CHAPTER IV
SYNTHESIS GAS PRODUCTION FROM REFORMING OF METHANE WITH CARBON DIOXIDE IN AN AC ELECTRIC DISCHARGE OVER Pt/ZrO$_2$

4.1 Abstract

Carbon dioxide reforming with methane was studied in the presence and absence of Pt/ZrO$_2$ under the discharge condition at atmospheric pressure. A small amount of oxygen was added to reduce carbon formation and sustain the discharge. Pt/ZrO$_2$ was examined solely to investigate its performance at various temperatures. The Pt/ZrO$_2$ catalyst was found to be active for carbon dioxide reforming with methane in the absence of the discharge only at very high temperatures (higher than 600 °C). Reforming with and without Pt/ZrO$_2$, the effects of temperature, applied frequency, and input low side voltage were investigated. It was found that the methane, oxygen and carbon dioxide conversions increased with increasing oxygen content in the feed gas; decreased with increasing temperature (except oxygen conversion with Pt/ZrO$_2$). The maximum conversions were found at a frequency of about 500-600 Hz (except for oxygen conversion with Pt/ZrO$_2$). At 500 Hz with Pt/ZrO$_2$, the oxygen conversion was about 71%. Without Pt/ZrO$_2$, the conversions increased with increasing input low side voltage. With Pt/ZrO$_2$, the optimum conversions were found at an input low side voltage of 48 V. For all cases, carbon dioxide conversion was always lower than methane conversion. This study shows that in the presence of the discharge plasma operation at low temperatures is favored in contrast to operation with the Pt/ZrO$_2$ catalyst. The conversions of methane and carbon dioxide in the absence Pt/ZrO$_2$ were usually higher than in the presence of catalyst. However oxygen conversion was higher with Pt/ZrO$_2$. The H$_2$/CO ratio was strongly dependent on the oxygen content in feed gas and temperature but nearly constant with changes in frequency and input low side voltage. Oxygen content of the feed stream, operating temperature, frequency and input low side voltage effected on CO/C$_2$ ratio. C$_2$ hydrocarbons could not be found in the presence of Pt/ZrO$_2$ without plasma. The coupling of methane and further dehydrogenation of ethane to

produce ethylene, acetylene and additional hydrogen only occurred in the presence of the plasma. Consequently, the H_2/CO ratio when carbon dioxide reforming of methane under corona discharge was higher than stoichiometric H_2/CO ratio of 1, while a H_2/CO ratio close to 1 was obtained when only Pt/ZrO_2 was used to activate this reaction.

4.2 Introduction

Conversion of methane to synthesis gas (carbon monoxide and hydrogen), which is a versatile feed stock for ammonia, methanol and Fischer-Tropsch synthesis processes and several other carbonylation and hydrogenation or reduction processes) (Choudhary et al., 1998) can be achieved by partial oxidation, steam reforming and carbon dioxide reforming. Because carbon dioxide is a major component of both greenhouse gases and many natural gas resources, especially in Asia, CO_2 reforming is a potentially useful reaction for reducing the impact of carbon dioxide and may become important. Substantial research has been done on methane catalytic reforming with carbon dioxide to produce synthesis gas. Carbon dioxide reforming of methane (reaction 4.1) has some advantages over steam reforming (reaction 4.2) such as producing a lower H_2/CO ratio, and the possibility of producing higher purity carbon monoxide (O'Connor and Ross, 1998). In addition, the 1:1 H_2/CO ratio produced from CO_2 reforming is applicable for GTL applications.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H = 247.0 \text{ kJ mol}^{-1} \qquad (4.1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = 229.7 \text{ kJ mol}^{-1} \qquad (4.2)$$

One should not consider the aspect of net CO_2 reduction as the driver, other factors must be considered. For example, the previously mentioned high CO_2 in natural gas resources may be stranded by the high cost of CO_2 removal, which may be reduced or eliminated by use of CO_2 reforming. Although the conversion of carbon dioxide and methane to synthesis gas has potential applications in industry and also has environmental advantages, it has only occasionally been practically commercialized. However, a major problem of CO_2 reforming with methane, resulting from the high carbon content in the feed stream, is the high level of carbon deposition (reactions 4.3 and 4.4) and deactivation of the catalyst.

