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 CO_2 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 CeO_2 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 CO_2 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 favor 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.

Keywords: Plasma-catalysis; Dielectric barrier discharge (DBD); Formaldehyde; Cu-Ce catalysts

Highlight

- Cu-Ce binary catalysts show excellent HCHO removal efficiency and CO_2 selectivity.
- Electronic excitations become more important with increasing specific energy density.
- Surface adsorbed oxygen plays an important role in plasma-catalytic reactions.
- Both gas phase and surface reactions contribute to HCHO removal.

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. CO_2 and H_2O) 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 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 γ-Al_2O_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 and CO_2 selectivity of formaldehyde, 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 AgCu/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 and 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 Section

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 600000 mL g^{-1} 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) which were

contained in a vessel heated in a water bath (60 ºC). 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.

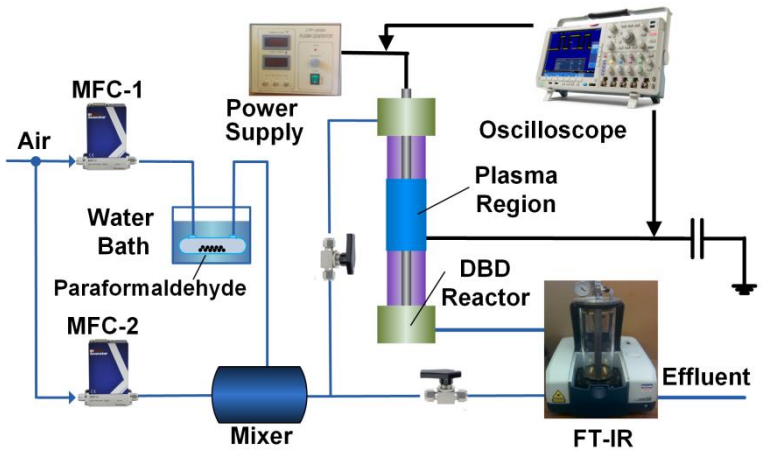


Fig. 1.

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 μF). 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:

$$SED\ (J\ L^{-1}) = \frac{P\ (W)}{Q\ (L/\mathrm{min})} \times$$

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 minutes, 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:

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

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:

$$CO_2\ selectivity\ (\%) = \frac{c_{co_2}}{c_{co} + c_{co_2}} \times 100$$

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), mean electron energy, reaction rate coefficients and energy

fractions of each plasma reaction channel. The reduced electric field was obtained from the experimental data, while an electron number density of 10^{19} m^{-3} was chosen as the initial condition for the calculation, which was within the same order of magnitude of experimental results (10^{18}–10^{21} m^{-3}) of air DBDs [24][25]. The cross section data of N_2 and O_2 used in this study was obtained from Phelps [26] and Lawton [27], while the effect of formaldehyde was excluded due to its low concentration (57.7 ppm) in the air flow (79% N_2 and 21% O_2). A list of chosen reactions has been given in Table S1 (Supporting Information).

2.3 Catalysts Preparation

A series of Cu-Ce mixed oxides with different Cu/Ce molar ratios (1:3, 1:1 and 3:1) were prepared using the citric acid method. The desired amount of copper nitrate, ceria nitrate and citric acid (99.9%, Alfa Aesar) were mixed and then dissolved in deionized water. The molar ratio of citric acid to metal salts was 1.5. The above solution was stirred at room temperature for 2 h, followed by drying in a water bath at 80 °C. The obtained samples were heated overnight at 110 °C and then calcined at 500 °C for 5 h. All the catalysts were sieved in 35-60 meshes for testing. Pure copper oxide and ceria oxide were prepared using a similar procedure.

2.4 Catalyst Characterization

N_2 adsorption and desorption experiments were carried out to determine the specific surface area, pore size distribution and average pore diameter of the catalysts using an Autosorb-1-C instrument (Quantachrome Instrument Crop). XRD patterns of the catalyst samples were recorded by a Rigaku D/max 2550PC system with a Cu-Kα radiation in the 2θ range from 10^o to 80^o. X-ray photoelectron

spectroscopy spectra were recorded with a Thermo ESCALAB 250 using Al Kα X-ray (hν = 1486.6 eV) at 150 W as a radiation source. Sample charging effect was eliminated by correcting the observed spectra with the C 1s binding energy (B. E.) value of 284.6 eV. Carbon deposition on the surface of spent catalysts was evaluated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in an air atmosphere using a Thermal MAX 500 instrument at a heating rate of 10 °C min^{-1} from 20 °C to 900 °C.

3. Results and Discussions

3.1 Catalyst properties

3.1.1 Structure of Cu-Ce catalysts

The isotherms of nitrogen adsorption/desorption for all the samples are of type IV, which is associated with capillary condensation in mesopores [28]. Type H3 hysteresis loops are observed closing at P/P_0 = 0.4 for all the catalysts, which indicate typical open slit-shaped pores with parallel walls and ink-bottle-shaped pores [29]. Table 1 shows the specific surface area (S_{BET}), total pore volume and average pore diameter of all the fresh catalysts. A synergy resulting from the interactions between Cu oxide and Ce oxide can be clearly observed. The specific surface area (33.0 – 64.4 m^2 g^{-1}) of the Cu-Ce catalysts is significantly enhanced compared to that of pure CuO (3.6 m^2 g^{-1}) and CeO_2 (10.3 m^2 g^{-1}). The highest S_{BET} and total pore volume were obtained for the Cu1Ce1 catalyst, while further increasing of the amount of Cu or Ce resulted in a decrease of the S_{BET} and pore volume of the catalysts.

Table 1.

Sample	S_{BET} (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (nm)	Crystallite size[a] (nm)	Lattice constant[b] (Å)	Ce^{3+} /Ce^{3+}+Ce^{4+} [c] (%)	O_{ads} /O_{ads} + O_{lat} [d] (%)
CuO	3.6	0.010	8.4	25.43	-	--	-
Cu3Ce1	33.0	0.044	6.7	5.12	5.4095	19.94	34.05
Cu1Ce1	64.4	0.081	4.4	4.58	5.4097	24.54	38.22
Cu1Ce3	41.7	0.063	6.2	4.77	5.4100	14.55	36.12
CeO_2	10.3	0.035	7.7	17.44	5.4104	9.78	26.70
Spent Cu1Ce1	60.8	0.078	4.8	4.58	5.4097	23.87	33.02

[a] All column data correspond to crystallite size of CeO_2 except for the first one, which corresponds to CuO.

