Conversion of carbon dioxide to carbon monoxide by pulse dielectric barrier discharge plasma

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Abstract: The conversion of carbon dioxide (CO₂) to carbon monoxide (CO) was investigated in a non-thermal plasma dielectric barrier discharge (DBD) reactor, and the effects of different process conditions on the CO₂ conversion were investigated. The results showed that the increase of input power could optimize the conversion of CO₂ to CO. The CO₂ conversion and CO yield were negatively correlated with the gas flow rate, but there was an optimum gas flow rate, that made the CO selectivity best. The carrier gas (N₂, Ar) was conducive to the conversion of CO₂, and the effect of N₂ as carrier gas was better than Ar. The conversion of CO₂ to CO was enhanced by addition of the catalyst (5A molecular sieve).

1. Introduction

The International Energy Agency states that the concentration of CO₂, the main greenhouse gas (GHG), has been increasing significantly in the atmosphere over the past century, while the impact of GHG on climate change is now admitted[1-4]. As an alternative to catalytic dry reforming reaction, non-thermal plasma appears as a promising technology, since highly energetic electrons generated by plasma at room temperature are able to initiate chemical processes[5-7]. Plasma-catalysis has been widely investigated for gaseous pollutant abatement[8,9] and dry reforming of methane[10-13]. The conversion of CO₂ using the plasma method can not only reduce its greenhouse effect, but also produce CO and other chemicals[14]. Up to now, different plasma sources have been used for CO₂ conversion, including DBD[15], corona discharge[16], glow discharge[17], microwave discharge[18], and gliding arc discharge[19]. Advantages of pulsed DBD treatment are: high destruction efficiency, no demands on temperature and pressure, insensitive to contamination, and no damage from high loads, simply installed, compact, little service, small scale. However, the plasma CO₂ dissociation process would be attractive only under specific conditions, which is, in the scenario of cheap[20] and clean (low carbon emissions) electricity production.

In this paper, in order to optimize the operating conditions for the conversion of CO₂ using DBD plasma reactor, we investigated the effects of discharge parameters, gas flow rate and different diluent gases. The CO₂ dissociation with or without molecular sieves type 5A as catalyst filled in the discharge area of the reactor was also investigated. The conversion of CO₂, as well as the yield efficiency and selectivity of CO, will be discussed with respect to these parameters on the plasma conversion of CO₂. Additionally, spectrum diagnosis studies have provided insight into the mechanism of CO₂ activation and the role of the catalyst in the reaction.
2. Experimental

Figure 1 shows the main components of the experimental equipment including a DBD reactor and a high voltage pulse generator. The homemade DBD reactor is a classical coaxial dielectric barrier discharge plasma type. A stainless steel wire mesh was wrapped around the outside of a corundum tube, with an external diameter of 25 mm and an inner diameter of 20 mm, and acted as a high voltage electrode. A stainless steel rod with an outer diameter of 10 mm was placed in the center of the corundum tube and used as a low-field electrode. The length of the discharge region and after glow region is 120 mm with a discharge gap fixed at 2 mm. The DBD reactor was supplied by a high voltage pulse power supply with a peak-to-peak voltage of 30 kV and a pulse frequency of 0-1000 Hz. The voltage across the external capacitor (47 nF) was measured to determine the charge passing through the DBD. All the electrical signals were sampled by a two-channel digital oscilloscope (DS1102E).

To obtain the desired concentration, the CO₂ and diluent gas flow rates were controlled by independent flow control valves. The flow rate was also controlled by the same specification of flow control valves. For the experiment in the reaction of CO₂ and diluent gases, the CO₂ was mixed with N₂ or Ar. The mixed gases stream then entered the DBD reactor. For each experiment, the conversion of CO₂ (X_CO₂) was defined as

\[ X_{\text{CO}_2} = \frac{n_{\text{in, CO}_2} - n_{\text{out, CO}_2}}{n_{\text{in, CO}_2}} \]  

(1)

the yield of CO (Y_CO) was defined as

\[ Y_{\text{CO}} = \frac{n_{\text{out, CO}}}{n_{\text{in, CO}_2}} \]  

(2)

and the selectivity of CO (S_CO) was defined as

\[ S_{\text{CO}} = \frac{n_{\text{out, CO}}}{n_{\text{in, CO}_2} - n_{\text{out, CO}_2}} \]  

(3)

where \( n \) is the total amount of molecules (mol). The active particles and reaction intermediates were analyzed by fiber-optic spectrometer (AvaSpec-2048FT-4-DT)[21]. The catalyst samples were measured by Fourier Transform Infrared Spectrometer (FTIR)[22].