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta H = 75 \text{ kJ mol}^{-1} \qquad (4.3)$$

$$2CO \rightarrow C + CO_2 \qquad \Delta H = -171 \text{ kJ mol}^{-1} \qquad (4.4)$$

Many types of catalysts have been studied to enhance this reaction (O' Connor and Ross, 1998; Wang and Ju, 1998; Stagg-Williams et al., 2000; Bradford and Vannice, 1999). Pt/ZrO_2 was found to be very stable for carbon dioxide reforming with methane when operated at moderate temperatures (Stagg-Williams et al., 2000; O' Connor and Ross, 1998). So far, no effective commercial catalysts are available which can be operated without carbon formation (Kogelschatz et al., 1998). Another drawback of catalytic carbon dioxide reforming with methane is the high process temperature required of more than 800 °C. Therefore, solving these problems to find ways to operate this process at milder reaction conditions is of great interest. This has been shown to be possible in other methane conversion studies without carbon dioxide, such as helping in the low temperature plasma-catalytic conversion of methane over Sr/La_2O_3 (Marafee et al., 1997) and other materials. The disadvantage of using electrical energy, that at best it may only be about 60 percent efficient, can be offset by process simplicity and cost, lower carbon formation and less excess energy that must be recovered and utilized only with considerable cost.

A plasma is a quasineutral gas consisting of charged and neutral gas molecules with a collective behavior in which the charged species follow the path of the electric field. Historically, plasma chemistry technologies started as equilibrium plasma processes using plasma jets for heating. Later, it was found that the non-equilibrium plasmas have more benefits for a set of technologies (Savinov et al., 1999). The non-thermal, also called cold, plasma having non-equilibrium properties (high electron temperature and low bulk gas temperature) can provide the capability of initiating chemical reactions at low temperatures and with lower energy input.

A non-equilibrium discharge is an effective tool to generate energetic electrons, which can initiate a series of plasma chemical processes such as ionization, dissociation, and excitation. Utilization of a non-equilibrium plasma as an initiation "catalyst" introduces no environmental problems, low cost, high selectivities, and energy-efficient synthesis in some cases. It is a volumetric process with high productivity, e.g. the interaction between accelerated charged particles (i.e. electrons and ions) and other chemical species (i.e. molecules and radicals) takes place throughout the whole plasma volume to promote the reactions, that are not possible in surface catalysis technologies (Mutaf-Yardimci et al., 1998). Using electric discharges will bring to the process not only the required heat, but also initiating species in the homogeneous phase speed to up elementary reactions. (Lesueur et al., 1994).

The activation of methane by electric fields was first reviewed more than 50 years ago (Glocker and Lind, 1939). Recently, non-equilibrium plasmas have been extensively studied as a possible way to initiate the reaction of methane to various products for industrial application because of its effectiveness in the activation of methane at low gas temperatures (Larkin et al., 1998(a); Larkin et al., 1998(b); Larkin el al., 2001; Thanyachotpaiboon et al., 1998; Yao et al., 2000; and Zhou et al., 1998(b)). A number of researchers are also interested in improving synthesis gas production from methane using electric discharges (Lesueur et al., 1994; Zhou et al., 1998(a)). The corona type discharge was chosen for this study due to its ability to operate at atmospheric pressure and higher. Applications for corona discharge processes have existed for over a hundred years. They play an important role in many industrial applications such as electrostatic precipitation, electro photography, static control in semiconductor manufacture, ionization instrumentation, generation of ozone and destruction of toxic compounds (Lowke and Morrow, 1994; and Chang et al., 1991).

A corona discharge is one of the promising techniques to reduce the conventional problem with synthesis gas production. In this work, a low temperature plasma reactor was used to facilitate carbon dioxide reforming of methane in the presence and absence of Pt/ZrO_2 catalysts. The effects of operating temperature, frequency and input low side voltage on conversions, H_2/CO and CO/C_2 were investigated.

4.3 Experimental

4.3.1 Plasma System

The flow rates of feed gases containing methane, carbon dioxide, and oxygen were controlled by a set of mass flow controllers supplied by SIERRA Instrument, Inc. The feed gases were introduced downward through the reactor and analyzed on-line by a Perkin-Elmer gas chromatograph, with thermal conductivity (TCD) and flame ionization (FID) detectors. The exhaust gas from the reactor was introduced into a condenser cooled by a mixture of dry ice and acetone that was used to remove the condensable products. Water was not quantified. All experiments were carried out at atmosphere pressure. The power supply unit consisted of an AC power supply for converting domestic AC power 220 V, 50 Hz, using a function generator for varying the frequency with a sinusoidal waveform. The output was then transmitted to a high voltage alternating current (HVAC) transformer. The HVAC could step up the low side voltage to the high side voltage by nominal factor of 125 at 60 Hz. This factor may not be constant with changes in frequency due to changes in power factor because of the capacitive nature of the reactor system. The electrodes were connected to the HVAC by stainless steel rods. The configuration of the reactor is shown in Figure 4.1. The discharge occurred in a quartz tube with an i.d. of 8 mm between two stainless steel electrodes. The upper wire electrode is centered axially within the reactor tube, while the lower electrode is a circular plate with eight holes to allow gas to pass through the reactor and is positioned perpendicular to the reactor axis. The gap distance between these two electrodes is 13 mm. The catalyst, which was placed on the lower electrode of the reactor, was 0.1 g. for all experiments. An Omega K-type thermocouple was place against of middle of outside wall of the reactor for monitoring the reaction temperature. Measurement of the gas temperature of the corona is complicated by the discharge, which can occur between the wire tip and the thermocouple. Therefore, the thermocouple was placed only after collecting all data. The gas discharge is usually initiated at room temperature and the gas is self-heated by the plasma. For this system, the conversions are defined as:

Conversion of methane = (moles of CH_4 consumed/moles of CH_4 introduced) x 100 %

Conversion of carbon dioxide = (moles of CO_2 consumed/moles of CO_2 introduced) x 100 %

Conversion of oxygen = (moles of O_2 consumed/moles of O_2 introduced) x 100 %

H_2/CO mole ratio = moles of H_2 produced/moles of CO produced

CO/C_2 mole ratio = moles of CO produced/moles of ethane, ethylene and acetylene produced

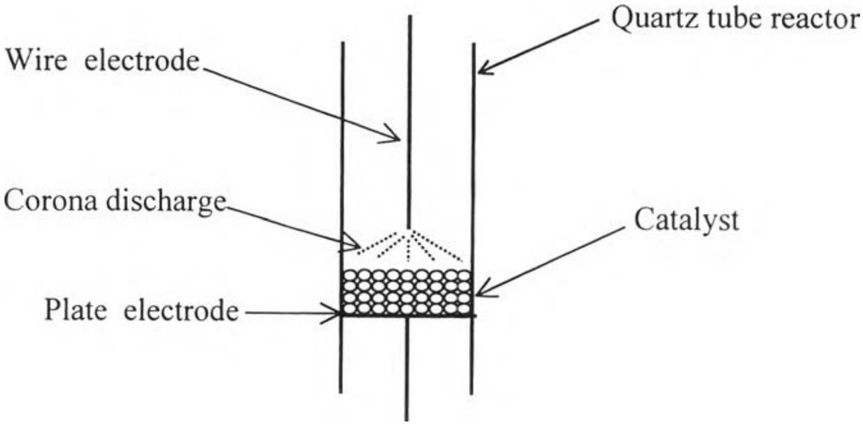

Figure 4.1 Corona discharge reactor configuration.

4.3.2 Catalyst Preparation

1 wt.% Pt/ZrO_2 catalyst was prepared by following the preparation technique of O'Connor and Ross (1998). The ZrO_2 support was prepared by calcining Zirconium (IV) hydroxide, 97% (Aldrich Chemical Company, Inc.) in flowing air at 800 °C for 15 h. The support was impregnated with a solution of Hexachloroplatinic (IV)- acid hexahydrate (40% Pt). Following equilibration overnight, the sample was then oven-dried at 120 °C for 2 h. The catalyst was subsequently calcined in air at 600 °C for 6 h. The percentage of platinum on the support was analyzed by atomic absorption spectroscopy. The analysis results of actual platinum loading was 1.00% Pt over ZrO_2.

4.4 Results and Discussion

4.4.1 Effect of Oxygen Content

Oxygen was added about 2-8 %. Oxygen has only a small effect on methane and carbon dioxide conversions in the range studied as shown in Figure 4.2. Evidently molecular oxygen is activated to form negative ions by dissociative attachment (reaction 4.5) and then this active negative oxygen ion further abstracts hydrogen from the methane molecule to form methyl radicals in the corona discharge (reaction 4.6), resulting in increasing methane conversion with increasing fraction of oxygen in the feed stream.