[b] Calculated from the characteristic peak of CeO_2 (111) crystal face located at $2\theta = 28.5°$ in the XRD patterns.

[c] Relative percentage of Ce^{3+} on catalyst surface are calculated from XPS data.

[d] Relative percentage of surface oxygen species (O_{ads}) are calculated from XPS data, while O_{lat} is lattice oxygen species of Cu-Ce catalysts.

Fig. 2 presents the XRD patterns of the fresh and spent catalysts. For the CuO catalyst, typical diffraction patterns of CuO phase (JCPDS 45-0937) can be clearly seen, while the CeO_2 and all fresh Cu-Ce catalysts show a typical cubic fluorite-type oxide structure (JCPDS 34-0394). No obvious reflections of a copper oxide phase are found in the Cu1Ce1 and Cu1Ce3 samples, which can be attributed to the well dispersed CuO on the surface of CeO_2 [30]. Further increasing of the Cu content leads to the formation of bulk CuO particles, since the characteristic peaks of CuO at 2θ = 35.5° and 38.5° are detected in the Cu3Ce1 catalyst. The diffraction peaks of all the Cu-Ce catalysts are broader compared to those of CuO and CeO_2, while the peak intensities of the Cu-Ce catalysts are smaller, indicating the decrease of CeO_2 crystallinity by Cu doping, which is in accordance with the calculated crystalline size of CeO_2 (Table 1) using the Scherrer's equation [31]

$$d = \frac{0.89\lambda}{(\beta - \beta o)\cos\theta} \quad (2)$$

where d is the average volume diameter of the crystallite, λ is the wavelength of the incident X-rays from the Cu source, θ is the X-ray incidence angle with respect to the sample surface, β is the peak width at half peak height (in radians) and β_0 is the instrumental line broadening.

Pure CeO_2 and CuO have a crystallite size of 17.44 nm and 25.43 nm, respectively, but it decreases significantly to 4.58-5.12 nm in the case of the Cu-Ce catalysts, which is in agreement with the results of N_2 adsorption-desorption experiments in this study. The XRD patterns of the Cu-Ce catalysts show a slight shift of about +0.3° for the characteristic peak of CeO_2 (111) crystal face located at 2θ = 28.5°. This behavior can be explained by the incorporation of CuO into the CeO_2 lattice and the partial substitution of Ce cations by Cu cations. Since the radius of Cu^{2+} (0.73 Å) is smaller than that of Ce^{4+} (0.97 Å), a contraction of the CeO_2 lattice would occur when Ce^{4+} is replaced by Cu^{2+} , as confirmed by the decrease of the lattice constant in Table 1.

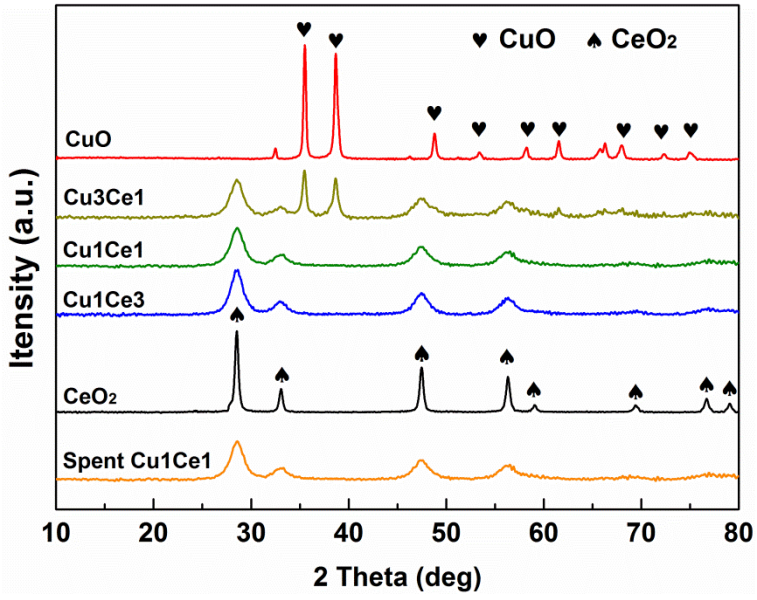
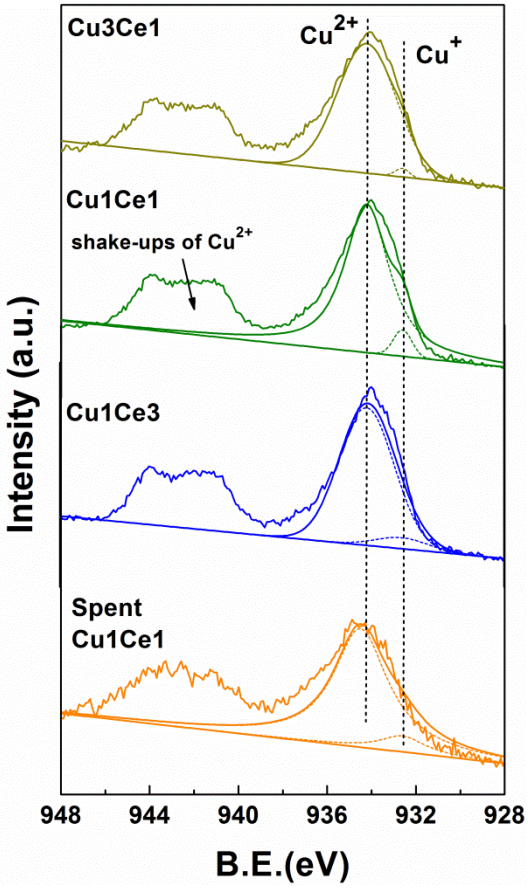


Fig. 2.

