Characteristics of atmospheric dielectric barrier discharge towards plasma-catalytic dry reforming of methane

X. Tu1, B. Verheyde2, S. Paulussen2, B. F. Sels1, P. A. Jacobs1

1Center for Surface Chemistry and Catalysis, Katholieke Universiteit Leuven, Leuven, Belgium
2Materials Technology, Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, Belgium

Abstract: In this paper, a cylindrical dielectric barrier discharge (DBD) reactor with water cooling has been developed for plasma-catalytic dry reforming. The influence of catalyst on the electrical characteristics of atmospheric DBD in CH4/CO2 mixture is investigated. The effects of input power, total feed flow rate, CH4/CO2 molar ratio and catalyst on the conversion and product selectivity of the dry reforming process are also studied.

Keywords: Dielectric barrier discharge, microdischarge, plasma catalysis, dry reforming

1. Introduction

Currently, the demand for effective renewable alternatives is becoming ever more urgent. The conversion and utilization of abundant low value inert gases like methane and carbon dioxide for energy production (synthesis gas, C2h, hydrocarbons and oxygenates) have exhibited promising potential. Up to now, the conventional catalytic dry reforming process still faces two main difficulties: firstly, high operating temperature is required due to the stable C-H bond of CH4 molecule; secondly, the formation of coke deposition on the surface of spent catalysts, causing their rapid deactivation.

Non-thermal plasma (NTP) is considered as an attractive alternative for converting greenhouse gases into syngas and valuable chemicals at lower temperature. Under NTP environment, the carrier gas is basically activated to create highly active species (electrons, atoms, ions and free radicals) for both the initiation and the propagation of chemical reactions. Due to the non-equilibrium character of NTP, the gas temperature remains low, while the highly energetic electrons with an electron temperature between 5000 and 20000 K enable reactions that thermodynamically would not occur at low gas temperature. Recently, the combination of plasma and heterogeneous catalyst for the hydrocarbon reforming has attracted great interest. Extensive efforts have been devoted to the plasma catalytic reactions concerning the conversion and product selectivity [1-4], whereas the interaction phenomena involved in the combination of catalyst with plasma have received less attention and required further study [3].

In this study, we develop a cylindrical dielectric barrier discharge (DBD) reactor for the plasma-catalytic dry reforming reactions. The effect of catalyst on the characteristics of the discharge in CH4/CO2 mixture is investigated. The conversion and product selectivity in the plasma dry reforming process are also studied under different operating conditions.

2. Experimental

The experimental setup is schematically shown in Fig. 1. A cylindrical DBD reactor with a water cooling unit is designed in this study. The outer electrode (Al foil, 10 cm in length) is connected to a high voltage output and the central electrode (stainless steel, 8 mm in diameter) is grounded. Borofloat glass tube is used as dielectric material with 11.5 mm i.d. and 15 mm o.d. The electrode gap is 1.75 mm and equals to the thickness of the glass tube. CH4 and CO2 are used as feed gas and injected into the discharge zone from the downstream of the reactor. The total gas flow rate is varied from 60 to 300 ml/min in this study. A sinusoidal ac power supply (AFS) with a maximum peak voltage of 40 kV and a variable frequency of 5-80 kHz is used. The DBD reactor is cooled through a circulation of deionized water unit. An optical fiber (Luxtron) is placed in the gas gap to measure the gas temperature in the discharge. In the case of plasma combined with catalyst, 0.5 g zeolite NaY (125-250 µm in diameter) is packed in the gas gap. The applied voltage is measured by a high voltage probe (Tektronics P6015A), while the total current is measured by a current monitor (Pearson Model 410). All the electrical signals are recorded by a 500MHz digital oscilloscope (Tektronics TDS3052). The catalyst is calcined at 600 °C for 5 hours and pelletized to a particle size of 125-250 µm. The reaction products are analyzed by a three-channel Compact GC (Interscience) equipped with a back flush system.
3. Results and discussion