$$O_2 + e^- \rightarrow 2O + e^- \rightarrow O^- + O \qquad (4.5)$$

$$CH_4 + O^- \rightarrow CH_3 + OH^- \qquad (4.6)$$

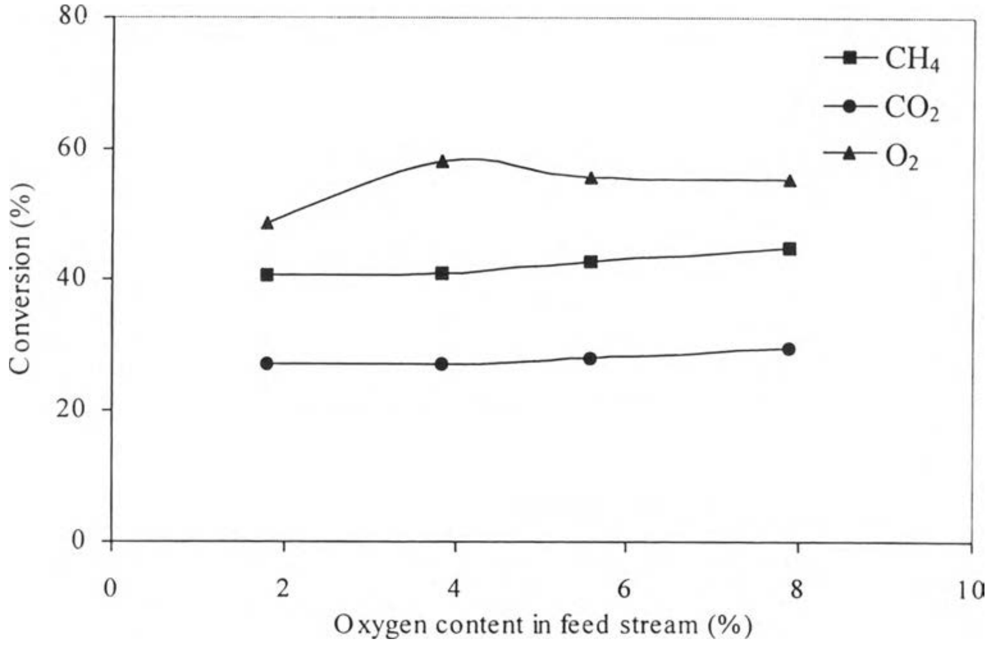

Figure 4.2 Effects of oxygen content on conversions. (overall flowrate, 50 sccm; applied frequency, 600 Hz; input low side voltage, 64 V; gap width, 1.3 cm and CH_4/CO_2 feed mole ratio, 1:1; and without catalyst)

Carbon deposition on the reactor was observed when adding oxygen less than 4 % in the feed stream because there is insufficient O^- to react with the carbon. An increase in the active negative oxygen (O^-) probably increases the rate of oxidation of methane and C_2 products to produce carbon monoxide, carbon dioxide, and water with no hydrogen production as suggested by the increasing CO/C_2 ratio and decreasing H_2/CO ratio as shown in Figure 4.3.

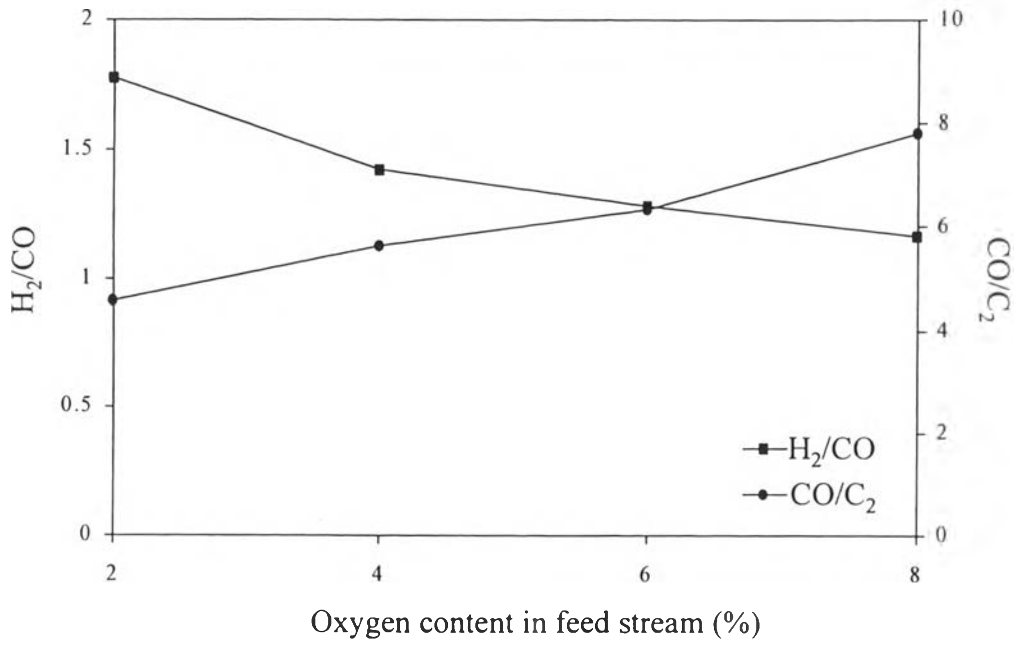

Figure 4.3 Effects of oxygen content on H_2/CO and CO/C_2. (overall flowrate, 50 sccm; applied frequency, 600 Hz; input low side voltage, 64 V; gap width, 1.3 cm and CH_4/CO_2 feed mole ratio, 1:1; and without catalyst)

4.4.2 Effect of Temperature

The activity of Pt/ZrO_2 for methane reforming with carbon dioxide at different temperatures is shown in Figure 4.4. The catalyst was not active at temperatures lower than 650 °C. The results showed that this catalyst was very effective for methane reforming with carbon dioxide at very high temperatures (about 900 °C). H_2/CO ratio increased from 0.5 to 1.0, close to stoichimetric ratio, with increasing operating temperature from 650 to 900 °C. C_2 hydrocarbon products were not found when only the catalyst was used to activate the reaction. This result indicated that there was no competing reaction, coupling of methane, as has been observed in methane corona discharge reactions.