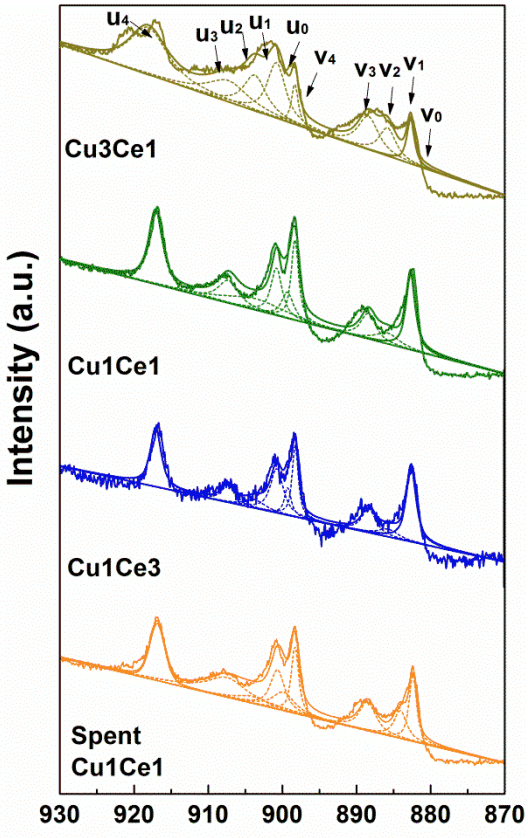
3.1.2 Surface analysis of Cu-Ce catalysts

XPS technique has been used to gain a better insight into the chemical states of all the elements on the surface of the Cu-Ce catalysts. Fig. 3 shows the XPS spectra of Cu 2p, Ce 3d and O 1s. The Cu 2p (Fig. 3a) spectra show a main peak of Cu $2p_{3/2}$ at around 934.0 eV, along with the shake-up peaks at 940-945 eV for all the Cu-Ce catalysts. The presence of the shake-up peaks and their binding energy demonstrate the existence of Cu^{2+} species on the catalyst surface [32]. Deconvolution of Cu $2p_{3/2}$ shows two peaks centered at 934.2 and 932.6 eV, respectively. The former can be identified as Cu^{2+} species, while the latter one belongs to a reduced Cu species (Cu^0 or Cu^+). It is difficult to distinguish the exact chemical state of the reduced surface Cu species using XPS since the binding energy of these two species is very close. However, it is believed that Cu^+ rather than Cu^0 exists as the main reduced Cu species on the catalyst surface since these catalysts were calcined in air [33]. Cu^+ species can also be formed from the substitution at the interfaces of the oxide phases due to the similar radius of Cu^+ and Ce^{4+} ions [30].

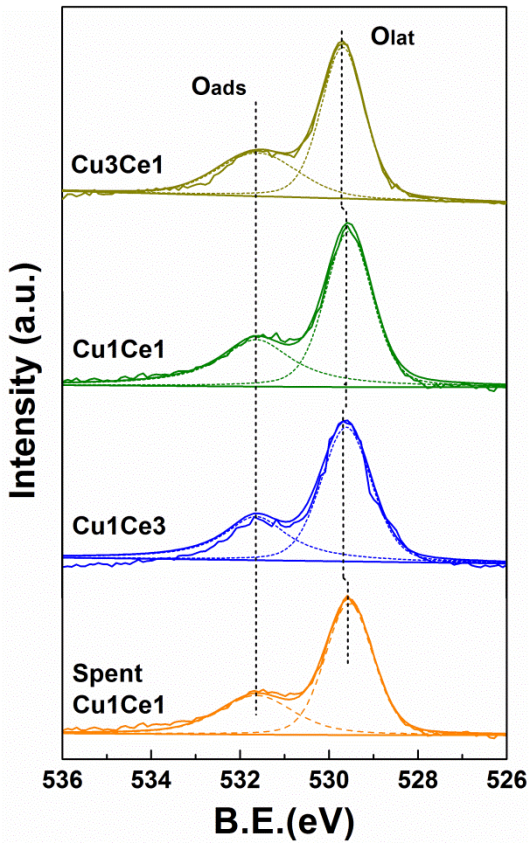
The XPS spectra of Ce 3d shows the spin-orbit splitting of Ce $3d_{5/2}$ and Ce $3d_{3/2}$, labeled as u and v, respectively (Fig. 3b). The spectra can be divided into ten peaks. The u_2, u_0, v_2 and v_0 peaks are assigned to Ce^{3+}, while the rest belong to Ce^{4+} [34]. The relative concentration of $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ ranges from 14.55% to 24.54% for the Cu-Ce catalysts, which suggests that CeO_2 is the main Ce species on the surface of the Cu-Ce catalysts. The XPS spectra of O 1s are shown in Fig. 3c. Two components are identified by deconvoluting the main peak at around 531 eV. The peaks at 529.6 eV are identified as lattice oxygen (O^{2-}) (denoted as O_{lat}), while those at 531.6 eV are assigned to the surface adsorbed oxygen (denoted as O_{ads}) [35]. The relative concentration of O_{ads} ranges from 34.05% to 38.22% as shown in Table 1, suggesting that lattice oxygen is the most abundant oxygen species on the surface of the Cu-Ce catalysts.


Cu3Ce1
Cu2+
Cu+
Cu1Ce1
shake-ups of Cu2+
Cu1Ce3
Spent
Cu1Ce1
Intensity (a.u.)
948
944
940
936
932
928
B.E.(eV)

(a)


u4
u3
u2
u1
u0
v4
v3
v2
v1
v0
Cu3Ce1
Cu1Ce1
Cu1Ce3
Spent
Cu1Ce1
Intensity (a.u.)
930
920
910
900
890
880
870

277 (b)



278

279 (c)

280 **Fig. 3.**

281

282 **3.2 Plasma-catalytic removal of formaldehyde**

283 Fig. 4 shows the effect of the Cu-Ce catalysts on the removal of formaldehyde as a function of
284 SED. The removal of formaldehyde increases with increasing SED regardless of the catalyst used.
285 Increasing the SED by raising the applied voltage is expected to effectively enhance the reduced
286 electric field (E/N), which changes the electron energy distribution function (EEDF) and enhances
287 the mean electron energy. This can be demonstrated by our calculation through solving the Boltzmann
288 equation using BOLSIG+. Taking the Cu1Ce1 catalyst for example, increasing the applied voltage
289 (peak-to-peak) from 4.86 kV to 6.48 kV significantly increases the SED from 288 J L^{-1} to 486 J L^{-1},

which enhances the reduced electric field from 90 Td to 120 Td and consequently increases the mean electron energy from 2.28 eV to 3.29 eV (shown in Fig. 5a). It is also found that by increasing the SED, the EEDF shifts with an increase in electron density in the high-energy tail of the distribution function (Fig. 5b). It is expected that increasing the SED also leads to an increase in the number of microdischarges per half cycle of the applied voltage. Although it is difficult to quantify the total number of microdischarges in a DBD system, previous work of Kim et al. has demonstrated through the use of an intensified charge coupled device (ICCD) camera that increasing the discharge power enhances the electric field, with the formation of more microdischarges in the plasma [36]. Snoeckx et al. has simulated the process of plasma-based dry reforming and found the number of micro-discharge pulses per half cycle has a great influence on the electron density, which in turn affects the calculated conversion and selectivity of the plasma process [25]. As a result of the combined effects induced by the increase of the SED, more chemically active species can be generated in the discharge via electron impacts to drive the plasma chemical reactions.

