

Plasma-catalysis for the conversion of greenhouse gases into value-added fuels and chemicals at ambient conditions

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Abstract: Non-thermal plasma technology has been regarded as a promising and effective alternative to the traditional catalytic route for the conversion of greenhouse gases (e.g. CO₂) into value-added fuels and chemicals at ambient conditions. Our recent work on the plasma-catalytic CO₂ conversion will be discussed in terms of reactant conversion, yield and selectivity of targeted product, carbon deposition on the spent catalysts in the plasma processes for CO₂ decomposition and CO₂ reforming of CH₄.

Keywords: Plasma-catalysis, Dielectric barrier discharge, CO₂ decomposition, CO₂ reforming of CH₄.

1. Introduction

Recently, the abatement of carbon dioxide (CO₂) has become a major global challenge as CO₂ is the main greenhouse gas and its emissions lead to the problems of climate change and global warming. Different strategies are being developed to tackle the challenges associated with CO₂ emissions, including carbon capture and storage (CCS), carbon capture and utilization (CCU), reducing fossil fuel consumption and boosting clean and renewable energy use. Rather than treated as a waste, CO₂ can be regarded as a low value raw chemical for the production of value-added fuels and chemicals (e.g., CO, CH₄, and methanol), which could offers beneficial ways to “use” in addition to permanently storing the emitted CO₂.

However, due to high stability of CO₂ molecule, it is a great challenge to thermally decompose CO₂. High temperatures (>3000 K) are required to get a reasonable CO₂ conversion, which incurs a high energy cost [1]. Non-thermal plasma provides an attractive alternative to the conventional catalytic route for the conversion of greenhouse gas into valuable fuels and chemicals due to its non-equilibrium properties, low power requirement and unique capacity to induce both physical and chemical reactions at low temperatures [2-5]. Moreover, combining non-thermal plasma with solid catalysts has great potential to enhance the conversion of feed gases, improve the selectivity towards the desirable products and to reduce the operating temperature of the catalyst which both increases the process energy efficiency and improves the catalyst stability by reducing poisoning, coking and sintering, therefore has attracted increasing interest for environmental and energy applications.

The use of dielectric barrier discharge (DBD) for conversion and utilisation of CO₂ has attracted significant interest due to the successful demonstration in ozone production for industrial application [6]. In addition, catalysts can be easily integrated into DBD to generate the potential plasma-catalysis synergy and enhance the plasma-catalytic reaction performance [4, 7]. We developed different plasma-catalysis system based on

DBD for CO₂ conversion, including plasma-photocatalytic decomposition of CO₂, CO₂ decomposition in a packed bed DBD reactor and dry reforming of CH₄. The effects of different process parameters and catalysts were investigated in detail.

2. Experimental setup and analysis

Fig. 1 shows the experimental system for plasma conversion of greenhouse gas. Two kinds of home-made plasma reactors are used: coaxial DBD and packed -bed DBD, which have the similar appearance and structure. In the coaxial DBD reactor, a quartz tube is used as the dielectric material. A smooth stainless steel (SS) or screw-type rod is placed in the centre of the quartz tube and used as the inner high voltage electrode, which is connected to the high voltage output of the power supply. The SS mesh or Al foil, used as the outer electrode, is wrapped over the quartz tube and grounded via an external capacitor. The DBD reactors are supplied by an AC high voltage power supply with a maximum peak voltage of 30 kV and a frequency of 5-20 kHz. The influence of the plasma processing parameters and reactor design has been investigated systematically in the previous work [8].

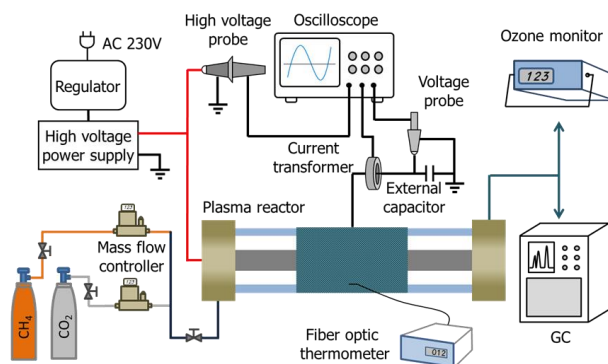


Fig. 1. Schematic diagram of the experimental setup.