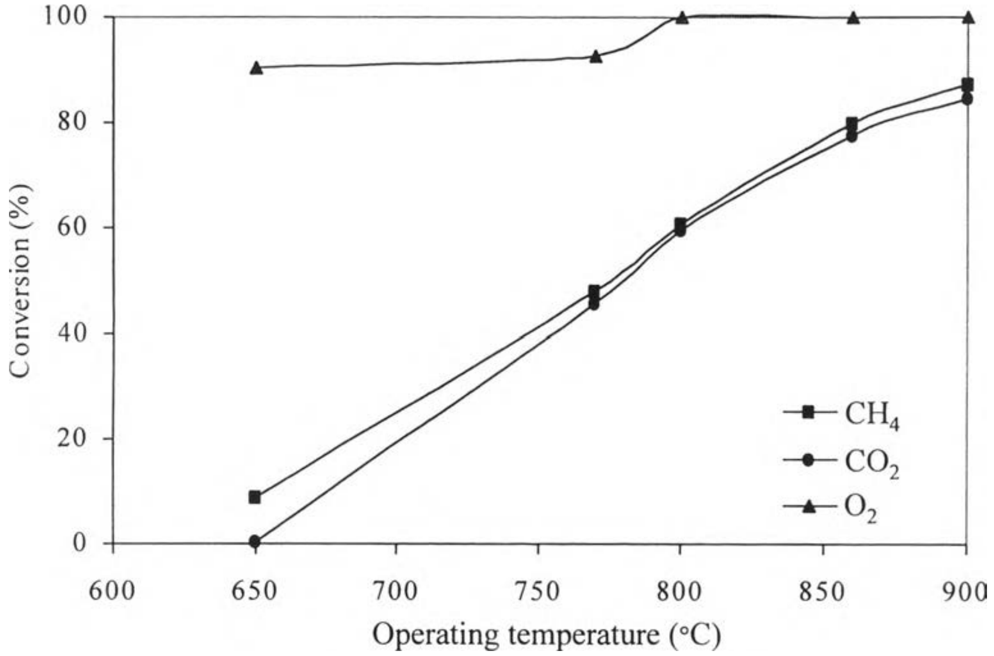

Figure 4.4 Effects of operating temperature of Pt/ZrO_2 catalyst without plasma on methane, carbon dioxide and oxygen conversions. (overall flowrate, 50 sccm; $CH_4/CO_2/O_2$ feed mole ratio, 12:12:1)

The comparison between the effect of using the plasma with and without Pt/ZrO_2 operated at different temperatures on methane reforming with carbon dioxide is shown in Figure 4.5. Both conversions of carbon dioxide and methane decreased gradually with increasing temperature, but oxygen conversion increased when using the plasma with Pt/ZrO_2. Without Pt/ZrO_2, the conversions of methane, carbon dioxide and oxygen decreased with increasing reaction temperature even though carbon dioxide reforming is an endothermic reaction. It can be concluded that the plasma reaction favors operation at room temperature rather than high temperatures. In the range of temperatures studied (lower than 650 °C), the catalyst did not assist the plasma to activate methane or carbon dioxide.