To get a better understanding of the initial steps of plasma chemistry, the effect of the reduced electric field on the fraction of energy transferred to different electron-molecule collision channels (e.g. elastic, rotational and vibrational excitations, electronic excitations and ionization) has been investigated (shown in Fig. 5c). In the E/N range of 90 Td to 120 Td, the discharge energy is mainly consumed by electronic, rotational and vibrational excitations. Electronic excitations become more important with increasing E/N as its energy fraction increases from 31.0 to 53.6%. Meanwhile, the discharge power consumed by the rotational and vibrational excitation channels is decreased from 68.6% to 45.6%. Only ~2.5% and ~0.3% of the energy contributes to the minor channels of elastic and ionization reactions, respectively. Electronic excitation reactions contribute to the generation of

N and O radicals and metastable N_2 via R1-R4 [24]:

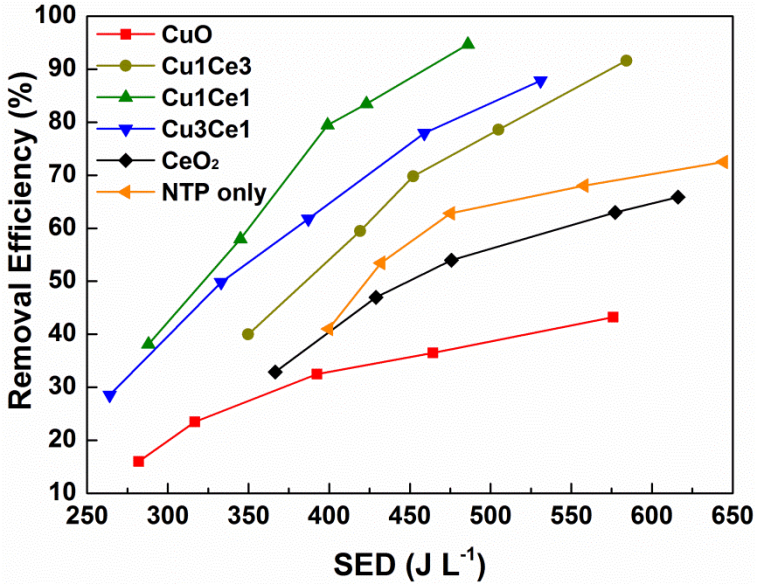
$$e + N_2 \rightarrow e + N_2(A),\ N_2(a^{'}) \quad \text{R1}$$

$$e + N_2 \rightarrow e + N + N \quad \text{R2}$$

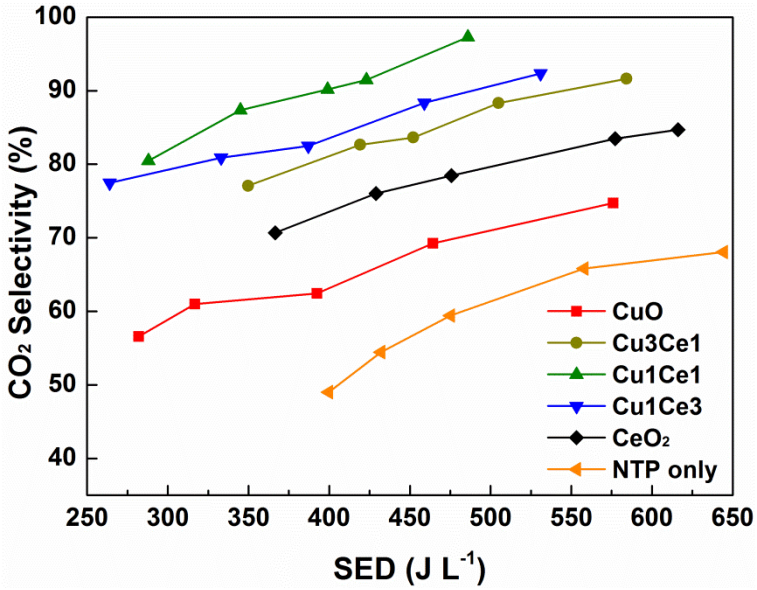
$$e + O_2 \rightarrow e + O + O \quad \text{R3}$$

$$e + O_2 \rightarrow e + O + O(1D),\ O(1S) \quad \text{R4}$$

where $N_2(a^{'})$ denotes the sum of N_2 metastable state of $N_2(a'^1\Sigma)$, $N_2(a^1\prod)$ and $N_2(w^1\Delta)$.

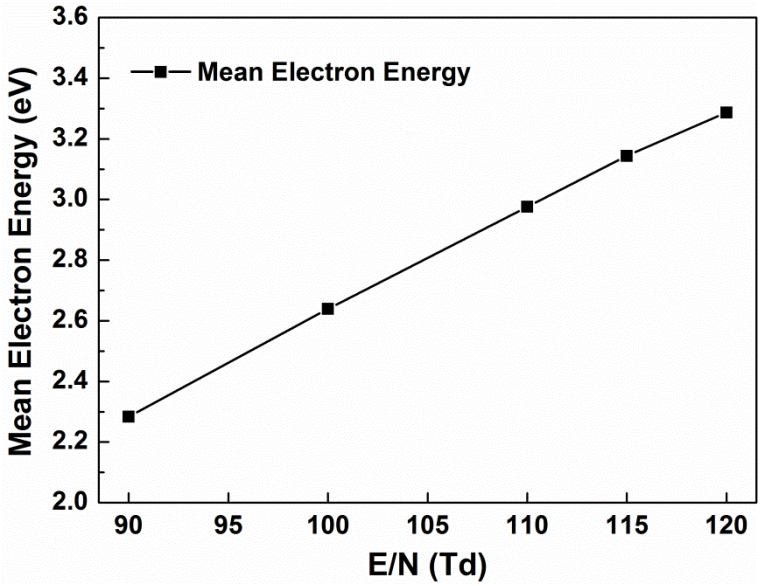


(a)