In the plasma-catalytic reaction, catalyst particles are placed along the bottom of the quartz tube. Based on the

configuration of the coaxial DBD reactor, a packed-bed DBD reactor is formed when packing materials are fully packed in the discharge volume. In these two reactors, quartz wool is used to support the catalysts or packing materials. To avoid the effect of quartz wool on the plasma chemical reactions, it is placed outside the plasma region. The gas products are analysed by a two-channel gas chromatography (Shimadzu 2014) equipped with a flame ionisation detector (FID) and a thermal conductivity detector (TCD). The concentration of ozone was measured by an ozone monitor (2B, Model 106-M). The temperature ($< 150\text{ }^{\circ}\text{C}$) in the DBD reactor was measured by a fibre optical thermometer (Omega, FOB102).

3. Plasma-photocatalytic decomposition of CO_2

A coaxial DBD was developed for the plasma-photocatalytic conversion of pure CO_2 into CO and O_2 at low temperatures [7]. The synergistic effect resulting from the combination of plasma and photocatalysts (BaTiO_3 and TiO_2) for CO_2 conversion was investigated from both physical and chemical perspectives. The catalyst pellets with a diameter of 1 mm were packed into the discharge gap along the bottom of the quartz tube. This packing method induces effective plasma-catalyst interactions, which might generate a synergistic effect and hence promote plasma-catalytic chemical reactions. Fig. 2 shows the effect of BaTiO_3 and TiO_2 photocatalysts on the conversion of CO_2 . It is clear that the presence of both catalysts in the discharge significantly enhanced the CO_2 conversion and energy efficiency of the plasma process. Packing BaTiO_3 pellets into the discharge gap exhibited exceptional performance with a remarkable enhancement of both CO_2 conversion (from 15.2% to 38.3%) and energy efficiency (from 0.24 mmol/kJ to 0.60 mmol/kJ) at a specific energy density (SED) of 28 kJ/L.

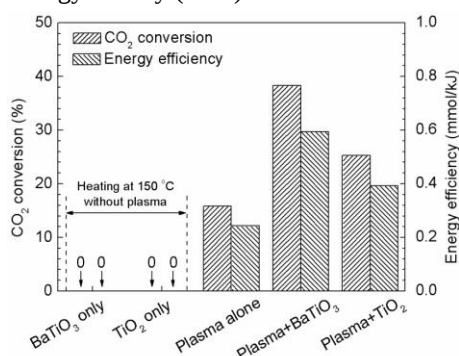


Fig. 2. Demonstration of the synergistic effect of plasma-catalysis for the conversion of CO_2 (SED = 28 kJ/L).

The results of a purely thermal experiment by heating both photocatalysts in a CO_2 flow at $150\text{ }^{\circ}\text{C}$ show no conversion and adsorption of CO_2 was observed, indicating the formation of a synergistic effect when combining plasma with photocatalysts at low temperatures. The electric field was increased by 10.9% and 9.0% with the presence of BaTiO_3 and TiO_2 in the discharge gap, respectively. Clearly, the enhancement of reaction

performance was more significant than the change in the electric field, which suggests that in addition to the plasma physical effect, the contribution of plasma-activated photocatalytic reaction to the synergy of plasma-catalysis cannot be ruled out. BaTiO_3 and TiO_2 are used as photocatalysts, which can be activated through the formation of electron-hole (e^-h^+) pairs with the aid of sufficient photonic energy ($h\nu$) with an appropriate wavelength to overcome the band-gap between the valence band and the conductive band. However, the intensity of UV emissions generated in the CO_2 DBD was significantly lower than that emitted from external UV sources (e.g. UV lamps) that are commonly used to activate photocatalysts in conventional photocatalytic reactions. This phenomenon suggests that the UV emissions generated by the CO_2 DBD only play a minor role in the activation of the BaTiO_3 and TiO_2 catalysts in the plasma-photocatalytic conversion of CO_2 , while the highly energetic electrons generated by plasma were considered as the main driving force to activate the photocatalysts for CO_2 conversion.