3.1 Effect of catalyst on discharge characteristics

Fig. 2 shows the applied voltage and current intensity of DBD in the mixture of CH\textsubscript{4} and CO\textsubscript{2} with/without catalyst pellets (zeolite NaY). It can be seen that the total current comprises the quasi-sinusoid displacement current superposed by numerous current pulse per half-cycle of the applied voltage. In the experiment, the filaments perpendicular to the electrodes are randomly distributed in the gas gap, while the jumping filaments can be observed with the naked eye. The discharges in CH\textsubscript{4}/CO\textsubscript{2} can be characterized as a typical filamentary regime with a microdischarge zone (<1/4T) in each half-cycle of the applied voltage, which is organized by numerous streamer clusters at different durations from 0.3 to 1 µs. Each streamer cluster consists of a great number of streamers with lifetime of around 30 ns. It is worth noting that the current peak in the discharge decreases greatly when the catalyst is packed in the gas gap. As shown in Fig. 2, the current peak value is 322 mA in the discharge combined with the catalyst, much lower than that (580 mA) in the discharge without catalyst. We can also see that the number of streamer cluster and streamer decreases prominently in the discharge in presence of the catalyst, which suggests the enhancement in the microdischarge stability in the DBD in combination with the catalyst. A similar result has been reported in earlier studies in which the corona discharge in the presence of catalyst was found to be stable compared to the gas discharge in the absence of the solid catalyst [1].

The amplitude spectra of the current signals are obtained by means of fast Fourier transform (FFT), as shown in Fig. 3. Whatever the discharge with or without catalyst pellets, the prominent peak situated at 30 kHz and its harmonics are clearly visible in all the FFT spectra. These frequencies are independent of any change of the gas flow rate and input power. They originate from the excitation frequency of the high voltage transformer. In the high frequency range at MHz level, several peaks between 1 and 3.5 MHz are also visible, which are directly related to the appearance of the streamer cluster with duration of 1 to 0.3 µs in the discharge. In addition, another frequency at around 30 MHz can be found in the FFT spectra. This frequency is attributed to the lifetime of a single microdischarge (30 ns) in the discharge. The gas flow rate, applied power and frequency of the transformer have little influence on such high frequency (30 MHz). Moreover, it is noted that the amplitude of the high frequencies at MHz level is much lower in the discharge with catalyst, which further confirms that the presence of the catalyst pellets in the gas gap effectively improves the stability of the microdischarge. The correlation analysis of the electrical signals also confirms the high frequency in the discharge.

Fig. 2 Applied voltage and current signals of DBD (CH\textsubscript{4}:100 ml/min, CO\textsubscript{2}:100 ml/min; power:100 W; frequency: 30 kHz) (a) without catalyst; (b) with catalyst.

Fig. 3 Effect of catalyst on the Fourier spectra of the current (CH\textsubscript{4}:100 ml/min, CO\textsubscript{2}:100 ml/min; power: 100 W; frequency: 30 kHz) (a) without catalyst; (b) with catalyst.

Fig. 4 Effect of catalyst on the applied voltage (peak-to-peak) and RMS value of DBD in CH\textsubscript{4}/CO\textsubscript{2} (CH\textsubscript{4}:100 ml/min, CO\textsubscript{2}:100 ml/min; power: 100 W)

The peak-to-peak voltage and voltage RMS value at different frequencies are presented in Fig. 4. At constant input power, the effect of frequency on the applied voltage can be observed. The peak-to-peak voltage and voltage RMS value increase with the decrease of the frequency from 30 to 10 kHz. Moreover, we found that the
presence of the catalyst pellets in the discharge zone leads to the decrease of both peak-to-peak and RMS values of the applied voltage. Such behavior can also be observed in our previous study of the Ar DBD operated at filamentary mode. The peak-to-peak voltage is also found to be much lower in the Ar discharge with catalyst than in the discharge without catalyst. In contrast, in the He DBD operated in a glow or a pseudoglow mode, the presence of the catalyst in the discharge gap increases the peak voltage, as well as the gas breakdown voltage, in comparison with the discharge in the absence of the catalyst. The results suggest that the effect of catalyst on the discharge characteristics maybe dependent on glow/pseudoglow or microdischarge mode in the discharge.

3.2 Plasma dry reforming
3.2.1 Effect of feed flow rate

The influence of total feed flow rate on the conversion of CH₄ and CO₂ is shown in Fig. 5. It can be seen that increasing the feed flow rate greatly reduces the conversion of CH₄ and CO₂. As the gas flow rate increases from 60 to 300 ml/min, the conversion rate of CH₄ and CO₂ decreases from 46 % and 35 % to 12.7 % and 11%, respectively. The yield of hydrogen also decreases remarkably from 11 % to 2 % with the rising of feed flow rate. Moreover, the increase of the feed flow rate results in the decrease of the selectivity of H₂ and CO. In contrast, the selectivity to C₂ hydrocarbons increases greatly with the gas flow rate, whereas the selectivity of C₃ and C₄ varies slightly under our operating conditions. The dependence of feed flow rate on the H₂/CO ratio is also very weak. The results suggest that a lower gas flow rate is beneficial to improving the conversion of CH₄ and CO₂ and producing syngas.