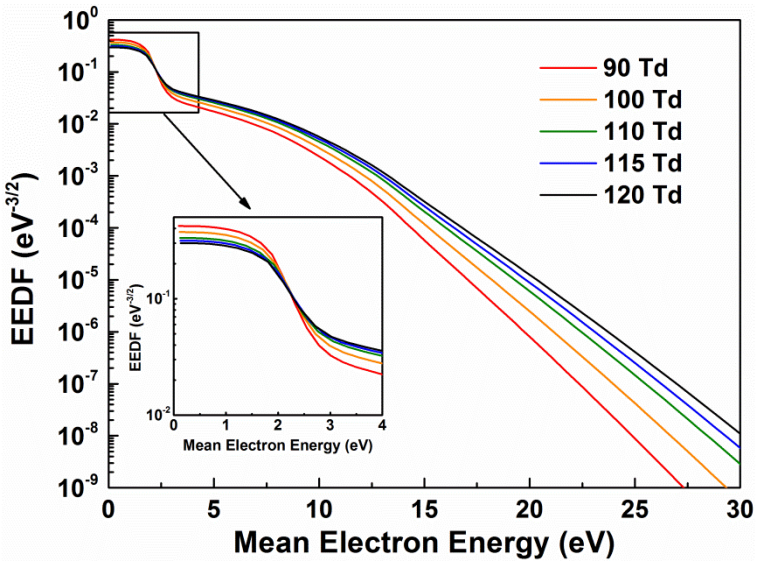


(b)

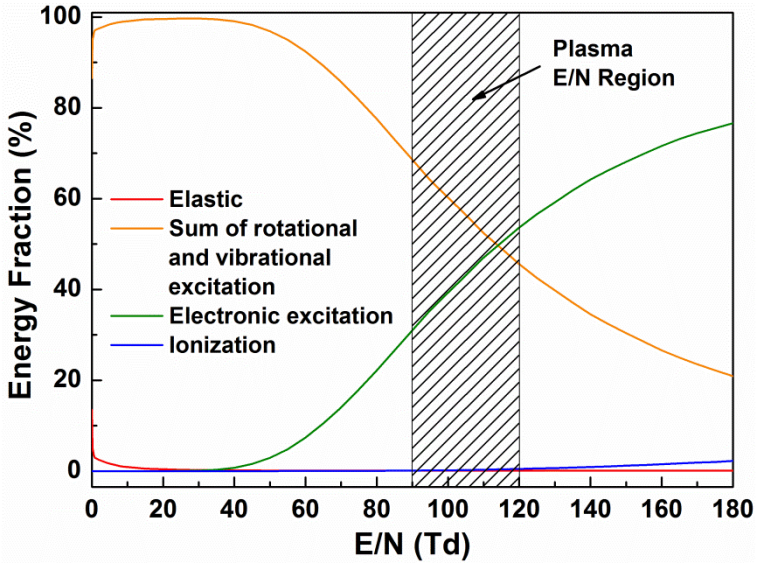
Fig. 4.


Mean Electron Energy
Mean Electron Energy (eV)
E/N (Td)
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
90
95
100
105
110
115
120

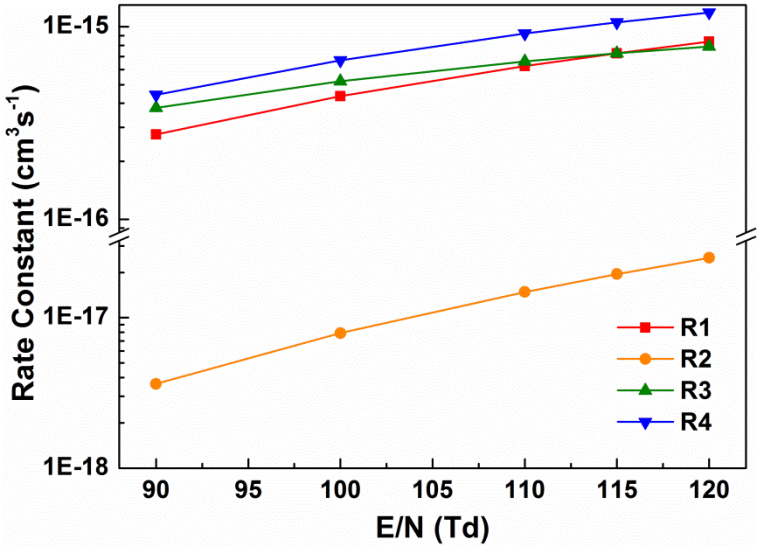
(a)


90 Td
100 Td
110 Td
115 Td
120 Td
EEDF (eV^-3/2)
Mean Electron Energy (eV)
Mean Electron Energy (eV)
0
5
10
15
20
25
30

(b)



(c)



(d)

Fig. 5.

As shown in Fig. 5d, the rate coefficient of the reactions R1-R4 is enhanced with the increase in SED, resulting in the formation of more reactive species. The reactive species with sufficient energy could collide and react with pollutant molecules. The rotational and vibrational excited N_2 and O_2 with insufficient energy are not able to rupture the pollutant molecules, but O_2 species may play a role in the oxidation of the intermediates to CO_2 and H_2O [24].