4. CO_2 decomposition in a packed bed DBD reactor

Direct conversion of undiluted CO_2 into CO and O_2 was carried out in a cylindrical DBD reactor with and without packing at low temperatures [1]. The effect of glass and BaTiO_3 beads on the physical characteristics of the discharge and chemical reaction performance was investigated to get a better understanding of plasma interactions with packing materials in CO_2 conversions.

Our results show that in the discharge with no packing, a typical filamentary discharge was clearly observed, which was also confirmed by the numerous peaks in the current signal. In contrast, packing BaTiO_3 or glass beads into the entire discharge area generated a typical packed-bed effect and leads to a transition in the discharge behaviour from a filamentary discharge to a combination of surface discharge and filamentary discharge. The addition of BaTiO_3 or glass beads into the DBD reactor was found to significantly reduce the amplitude of the current peaks. In a packed-bed DBD reactor, filaments can only be generated in the small gap between the pellet-pellet and the pellet-quartz wall, while surface discharge can be formed on the surface of pellets near contact points between pellets.

The gap voltage of the CO_2 discharge in the packed bed DBD reactor was much lower than that of the discharge with no packing. The breakdown voltage of the discharge was also significantly decreased packed with BaTiO_3 and glass beads, which can be ascribed to the reduced electrode gap and reduced pressure due to the packing of solid materials into the discharge gap.

In addition, the presence of the packing materials in the discharge significantly improved the average electric field strength. The material (BaTiO_3) with a higher dielectric constant had a more significant effect on the electric field of the discharge. For example, the average electric field strength (3.27 kV/mm) in the DBD reactor fully packed with the BaTiO_3 beads was almost doubled compared to that of the discharge with no packing (1.75 kV/mm) at the

same discharge power of 40 W, which resulted in the significant enhancement in CO₂ conversion, as shown in Fig. 3. Compared to the plasma reaction with no packing, the addition of BaTiO₃ and glass beads to the plasma system increased the conversion of CO₂ by around 75.0% and 35.0%, respectively. It is found that the conversion of CO₂ was not a function of dielectric constant when the packing pellets with different dielectric constants were placed in the plasma reactor. It is believed that plasma discharges can generate strong UV radiation without using extra UV sources (e.g. UV lamps) to activate photocatalysts, such as BaTiO₃. The electrons with a high energy (> 3.0 eV for BaTiO₃) generated by the CO₂ discharge can trigger electron impact activation of BaTiO₃ photocatalysts to form electron-hole pairs, which contributed to the enhanced conversion of CO₂ [7].

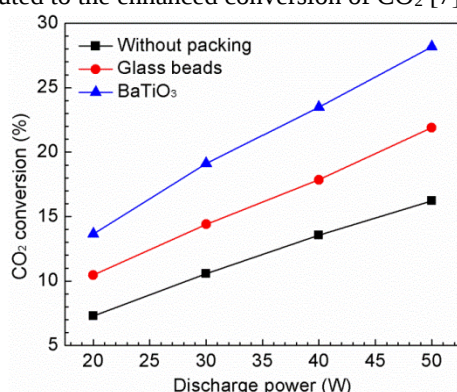


Fig. 3. Effect of packing materials on CO₂ conversion (feed flow rate: 50 ml/min; frequency: 9 kHz).