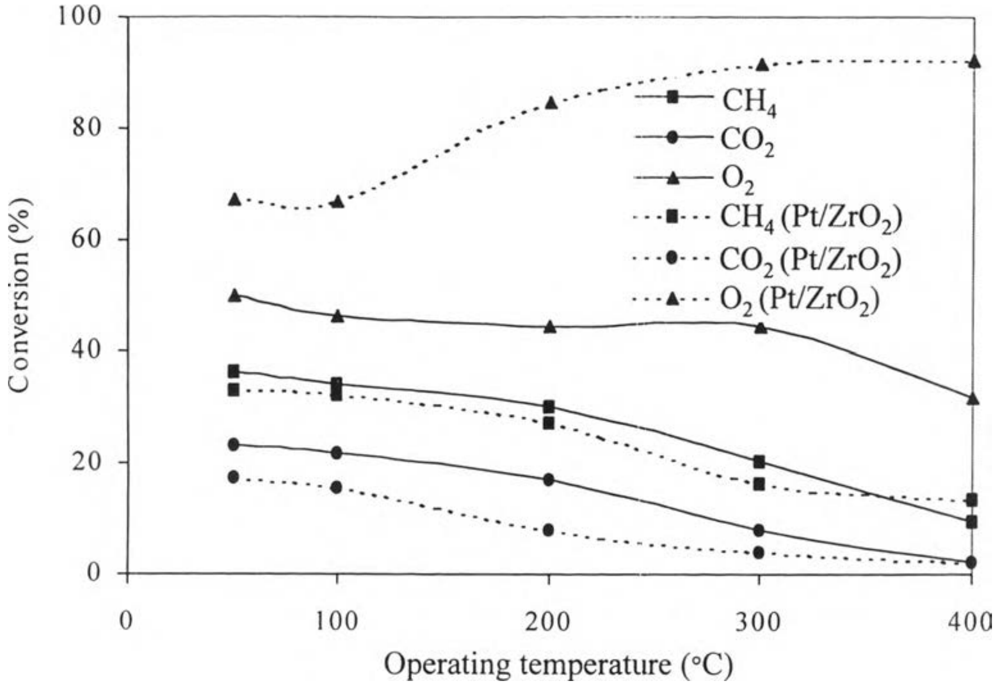

Figure 4.5 Effects of operating temperature on conversions. (overall flowrate, 50 sccm; applied frequency, 600 Hz; input low side voltage, 56 V; gap width, 1.3 cm; $CH_4/CO_2/O_2$ feed mole ratio, 12:12:1; and with/without catalyst)

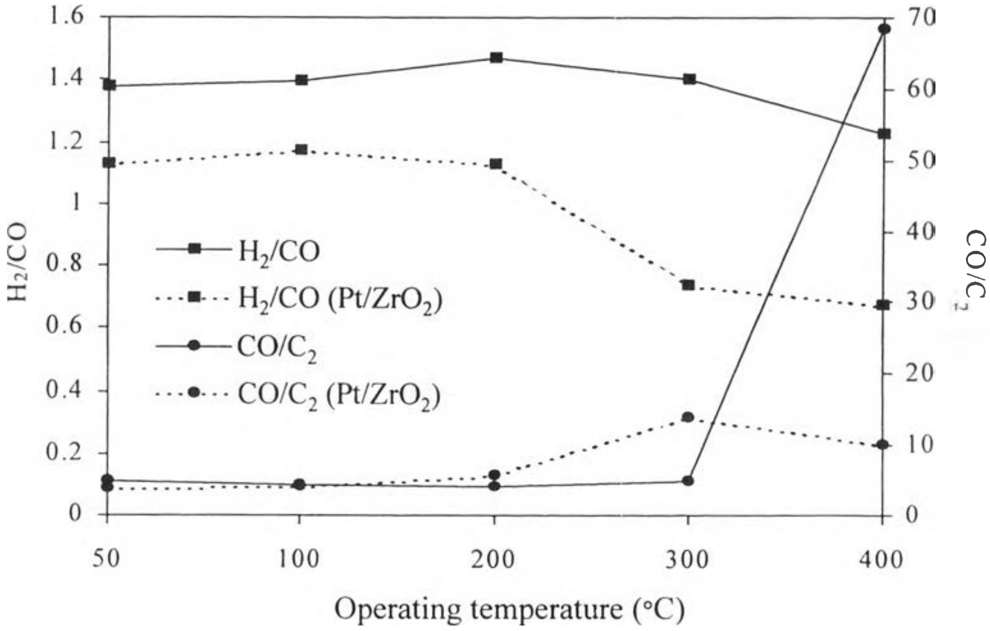

Figure 4.6 Effects of operating temperature on H_2/CO and CO/C_2. (overall flowrate, 50 sccm; applied frequency, 600 Hz; input low side voltage, 56 V; gap width, 1.3 cm; $CH_4/CO_2/O_2$ feed mole ratio, 12:12:1; and with/without catalyst)

As previously mentioned, the coupling of methane by the plasma is more effective at a low temperature. Further dehydrogenation of ethane to produce ethylene, acetylene and hydrogen also decrease with increasing operating temperature, as shown in Figure 4.6, thus causing the CO/C_2 ratio to increase and the H_2/CO ratio to decrease. Interestingly, for the catalytic plasma system, the CO/C_2 ratio increased dramatically when the temperature increased from 300 °C to 400 °C indicating the catalytic activity for the methane oxidation depending on the reaction temperature.