Compared to the plasma process with no catalyst, the combination of plasma with the Cu-Ce binary catalysts significantly enhances the removal efficiency of HCHO, while the presence of CuO or CeO_2 in the DBD reactor has a negative effect on the removal of HCHO. In addition, all the catalyst samples show an enhanced CO_2 selectivity when combined with the plasma. The highest formaldehyde removal efficiency (94.7%) and CO_2 selectivity (97.3%) were achieved using the Cu1Ce1 catalyst at the SED of 486 J L^{-1}, as shown in Fig. 4. These results suggest that the interactions between Cu and Ce species could change the properties of the catalysts, and consequently enhance the performance of the plasma-catalytic oxidation of formaldehyde. As shown in Table 1, the Cu-Ce catalysts have a larger specific surface area and pore volume compared to the pure CuO and CeO_2 samples. It is generally recognized that adsorption is the initial step of heterogeneous catalysis. Higher adsorption capacity is expected for the Cu-Ce catalysts due to their larger specific surface area which can provide more adsorption sites and prolong the retention time of formaldehyde in the plasma due to the diffusion of pollutants within the pores. In a single-stage plasma-catalysis system where the catalyst is directly in contact with the plasma, reactive species can also be generated in the pores of the catalysts, thus the probability of reactions between the adsorbed pollutant molecules and reactive species in the plasma-catalysis system is enhanced [37]. Guaitella et al. found that the adsorption of C_2H_2 and active species increased with increasing catalyst porosity, which led to a higher oxidation of C_2H_2 in the plasma-catalytic reactions [38]. These results are in good agreement with the findings of this work as the specific surface areas and pore volumes follow the same order as the removal efficiency and CO_2 selectivity: Cu1Ce1 > Cu1Ce3 > Cu3Ce1. It is worth noting that high removal efficiency of 92.9% and CO_2 selectivity of 96.4% are achieved in the plasma-catalytic removal of HCHO over the Cu1Ce1 catalyst at a SED of 486 J L^{-1} after reaction for 5 h, showing the satisfied

activity and stability of the Cu1Ce1 catalyst under the experimental conditions. The carbon deposition (calculated from the TGA curve) on the spent Cu1Ce1 catalyst after 5 h reaction at the SED of 486 J L^{-1} was 0.15%. This weak coke formation could be the reason for the slightly decreased removal efficiency and CO_2 selectivity. The specific surface area and pore volume of the Cu1Ce1 catalyst was found to have weakly decreased after the reaction, while the average pore diameter of the catalyst was slightly increased, as shown in Table 1. These changes could be attributed to the block of micro-pores on the Cu1Ce1 catalyst by the carbon deposition. The XRD pattern of the spent Cu1Ce1 catalyst (Fig. 2) shows no significant differences compared to that of the fresh catalyst, indicating the crystallite structure of the catalyst is not changed by the plasma treatment [39].

Previous studies reported the formation of oxygen vacancies on the surface of Cu-Ce catalysts [40][41]. It is believed that the oxygen vacancies act as adsorption–desorption centers for gas phase oxygen species, which favors the generation of surface adsorbed oxygen species (O_{ads}) on the Cu-Ce catalysts for the oxidation of formaldehyde [42]. The presence of Ce^{3+} on the surface of the Cu-Ce catalysts confirms the formation of oxygen vacancies. The relative concentration of Ce^{3+} in the Cu-Ce catalysts is found to be much higher than that of pure CeO_2 (9.78%), while the Cu1Ce1 catalyst shows the highest Ce^{3+} concentration, which perfectly matches the reaction performance of the plasma-catalytic process. Note that the partial substitution of Ce^{4+} by Cu^{2+} could also lead to the formation of oxygen vacancies or the reduction of Ce^{4+} to Ce^{3+} to retain charge balance [43]. The relative concentration of Ce^{3+} in the spent Cu1Ce1 catalyst is slightly less (23.87%) than that of the fresh catalyst (24.54%), indicating that part of the Ce^{3+} are oxidized to Ce^{4+} during the plasma-catalytic process [44].

Moreover, the Cu-O and Ce-O chemical bonds can be weakened in the Cu-Ce catalysts due to

383 the electron effect to form more reactive oxygen species and enhance their mobility. As confirmed by
384 XPS results of O 1s, the relative concentration of the surface adsorbed oxygen species O_{ads} in the Cu-
385 Ce samples was higher than that of pure CeO_2, whilst the highest O_{ads} concentration of 38.22% was
386 observed in the fresh Cu1Ce1 catalyst with the best reaction performance. The concentration of O_{ads}
387 decreased to 33.02% after the plasma reaction of 5 h, which indicates that the surface adsorbed oxygen
388 species play an important role in the oxidation of formaldehyde on the catalyst surface. The presence
389 of a higher concentration of O_{ads} tends to generate more active oxygen species, which could result in
390 high removal efficiency via surface reactions [41]. A perfect correlation between the reaction
391 performance and the O_{ads} concentration for different catalysts is observed in this work.
392 The redox properties of the catalysts generated from the interactions between Cu and Ce species
393 play an important role in the oxidation reactions. Previous studies showed that the redox pairs of
394 Cu^{2+}/Cu^{+} and Ce^{4+}/Ce^{3+} were involved in the electron transfer process from Ce^{4+} to Cu^{2+} within the
395 Cu^{2+}-O-Ce^{4+} connections in the Cu-Ce catalysts. The Cu^{2+}-O-Ce^{4+} connections could bridge the
396 oxygen transfer within the structure and reduce the redox potential of the Cu species, which ensures
397 the improvement of reducibility for both Cu and Ce oxides in the Cu-Ce samples for the plasma-
398 catalytic oxidation reactions [45].
399
400 **3.3 Reaction mechanisms**
401 The main gaseous products from the plasma-catalytic reactions were CO, CO_2 and H_2O, while
402 minor products such as HCOOH were also observed. Ozone was not detected for any of the catalysts,
403 which might be decomposed due to heating or catalytic decomposition, or consumed in the plasma
404 oxidation process [46]. In this work, the removal of low concentration formaldehyde in the plasma-

catalysis system can be attributed to both plasma gas phase reactions and plasma-assisted surface reactions on the catalyst surface. The gas phase reactions for the removal of formaldehyde are mainly induced by plasma generated reactive species such as O, O(1D), OH, N and metastable N_2, as shown in R5-R7 [47], while the direct electron-impact collisions only weakly affect the reaction due to the low concentration of formaldehyde in the carrier gas.