Plasma decomposition of CO₂ into CO and O₂ was also performed in a BaTiO₃ packed-bed DBD reactor in the presence of different catalysts [9]. Compared to the reaction with BaTiO₃ only in the reference mode, the addition of γ -Al₂O₃ or 10 wt% Ni/ γ -Al₂O₃ catalyst to the BaTiO₃ packed DBD reactor enhanced CO₂ conversion. Coupling of the discharge with the 10 wt% Ni/ γ -Al₂O₃ catalyst showed higher CO₂ conversion than that with the γ -Al₂O₃ support. The results showed that the location of the catalyst bed played a key role in determining the process performance. Compared with the other packing modes, placing an extra packing bed (γ -Al₂O₃ or Ni/ γ -Al₂O₃) upstream of the BaTiO₃ bed showed higher CO₂ conversion, as shown in Fig. 4. Due to the presence of different reactant compositions before entering the extra packing bed for different packing modes, the recombination of CO and O to form CO₂ was more likely to happen on the catalyst or support surface in mid- and downstream modes, which led to lower CO₂ conversion than that obtained in the upstream packing mode. Compared with the γ -Al₂O₃ support, the coupling of the DBD with the Ni catalyst shows a higher CO₂ conversion, which can be attributed to the presence of Ni active species on the catalyst surface. The argon plasma treatment of the reacted Ni catalyst provides extra evidence to confirm the role of Ni active species in the conversion of CO₂.

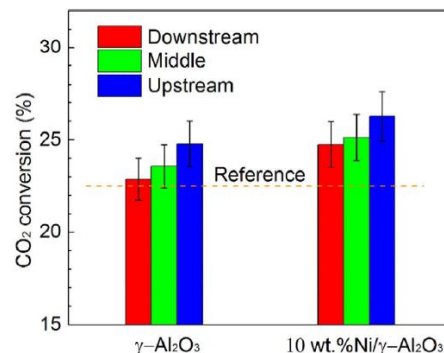


Fig. 4. Effect of catalyst and support on CO₂ conversion for different packing modes (discharge power: 40 W; CO₂ flow rate: 30 ml/min).

5. Plasma-catalytic CO₂ reforming of CH₄

CO₂ (Dry) reforming of methane has been regarded as a promising and attractive process which utilizes these two abundant greenhouse gases as feedstock to produce value-added fuels and chemicals. This reaction can be carried out using feedstock in the form of landfill gas, biogas or flared shale gas, which maximizes the energy utilization and minimizes the negative environmental impact.

The effect of supports (γ -Al₂O₃, MgO, SiO₂ and TiO₂) in the Ni based catalysts was also investigated. Different catalyst characterizations were used to understand the effect of catalyst properties on the plasma-catalytic dry reforming reaction [10]. A maximum CO₂ conversion of 26.2% and CH₄ conversion of 44.1% were achieved when using the Ni/ γ -Al₂O₃ catalyst at a specific energy density (SED) of 72 kJ/l. Compared to other Ni catalysts, placing the Ni/ γ -Al₂O₃ catalyst in the DBD produced more syngas and C₃-C₄ hydrocarbons, but less C₂H₆. The lowest energy cost (EC) for biogas conversion and syngas production, as well as the highest energy efficiency and fuel production efficiency (FPE), were achieved when using the Ni/ γ -Al₂O₃ catalyst in the plasma process. The Ni/ γ -Al₂O₃ catalyst also showed the lowest surface carbon deposition of 3.8%, after running the plasma-catalytic reforming process for 150 min at a SED of 60 kJ/l (see Fig. 5).

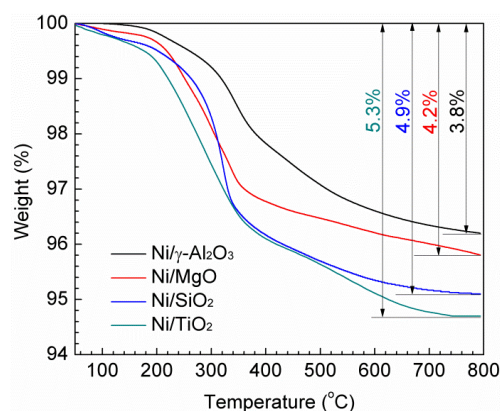


Fig. 5. TG results of different Ni catalysts after reaction at a SED of 60 kJ/l for 150 min.

The carbon deposition on these Ni catalysts was not only lower than that used in thermal catalytic dry reforming, but also lower than the carbon deposition reported in previous plasma-catalytic dry reforming processes. Compared to other Ni catalysts, the enhanced performance of the Ni/ γ -Al₂O₃ catalyst can be attributed to its higher specific surface area, higher reducibility and more, stronger basic sites on the catalyst surface.

6. Acknowledgement

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