4.4.3 Effect of Frequency

Without the catalyst, the maximum methane and carbon dioxide conversions are found at 600 Hz. The maximum conversions of methane and carbon dioxide shift from 600 Hz to 500 Hz under the presence of the catalyst as shown in Figure 4.7.

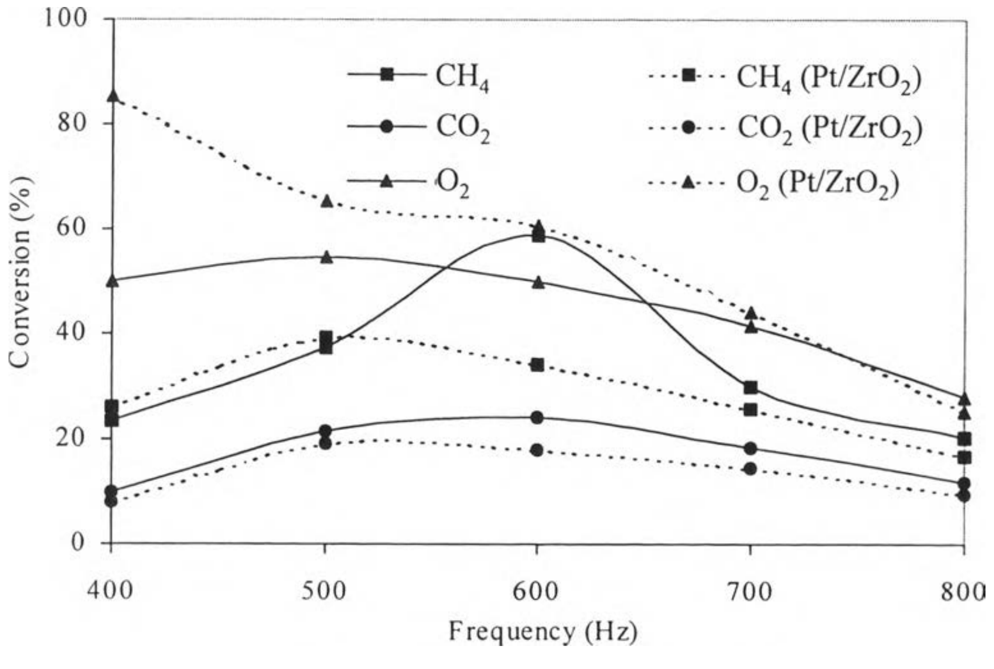

Figure 4.7 Effects of applied frequency on conversions. (overall flowrate, 50 sccm; input low side voltage, 56 V; gap width, 1.3 cm; CH_4/CO_2/O_2 feed mole ratio, 12:12:1; and with/without catalyst)

The main effect of frequency on the conversions and selectivities results from the space charge (electrons and ions) characteristics of the discharge, even though the power is constant. As the AC discharge is applied, each electrode performs alternatively as anode or cathode. The alternating behavior has proven effectively in eliminating contaminant accumulation on the electrodes, which shows that the system behavior is significantly different with AC discharges than with DC (Liu *et al.*, 1996).