3. Results and discussion

3.1. Effects of input power

Increasing the input power by only changing the applied voltage does not change the average electric field of the plasma, since the gas voltage and breakdown voltage of the CO₂ in the DBD reactor is
almost constant with the increase in the input power[23] (calculated from the Lissajous figure[24]). The conversion of CO$_2$, yield and selectivity of CO at 150 ml/min flow rate and 700 Hz pulse frequency power supply as a function of input power were investigated for the pure CO$_2$ (black lines in Figure 2) and for CO$_2$ mixed with either Ar (red lines) or N$_2$ (blue lines) in a 1:1 molar ratio. Figure 2 (a) (b) shows that when the input power is increased, the conversion of CO$_2$ and yield of CO increase. The conversion of CO$_2$ and yield of CO are higher in the presence of diluent gases and N$_2$ is more conducive to enhancing CO$_2$ conversion rate compared to Ar.

This effect may be attributed to the fact that electrical energy can produce electrons with much higher average kinetic energies than the surrounding gas-phase ions and molecules. These energetic electrons can interact with the CO$_2$ gas to produce highly reactive species (i.e., radicals, anions, cations, and secondary electrons) that will preferentially destroy CO$_2$[25]. With the increase in the input power, the density of high-energy electrons increases and the electron energy distribution function varies. Thus, the opportunity for collisions between CO$_2$ and reactive species is increased. This assumption can explain the increase in CO$_2$ conversion and CO production with the increase in the input power. However, the selectivity of CO increases to a maximum at 50W and then decreases with the increasing of input power, as we can see from Figure 2 (c). This result could due to CO$_2$ and generated CO being partially ionized to generate carbon in the reactor with the increase of input power. The results of the emission spectrum showed that the reaction produced CO$_2^+$ (290 nm), C (312 nm), O (800–820 nm), CO (561 nm), C$_2$ (512 nm) and other particles in the presence of N$_2$ and plotted in Figure 3. Because conversion of CO$_2$ in a DBD reactor generally follow two reaction pathways involving electron impact[26],

$$\text{CO}_2 + e^- \rightarrow \text{CO} + \text{O} + e$$  \hspace{1cm} (4)

$$\text{CO}_2 + e^- \rightarrow \text{C} + \text{O}_2 + e$$  \hspace{1cm} (5)

The formation of solid carbon on the corundum tube wall and the inner surface of electrode can also result from carbon monoxide or carbon dioxide dissociation[5] (Eqs. (5) and (6)).
3.2. Effects of gas flow rate

In order to probe the effects of the gas flow rate of CO\textsubscript{2} on conversion of the dissociation reaction, data were taken for six different pure CO\textsubscript{2} flow rates: 50, 100, 150, 200, 250 and 300 ml/min. The data were obtained with input power 50W and a pulse frequency of 700Hz using the DBD reactor. The effect of gas flow rate on the CO\textsubscript{2} conversion, yield and CO selectivity is plotted in Figure 4. It can be shown that the conversion of CO\textsubscript{2} and CO yield decrease with the increase of gas flow rate. CO\textsubscript{2} conversion reduced from 23.31% to 13.11% and CO yield reduced from 16.48% to 8.2% with an increase in flow rate from 50 to 300 ml/min. With higher flow rate, the mean residential time of gas was smaller, which leads to lower conversion efficiency. However, the selectivity of CO increases to a maximum 79.51% at 150 ml/min and then decreases with the increasing of gas flow rate.