3.2.2 Effect of applied power

Fig.6 (a) presents the effect of input power on the conversion of dry reforming reaction. It can be seen clearly that increasing input power leads to the increasing in the conversion of CH₄ and CO₂. The conversion rate of CH₄ and CO₂ can rise up to 47.6 % and 37.4 % at applied power of 150 W. The conversion rate of CH₄ is found to be much higher than that of CO₂ under our operating conditions. Increasing input power could effectively enhance the electrical field, electron temperature, electron density and gas temperature in the discharge, which contributes to the improvement of conversions of both gases. In addition, the increase of power produces more active species, such as O, H, OH, which could also break the C-H bond in CH₄ and produce more methyl radicals. The influence of applied power on the gas selectivity is presented in Fig. 6(b). We can see that the selectivity of H₂ slightly increases when the input power varies from 120 to 150 W. The yield of H₂ is enhanced by about 10 % when the power is 30 W up. The selectivity of CO also shows the similar variation. In addition, it can be noted that the rising in the power decreases the selectivity to light hydrocarbons (C₂, C₃) and improves the selectivity to C₄ simultaneously. In this study, the maximum C₂ and C₃ selectivity of 36 % and 14.8 % can be achieved at input power of 120 W. The results suggest that the increase of power destroys the light hydrocarbons and converts them to higher hydrocarbons and hydrogen.
3.2.3 Effect of CH$_4$/CO$_2$ ratio

In this study, the effect of CH$_4$/CO$_2$ ratio on the conversion and product selectivity in the plasma dry reforming process is investigated, as plotted in Fig. 7. The conversion rate of CH$_4$ decreases from 39.1 to 17.2 % with increasing CH$_4$/CO$_2$ ratio from 1/3 to 3, whereas the conversion of CO$_2$ slightly decreases from 18 to 15 %. The low concentration of CH$_4$ leads to the improvement of the selectivity and yield of H$_2$. As shown in Fig. 7, the highest H$_2$ yield of 8.5 % is obtained at CH$_4$/CO$_2$ ratio of 1/3. Meanwhile, the high content of CO$_2$ in the mixture contributes to the high selectivity of CO, which increases from 14 % to 39.6 % when the percentage of CO$_2$ increases from 25 to 75%. It is further found that the H$_2$/CO ratio increases considerably with the CH$_4$/CO$_2$ ratio. The rising in CH$_4$ concentration also increases the selectivity of C$_2$ hydrocarbons, particularly for C$_2$H$_6$.

3.2.4 Effect of catalyst

0.5 g zeolite NaY is packed in the electrode gap for the plasma-catalytic dry reforming. At input power of 140 W and flow rate of 200 ml/min (CH$_4$/CO$_2$ ratio=2), the conversion rate of CH$_4$ and CO$_2$ slightly decreases from 22.8 % and 15 % (without catalyst) to 18.7 % and 11.7 % (with catalyst), respectively. It is found that the selectivity of H$_2$ (28.6 %), CO (27.4 %), C$_2$ (57.1 %) increases in the presence of catalyst in the discharge, while the C$_3$ selectivity decreases.

4. Conclusion

In this study, the plasma-catalytic reaction of CH$_4$ and CO$_2$ has been carried out by using a cylindrical DBD reactor with a water cooling unit. The effect of the catalyst (zeolite NaY) packed in the gas gap on the electrical characteristics of the discharge in CH$_4$/CO$_2$ mixture has been investigated. The results show that the discharge in CH$_4$/CO$_2$ is operated in a filamentary mode with a micro-discharge zone in each half-cycle of the applied voltage, which is organized by numerous streamer clusters at different frequencies from 1 to 3.5 MHz. The presence of the catalyst in the gas gap leads to the remarkable decrease of the peak-to-peak values of the applied voltage and current intensity in the discharge. Compared with the discharge without catalyst, the number of streamer clusters and streamers also decreases greatly in the DBD in combination with the catalyst. The plasma dry reforming of CH$_4$ and CO$_2$ has been further studied under different operating conditions. The highest conversion rates of CH$_4$ and CO$_2$ are 47.6 % and 37.4 % at input power of 150 W, CH$_4$/CO$_2$ molar ratio of 2, and total feed flow rate of 60 ml/min, while the H$_2$ and CO selectivity of 30 % and 32.3 % can be achieved.

References