



Plasma-catalytic removal of formaldehyde over Cu–Ce catalysts in a dielectric barrier discharge reactor



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ABSTRACT

In this study, a coaxial dielectric barrier discharge (DBD) reactor has been used for plasma-catalytic removal of low concentration formaldehyde over a series of Cu–Ce oxide catalysts prepared by the citric acid sol–gel method. The effect of the Cu/Ce molar ratio on the removal of formaldehyde and CO₂ selectivity has been investigated as a function of specific energy density (SED). In comparison to the plasma-only process, the combination of plasma with the Cu–Ce binary oxide catalysts significantly enhances the reaction performance, while the presence of CuO or CeO₂ in the DBD reactor has a negative effect on the removal of HCHO. This suggests that the interactions between Cu and Ce species change the properties of the catalysts and consequently affect the performance of the plasma-catalytic process. The highest removal efficiency of 94.7% and CO₂ selectivity of 97.3% were achieved when the Cu₁Ce₁ catalyst (Cu/Ce = 1:1) was placed in the DBD reactor at the SED of 486 J L⁻¹. The interaction between Cu and Ce species results in a larger specific surface area and pore volume, along with a greater formation of surface adsorbed oxygen (O_{ads}), which favors the oxidation of formaldehyde in the plasma process. In addition, the redox cycles between Cu and Ce species facilitate the formation of additional active oxygen atoms and contribute to the plasma-catalytic oxidation reactions. Plausible reaction mechanisms involved in the plasma-catalytic oxidation of HCHO have been proposed.

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1. Introduction

Formaldehyde (HCHO) is a hazardous air pollutant that is mainly emitted from industrial processes such as the manufacturing of wood products and building materials, and combustion processes. As one of the toxic volatile organic compounds (VOCs), the emission of formaldehyde has become a great concern in our society due to its harmful effects on our health and environment, especially as a suspected carcinogen. Significant efforts have been devoted to the development and investigation of various pollution remediation technologies including adsorption, membrane separation, biological process, thermal combustion and catalytic oxidation for the removal of formaldehyde. However, conventional technologies are not cost-effective for the removal of low concentration VOCs

(e.g., formaldehyde) in high volume waste gas streams. For example, thermal processes require large amounts of energy for heating the high volume gas flow to clean only a low concentration of environmental pollutants.

Non-thermal plasma (NTP) has been regarded as a promising method for the removal of a wide range of low concentration volatile organic compounds (VOCs) due to its non-equilibrium character, fast reaction, low energy cost and unique ability to initiate both physical and chemical reactions at low temperatures [1]. Energetic electrons generated in non-thermal plasma can collide with carrier gases, forming highly reactive species such as free radicals and excited atoms, molecules and ions. These species are capable of breaking most chemical bonds or initiating chemical reactions, leading to the removal of various VOC pollutants [2–5]. However, the selectivity toward the desired final products (e.g., CO₂ and H₂O) through deep oxidation is typically low when using plasma discharge alone, whilst the formation of unwanted by-products is inevitable [3,5]. Recently, a hybrid plasma-catalysis technology has been developed to combine the advantages of high selectivity from catalysis with the low temperature, fast reaction provided by non-thermal plasma [6–8]. The integration of plasma

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and catalysis has great potential to reduce the operating temperature of catalyst activation, enhance the removal efficiency of the gas pollutant and increase the selectivity of the desired final products to minimise the formation of unwanted by-products (such as NO_x); all of which contribute to enhancing the energy efficiency of the process [8–10].

Catalysts are regarded as one of the most important factors to determine the reaction performance of a plasma-catalysis system. Different catalysts including $\gamma\text{-Al}_2\text{O}_3$, TiO_2 , zeolite 13X and NaNO_2 coated raschig rings, have been shown to enhance the process performance for the plasma-catalytic oxidation of formaldehyde [11,12]. Ding et al. found that the presence of Ag/CeO_2 catalysts in a dielectric barrier discharge (DBD) significantly improved the removal efficiency of formaldehyde and CO_2 selectivity, which can be attributed to the formation of plasma-enhanced catalytic redox cycles between Ag and Ce species [13]. Zhao et al. also reported a similar interaction effect from Ag and Cu in the $\text{AgCu}/\text{HZSM-5}$ for formaldehyde removal in a cycled storage-discharge (CSD) system [14]. However, high costs of noble metals could limit the use of these catalysts for industrial applications. Up until now, the knowledge of supported metal oxide catalysts, especially the binary oxide catalysts, for the plasma-catalytic oxidation of formaldehyde is rather limited [15,16].

Cu-based catalysts have been widely used in the oxidation of VOCs due to their sufficient catalytic activity and relatively low cost [17]. Cerium oxide (CeO_2) has been regarded as an effective promoter in thermal catalytic reactions due to its high oxygen storage capacities and redox properties between Ce^{4+} and Ce^{3+} . CeO_2 can also act as a local source/sink of oxygen species due to its high bulk oxygen mobility and oxygen vacancies [18]. Cu–Ce mixed oxides have been regarded as promising catalysts for thermal catalytic oxidation of VOCs, such as benzene and toluene, due to the strong interactions between Cu and Ce species [19,20]. However, the combination of Cu–Ce oxide catalysts with non-thermal plasmas for the oxidation of VOCs has not yet been reported [21]. It is still not clear how the interactions between Cu and Ce species will affect the plasma-catalytic oxidation process.