The results may be explained as: the increase of flow rate having a negative effect on the main reaction and side reaction respectively. With higher flow rate, the mean residential time of gas was smaller, which leads to lower conversion efficiency[27]. When the flow rate is less than 150 ml/min, the experiment is dominated by the main reaction, which generates CO. As the flow rate increases above 150 ml/min, the side reaction, which generates carbon, becomes more dominant.
3.3. Effect of carrier gas

Figure 5 shows the CO₂ conversion, yield and selectivity of CO of the plasma processing of CO₂ with different carrier gases at an input power of 50 W and a total flow rate of 200 ml/min. It is evident that when carrier gas concentration increases, the conversion of CO₂ becomes gradually higher. With the increase in the N₂ and Ar concentration from 0 to 50%, the CO₂ conversion increased to 21.32% and 19.37%, respectively. When the ratio of the carrier gas and CO₂ is less than 50%, the CO yield with Ar is slightly lower than the yield without it. However, when increasing N₂ reaches a certain percentage, the yield of CO will be higher than the yield without N₂.

S. L. Brock[28] et al. showed that the carrier gas is more easily activated than CO₂. The use of diluent gases has a function of optimizing discharge conditions so that CO₂ molecules are more easily converted to active oxygen atoms and CO. Besides, adding a carrier gas leads to the reduction of the absolute flow rate of CO₂, so the opportunity for collisions between CO₂ and energetic electrons is increased at the same input power. It is interesting to note that N₂ as the diatomic molecule has a larger collision area than Ar, which is a monatomic molecule, so an N₂ activated molecule may have a greater collision probability with CO₂ molecules and thus promote the conversion of CO₂ and yield of CO. The reason for the decrease of CO yield with Ar carrier gas may be due to a change in the discharge status in the reactor.

![Figure 5. Effect of carrier gas on CO₂ conversion, CO yield and selectivity of CO](image)

As can be seen from Figure 5 (c), it shows a maximum selectivity of CO at 20% carrier gas concentration. After the addition of the carrier gas, the active substance increased to promote the conversion of CO₂ to CO in the reaction system. However, when the carrier gas is added excessively, a large number of active particles will collide with CO, which leads to further conversion of CO molecules.
3.4. Effect of catalyst

Figure 6 shows the conversion of CO\textsubscript{2} by high-voltage pulse discharges combined with 3 g of 5A molecular sieve at a pure CO\textsubscript{2} flow rate of 150 ml/min and a pulse frequency of 700 Hz in the DBD reactor. It can be observed that the conversion of CO\textsubscript{2} is apparently enhanced in the presence of catalyst with the increase in the input power. Although the yield of CO also increased, the increment is small. Compared with no packing catalyst, CO selectivity decreased. Also, in both cases selectivity increases first and then decreases with the increasing input power.

These apparent synergistic effects may be attributed to the following reasons: (1) In the DBD reactor packed with molecular sieve, the high frequency of surface collisions involving reactive and or energetic species may suggest that surface mediated processes could also affect the overall conversion efficiency. (2) The high dielectric constant of the catalyst serves to enhance the electric field in the interstitial regions throughout the entire reactor volume. During the course of a voltage cycle, irregular regions around the molecular sieve pass through the Paschen limit and a corona forms. The molecular sieve in effect spreads the discharges that are dispersed from the central electrode to the molecular sieve, ensuring that the entire gas flow is exposed to the electric field. (3) The 5A molecular sieve shows a significant interaction with CO. Molecular sieves have a certain degree of CO adsorption.

![Figure 6. Effect of catalyst on CO\textsubscript{2} conversion, CO yield and selectivity of CO](image)

4. Conclusion

Plasma conversion of CO\textsubscript{2} may prove to be an effective and energy efficient technique for CO\textsubscript{2} remediation if the parameters governing the plasmochemical reactions can be optimized. In this study, the effects of the key plasma process parameters (input power, gas flow rate, carrier gas and catalyst) and their interactions on plasma conversion of CO\textsubscript{2} in a coaxial DBD reactor has been investigated. The results show that the conversion of CO\textsubscript{2} increases with increasing input power and added carrier gas, but decreases with the increase of gas flow rate. The yield of CO was negatively correlated with the gas flow rate, but there was an optimum value, which made the CO selectivity best. The carrier gas (N\textsubscript{2}, Ar) was conducive to the conversion of CO\textsubscript{2}, and the effect of N\textsubscript{2} as carrier gas was better than Ar. The CO\textsubscript{2} conversion and CO yield were enhanced by addition of molecular sieve. In conclusion, this
study demonstrates the feasibility of utilizing pulsed dielectric barrier discharges combined with different process parameters to convert CO₂ to CO. More studies are underway to further improve the efficiency of plasma CO₂ conversion.

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