$$N_2(A),\ N_2(a') + HCHO \rightarrow N_2 + HCO + H \quad \text{R5}$$

$$O,\ O(1D) + HCHO \rightarrow HCO + OH \quad \text{R6}$$

$$OH + HCHO \rightarrow HCO + H_2O \quad \text{R7}$$

As shown in R5-R7, HCO is the main intermediate from the initial steps of HCHO oxidation. HCO species can be further oxidized by reactive species such as O and O(1D) to form end-products CO, CO_2 and H_2O [13]. HCOOH is a common byproduct in plasma processing of HCHO [16]. HCOOH may also be formed from the oxidation of HCHO by O and O(1D) (R8) or the recombination of HCO with OH (R9):

$$HCHO + O,\ O(1D) \rightarrow HCOOH \quad \text{R8}$$

$$HCO + OH \rightarrow HCOOH \quad \text{R9}$$

Plasma-assisted surface reactions also contribute to the oxidation of HCHO, while thermal catalytic activation of HCHO can be ignored due to the relatively low temperature plasma process (< 100 ^{o}C) used in this study. In this single-stage plasma catalysis system where the Cu-Ce catalysts are directly in contact with the discharge, both HCHO and intermediates from the gas phase reactions can be adsorbed onto the catalyst surfaces. Short-lived active species (e.g. O) generated close to or on the catalyst surface can participate in the surface reactions. It was reported that the adsorption-desorption equilibrium can be significantly influenced by plasma [48]. Vibrational excited species

generated in plasma may also promote the adsorption of pollutants onto the catalyst surface at low temperatures [49]. The enhanced adsorption process increases the collision possibility of pollutants and active species, leading to an acceleration of the plasma chemical reactions. The adsorbed species could also react with adjacent reactive oxygen species from oxygen vacancies or gas-phase O atoms, forming intermediates such as HCO and HCOOH, before finally being oxidized to end-products such as CO_2 and H_2O. Meanwhile, Cu^{2+} sites on the catalyst surface could be reduced to Cu^{+} and re-oxidized to Cu^{2+} by the adsorbed oxygen or the lattice oxygen from CeO_2, which suggests Ce^{4+} acts as an oxygen source for the oxidation of HCHO [50]. The consumed oxygen species on the catalysts can be replenished by capturing oxygen molecules and reactive oxygen species generated in the plasma. The fast redox between Ce^{4+} and Ce^{3+} determines the oxygen storage capacity, which is important for the formation of surface oxygen species. Both Cu and Ce are able to shift between various oxidation states, while the interaction between Cu and Ce plays a significant role to enclose the redox reaction cycle, which determines the catalytic performance [45]:

$$Cu^{2+} / Cu^{+} \rightleftharpoons O_2^{2-}/O^{-} \rightleftharpoons Ce^{4+} / Ce^{3+} \qquad \text{R10}$$

The plausible reaction mechanisms in the plasma-assisted surface oxidation of HCHO are presented in Fig. 6:

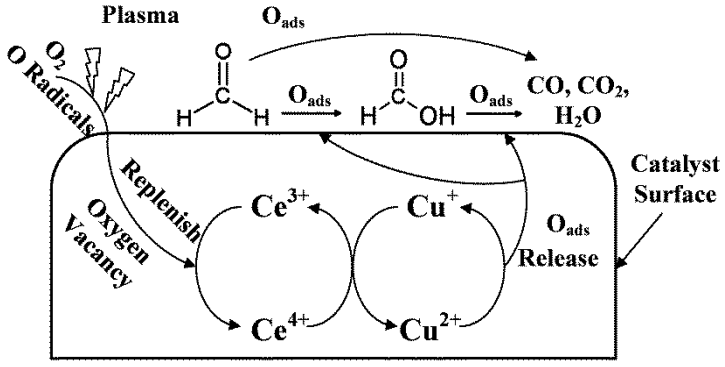


Fig. 6.

4. Conclusions

In this study, the effects of the Cu-Ce catalysts and SED on the plasma-catalytic removal of formaldehyde have been investigated in terms of the removal efficiency and CO_2 selectivity. Compared to the plasma process in the absence of a catalyst, the presence of CuO or CeO_2 catalyst in the plasma decreases the removal efficiency of HCHO, while the combination of plasma with the Cu-Ce binary metal oxide catalysts significantly enhances the reaction performance regardless of the SED. This can be ascribed to the interactions between Cu and Ce species over the catalyst surface. The Cu1Ce1 catalyst (Cu/Ce=1:1) shows the best reaction performance among all the catalysts with the highest removal efficiency of 94.7% and CO_2 selectivity of 97.3% at the SED of 486 J L^{-1}. The combination of Cu and Ce oxides results in larger specific surface area and characteristic pore volume and smaller crystalline size, all of which contribute to the plasma-catalytic oxidation of formaldehyde. The interactions between Cu and Ce oxides also increase the formation of surface adsorbed oxygen species and facilitate the redox cycles between Cu and Ce species, which plays a key role in the plasma-induced surface reactions and significantly improves the removal efficiency of formaldehyde. In this work, the removal of low concentration formaldehyde in the plasma-catalytic process can be attributed to both plasma gas phase reactions and plasma-assisted surface reactions on the catalyst surface.

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References

[1] H.L. Chen, H.M. Lee, S.H. Chen, M.B. Chang, Ind. Eng. Chem. Res. 47 (2008) 2122-2130.

[2] H.H. Kim, Plasma Process. Polymers 1 (2004) 91-110.

[3] R. Aerts, X. Tu, W. Van Gaens, J.C. Whitehead, A. Bogaerts, Environ. Sci. Technol. 47 (2013) 6478-6485.

[4] X. Tu, H. J. Gallon, J. C. Whitehead, J. Phys. D: Appl. Phys. 44 (2011) 482003.

[5] R. Aerts, X. Tu, C. De Bie, J. C. Whitehead, A. Bogaerts, Plasma Process. Polymers 9 (2012) 994-1000.

[6] J. Van Durme, J. Dewulf, C. Leys, H. Van Langenhove, Appl. Catal. B: Environ. 78 (2008) 324-333.

[7] E. C. Neyts, A. Bogaerts, J. Phys. D: Appl. Phys. 47 (2014) 224010.

[8] J. C. Whitehead, Pure Appl. Chem. 82 (2010) 1329-1336.

[9] X. Tu, J.C. Whitehead, Appl. Catal. B: Environ. 125 (2012) 439-448.

[10] X. Tu, H. J. Gallon, M. V. Twigg, P. A. Gorry, J. C. Whitehead, J. Phys. D: Appl. Phys. 44 (2011) 274007.

[11] K. Hensel, Z. Machala, A. Mizuno, 2rd International Workshop on Cold Atmospheric Pressure Plasmas: Sources and Applications, 85-88, Bruges, Belgium, 2005.

[12] W.J. Liang, J. Li, J.X. Li, T. Zhu, Y.Q. Jin, J. Hazad. Mater. 175 (2010) 1090-1095.