In this study, a series of Cu–Ce oxide catalysts with different molar ratios have been prepared by a citric acid method. The effect of these catalysts on plasma-catalytic removal of formaldehyde as a function of specific energy density (SED) has been investigated in terms of formaldehyde removal efficiency and CO_2 selectivity. Catalyst characterization has been carried out using a wide range of analytic techniques such as Brunauer–Emmett–Teller (BET) surface measurement, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to get a better understanding of the roles of these catalysts in the plasma-catalytic process. Plausible reaction mechanisms and pathways have also been proposed and discussed.

2. Experimental

2.1. Experimental setup

Fig. 1 shows the schematic diagram of the experimental setup. A 60 mm-long aluminum foil (ground electrode) was wrapped over a quartz tube with an inner diameter of 8 mm and wall thickness of 1 mm. A stainless steel rod with an outer diameter of 4 mm was placed in the axis of the quartz tube and acted as a high voltage electrode. As a result, the length of the discharge zone was 60 mm with a discharge gap of 2 mm. Catalysts (100 mg, 35–60 mesh) were packed in the discharge region and held by quartz wool, corresponding to a gas hourly space velocity (GHSV) of $600,000 \text{ mL g}^{-1} \text{ h}^{-1}$. In this study, simulated dry air was used as carrier gas. Gaseous formaldehyde was acquired by feeding a dry air stream through paraformaldehyde powders (99.9%, Alfa Aesar)

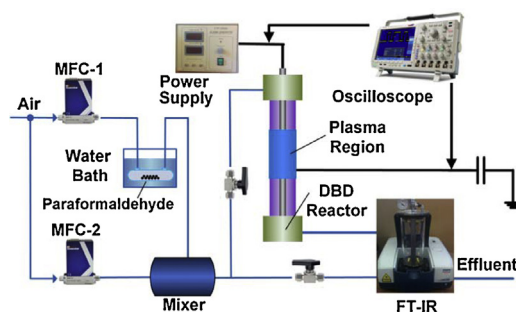


Fig. 1. Schematic diagram of the experimental setup.

which were contained in a vessel heated in a water bath (60°C). The total flow rate for the experiments was fixed at 1 L min^{-1} with a corresponding residence time of 0.23 s in the discharge area. The initial concentration of formaldehyde was kept at 57.7 ppm.

The DBD reactor was supplied by an AC high voltage power supply with a maximum peak voltage of 30 kV and a frequency of 10 kHz. A high voltage probe (Testec, HVP-15HF, 1000:1) was used to measure the applied voltage of the discharge, while a Tektronix P5100 probe was used to measure the voltage across the external capacitor C_{ext} ($0.47 \mu\text{F}$). All the electrical signals were monitored by a digital oscilloscope (Tektronix 3034B). V–Q Lissajous method was used to calculate the discharge power (P) of the DBD reactor. In the present work, specific energy density has been defined as energy dissipated to the plasma per unit volume:

$$\text{SED}(\text{J/L}) = \frac{P(\text{W})}{Q(\text{L/min})} \times 60$$

where P is the discharge power and Q is the total flow rate.

Effluent compositions were analyzed online using a Fourier transform infra-red (FTIR) spectrometer (Jasco FT/IR-4200, resolution of 2 cm^{-1}) equipped with a 1–16 m variable gas cell (PIKE Technologies). The effective pathlength of the gas cell used in this study was 5.3 m. Measurements were carried out after running the plasma system for about 40 min, when a steady-state had been reached. All the signals were obtained by averaging 128 scans. Quantitative analysis was carried out by comparing the obtained signals with the standard FTIR spectra from Pacific Northwest National Laboratory (PNNL) database. The removal efficiency of formaldehyde is defined as:

$$\eta_{\text{HCHO}} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\%$$

where C_{in} and C_{out} are inlet and outlet concentrations of formaldehyde, respectively.

The selectivity of carbon dioxide (CO_2) is defined as follows:

$$\text{CO}_2 \text{ selectivity}(\%) = \frac{C_{\text{CO}_2}}{C_{\text{CO}} + C_{\text{CO}_2}} \times 100\%$$

where C_{CO} and C_{CO_2} are CO and CO_2 concentrations in the effluent, respectively.

2.2. Model description

A Boltzmann equation solver called BOLSIG+ was used to calculate the electron energy distribution in the plasma together with the energy deposition in various electron-induced collisions [22,23]. Based on the classical two term approximation, BOLSIG+ provided steady solutions to the Boltzmann equation in the selected range of the reduced electric field (E/N , ratio of electric field to the number density of carrier gas molecules, in Td) and gave outputs of the corresponding electron energy distribution function (EEDF),

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