being explored and improved. In this regard, the combination of non-thermal plasma and heterogeneous catalysis has emerged as a potential candidate for the treatment of dilute waste gas streams containing VOCs from paint, semiconductor and food industry [5-7]. In a plasma-catalytic system, the catalyst can be located either inside or downstream of the discharge. Depending on this location, different mechanisms can induce a synergy and cause an improvement of the energy efficiency and CO₂-selectivity. Also, a reduced formation of unwanted by-products and a better carbon balance have been reported [7].

In this study the abatement of trichloroethylene (TCE) is investigated with a DC excited corona/glow discharge combined with CeO₂ catalyst downstream. TCE is a chlorinated solvent that is often used as a degreasing agent in semiconductor and metal industry. According to the International Agency for Research on Cancer (IARC), TCE is potentially carcinogenic to humans and its emission into the atmosphere should therefore be reduced. In order to minimize the energy cost of the abatement, combination of low energy density plasma and moderate catalyst temperature have been examined.
2 Experimental

The experimental set-up is identical as the one used in [8]. Therefore, only a brief summary is given here. Dry synthetic air was fed to a TCE bubbling bottle located in an ice-water bath. All experiments were carried out with a total air flow of 500 mL/min containing 500 ppm TCE. The TCE abatement and the identification of by-products were determined with a FT-IR spectrometer (Bruker, Vertex 70). Spectra were taken after steady state condition and consisted of 10 averaged measurements. The formation of ozone was analyzed by an UV ozone monitor (Envitec, model 450).

![Figure 1: Schematic diagram of the experimental set-up.](image)

The plasma source is based on the concept of a multi-pin-to-plate negative DC corona/glow discharge. The plasma source consists of 10 aligned cathode pins with a discharge gap of 10 mm. The discharge is powered with a DC power supply (Technix, SR40-R-1200) and generated at atmospheric pressure and room temperature. The plasma voltage and discharge current varied between 8.0–10.5 kV and 0.04–0.20 mA, respectively.

Cerium oxide (commercial catalyst) was calcinated for 4 h at 500 °C under a stream of dry synthetic air with a flow of 200 mL/min. For all tests, 1 g of MnO₂ powder was introduced in a cylindrical glass reactor located in a temperature controlled vertical tubular oven operating in the temperature range of 100 – 250 °C. The oven was heated in a period of 60 min to the desired value. The measurements were then performed after thermal balance was reached.

3 Results and discussion

3.1 TCE abatement with non-thermal plasma

Figure 1 shows the TCE abatement and COₓ selectivity as a function of the energy density. The abatement increases with increasing energy density due to a higher density of energetic electrons which trigger the formation of radicals capable of decomposing TCE. For an energy density of 240 J/L the abatement and COₓ selectivity reach a maximum at 85 % and 17 %, respectively. This low selectivity is related to the formation of unwanted and toxic byproducts such as phosgene and dichloroacetylchloride [9].
Figure 2: TCE abatement and CO\textsubscript{x} selectivity as a function of the energy density.

### 3.2 TCE abatement with CeO\textsubscript{2}

Figure 3 shows the TCE abatement as a function of the catalyst temperature with CeO\textsubscript{2}. The catalyst activity was evaluated for the temperature range of 100 – 300°C. The abatement increases with catalyst temperature and shows the typical S-curve. At 300°C the catalyst is able to abate 42% of the initial TCE concentration. The CO\textsubscript{x} selectivity reaches 42% at this temperature.

Figure 3: TCE abatement as a function of the catalyst temperature.

### 3.3 TCE abatement with plasma-catalysis

Figure 3 shows the TCE abatement as a function of the catalyst temperature for two cases of energy density (40 – 80 J/L). In order to reduce the energy cost of the process, we chose to use low energy density plasma in combination with moderate catalyst temperature. Therefore, we operated the discharge at 40 J/L and 80 J/L and examined the process for catalyst temperatures between 100 – 300°C. The plasma-catalytic abatement
increases almost linearly with the catalyst temperature. By increasing the energy density of the plasma to 80 J/L the abatement improves with 10 – 30 %.

Figure 4: TCE abatement as a function of catalyst temperature for two cases of energy density (40 – 80 J/L)

Figure 5 shows the CO\textsubscript{x} selectivity as a function of the catalyst temperature for the same energy densities. The CO\textsubscript{x} selectivity reaches a maximum of 48 % at 300°C which shows that the plasma discharge in combination with CeO\textsubscript{2} shows potential to remove dilute TCE from air streams.

Figure 5: CO\textsubscript{x} selectivity as a function of catalyst temperature for two cases of energy density (40 – 80 J/L)

Future experiments will include a long term test (100 h) to test the stability of CeO\textsubscript{2} followed by a full characterization of the catalyst to examine if the catalyst morphology has changed and if catalyst poisoning has occurred.
4 Conclusions

The plasma-catalytic abatement of TCE showed a great improvement of the CO\textsubscript{x} selectivity compared to the plasma alone system. By examining the effect of catalyst temperature, we found that low energy density plasma in combination with moderate catalyst temperature successfully abated dilute TCE in air streams.

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