[13] H.X. Ding, A.M. Zhu, F.G. Lu, Y. Xu, J. Zhang, X.F. Yang, J. Phys. D: Appl. Phys. 39 (2006) 3603-3608.

[14] D.Z. Zhao, X.S. Li, C. Shi, H.Y. Fan, A.M. Zhu, Chem. Eng. Sci. 66 (2011) 3922-3929.

[15] Y. Wan, X. Fan, T. Zhu, Chem. Eng. J. 171 (2011) 314-319.

[16] X. Fan, T. Zhu, Y. Sun, X. Yan, J. Hazard. Mater. 196 (2011) 380-385.

[17] H.L. Tidahy, S. Siffert, F. Wyrwalski, J.F. Lamonier, A. Aboukais, Catal. Today 119 (2007) 317-320.

[18] R. Qu, X. Gao, K. Cen, J. Li, Appl. Catal. B: Environ. 142-143 (2013) 290-297.

[19] S.M. Saqer, D.I. Kondarides, X.E. Verykios, Appl. Catal. B: Environ. 103 (2011) 275-286.

[20] C. Hu, Chem. Eng. J. 168 (2011) 1185-1192.

[21] H.J. Li, X.Y. Jiang, X.M. Zheng, Appl. Surface Sci. 280 (2013) 273-281.

[22] G.J.M. Hagelaar, L.C. Pitchford, Plasma Sources Sci. Technol. 14 (2005) 722-733.

[23] S. Pancheshnyi, S. Biagi, M.C. Bordage, G.J.M. Hagelaar, W.L. Morgan, A.V. Phelps, L.C. Pitchford, Chem. Phys. 398 (2012) 148-153.

[24] A. Fridman, Plasma chemistry, Cambridge University Press, 2008.

[25] R. Snoeckx, R. Aerts, X. Tu, A. Bogaerts, J. Phys. Chem. C 117 (2013) 4957-4970.

[26] A.V. Phelps, L.C. Pitchford, Phys. Rev. A 31 (1985) 2932-2949.

[27] S.A. Lawton, A.V. Phelps, J. Chem. Phys. 69 (1978) 1055.

[28] B.C. Lippens, J. De Boer, J. Catal. 4 (1965) 319-323.

[29] K.S. Sing, Pure Appl. Chem. 57 (1985) 603-619.

[30] G. Avgouropoulos, T. Ioannides, H. Matralis, Appl. Catal. B: Environ. 56 (2005) 87-93.

[31] X. Tu, H. J. Gallon, J. C. Whitehead, Catal. Today 211 (2013) 120-125.

[32] D. Mrabet, A. Abassi, R. Cherizol, T.-O. Do, Appl. Catal. A: General 447 (2012) 60-66.

[33] W. Liu, M. Flytzani-Stephanopoulos, J. Catal. 153 (1995) 317-332.

[34] M. Skoda, M. Cabala, I. Matolinova, T. Skala, K. Veltruska, V. Matolin, Vacuum 84 (2009) 8-12.

[35] J.C. Dupin, D. Gonbeau, P. Vinatier, A. Levasseur, Phys. Chem. Chem. Phys. 2 (2000) 1319-1324.

[36] H.H. Kim, A. Ogata, Eur. Phys. J. Appl. Phys. 55 (2011) 13806.

[37] F. Holzer, Appl. Catal. B: Environ. 38 (2002) 163-181.

[38] O. Guaitella, F. Thevenet, E. Puzenat, C. Guillard, A. Rousseau, Appl. Catal. B: Environ. 80 (2008) 296-305.

[39] X. Tang, K. Li, H. Yi, P. Ning, Y. Xiang, J. Wang, C. Wang, J. Phys. Chem. C 116 (2012) 10017-10028.

[40] G. Marbán, A.B. Fuertes, Appl. Catal. B: Environ. 57 (2005) 43-53.

[41] G. Zhou, H. Lan, T. Gao, H. Xie, Chem. Eng. J. 246 (2014) 53-63.

[42] M. Roxana Morales, F.N. Agueero, L.E. Cadus, Catal. Lett. 143 (2013) 1003-1011.

[43] A. Martinezarias, D. Gamarra, M. Fernandezgarcia, X. Wang, J. Hanson, J. Rodriguez, J. Catal. 240 (2006) 1-7.

[44] W. Shan, M. Fleys, F. Lapicque, D. Swierczynski, A. Kiennemann, Y. Simon, P.-M. Marquaire, Appl. Catal. A: General 311 (2006) 24-33.

[45] U. Menon, H. Poelman, V. Bliznuk, V.V. Galvita, D. Poelman, G.B. Marin, J. Catal. 295 (2012) 91-103.

[46] F. Holzer, F.D. Kopinke, U. Roland, Plasma Chem. Plasma Process.25 (2005) 595-611.

[47] N. Blin-Simiand, S. Pasquiers, F. Jorand, C. Postel, J.R. Vacher, J. Phys. D: Appl. Phys. 42 (2009) 122003.

[48] N. Blin-Simiand, P. Tardiveau, A. Risacher, F. Jorand, S. Pasquiers, Plasma Process. Polymers 2 (2005) 256-262.

[49] T. Nozaki, H. Tsukijihara, W. Fukui, K. Okazaki, Energy & Fuels 21 (2007) 2525-2530.

[50] C. He, Y. Yu, C. Chen, L. Yue, N. Qiao, Q. Shen, J. Chen, Z. Hao, RSC Advances 3 (2013) 19639.

Figure captions

Fig. 1. Schematic diagram of the experimental setup.

Fig. 2. XRD patterns of fresh and spent catalysts.

Fig. 3. XPS spectra of fresh and spent Cu-Ce binary catalysts (a) Cu 2p; (b) Ce 3d; (c) O 1s.

Fig. 4. Effect of different catalysts on (a) removal efficiency of formaldehyde; (b) CO_2 selectivity as

a function of SED.

Fig. 5. (a) Calculated mean electron energy; (b) EEDF; (c) energy fraction consumed in different electron impact reactions; (d) rate constants of reactions for the formation of N and O radicals in the plasma-catalysis system over the Cu1Ce1 catalyst (E/N: 90 - 120 Td; SED: 288-486 J L^{-1}).

Fig. 6. Plausible reaction mechanisms on catalyst surface.

Table Captions

Table. 1. Physicochemical characteristics of the catalysts**.**