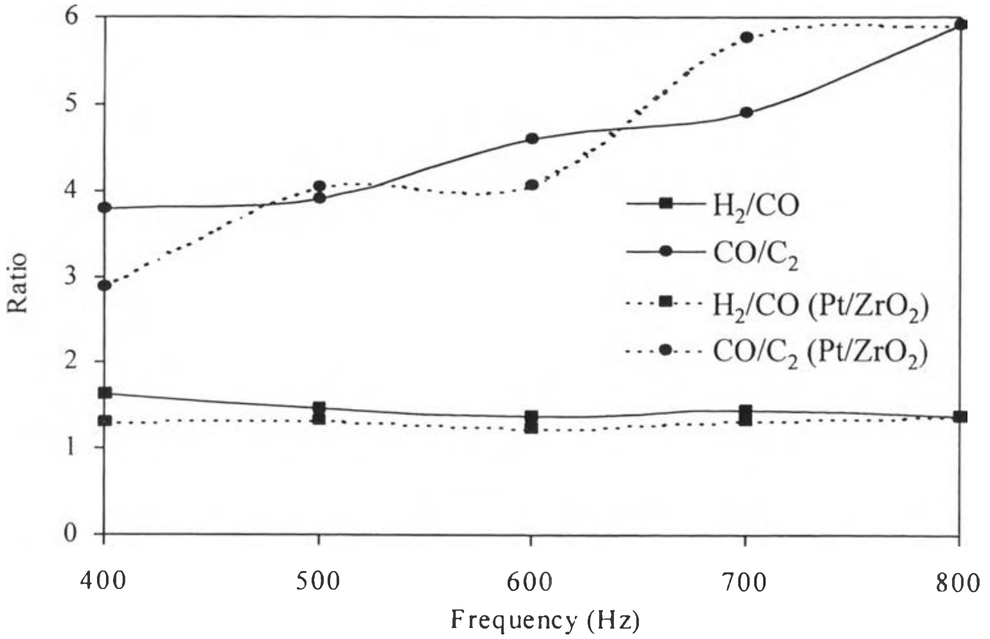

Figure 4.8 Effects of applied frequency on H_2/CO and CO/C_2. (overall flowrate, 50 sccm; input low side voltage, 56 V; gap width, 1.3 cm; $CH_4/CO_2/O_2$ feed mole ratio, 12:12:1; and with/without catalyst)

Acceleration of the remaining space charge by the reversing electric field can decrease the amount of current needed to sustain the discharge. The capacitive nature of the reactor creates a phase lag between the voltage and current waveforms and this increases with higher frequency, thus reducing the power factor and discharge power at constant applied voltage. For this reason, the conversion of methane and oxygen increased with decreasing frequency until about 400-500 Hz. Carbon began to form in the reactor when the frequency was decreased lower than 400 Hz. Since this carbon is electrically conductive, the current tends to flow almost entirely through these carbon deposits. This reduces the number of discharge streamers and limits the number of energetic electrons that can interact with the feed gases in the reaction zone resulting in obstruction methane conversion as well as the reaction rate. The frequency has no strong effect on the H_2/CO mole ratio in the presence or absence Pt/ZrO_2 as shown in Figure 4.8.

4.4.4 Effect of Applied Voltage

To investigate the effect of applied voltage on the system, the applied low side voltage was varied from 32 to 72 V corresponding about 4,000-9,000 V in the reaction zone. In contrast to increase in the frequency, all conversions increased with increasing applied voltage without catalyst (Figure 4.9).

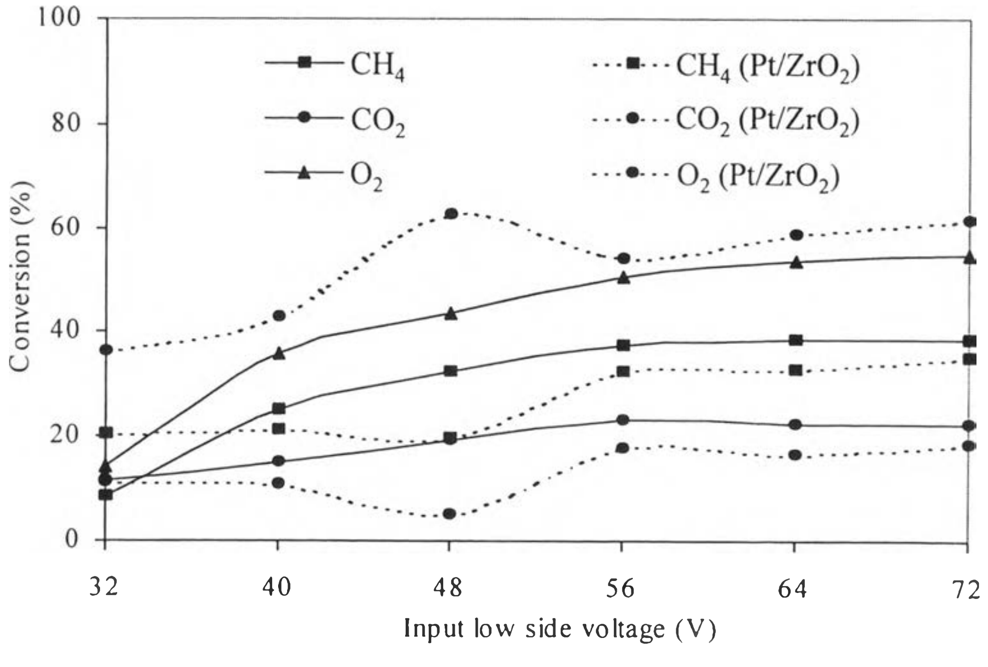

Figure 4.9 Effects of input low side voltage on conversions. (overall flowrate, 50 sccm; applied frequency, 600 Hz; input low side voltage, 56 V; gap width, 1.3 cm $CH_4/CO_2/O_2$ feed mole ratio, 12:12:1; and with and without catalyst)

As shown in Figure 4.10, the H_2/CO mole ratio remained almost constant at about 1.4 with increasing voltage under the presence and absence catalyst. When the system had no Pt/ZrO_2, the CO/C_2 ratio was also constant. The current increased from 0.51 to 0.80 A and from 0.57 to 0.83 A with increasing input low side voltage with and without catalyst, respectively. The current of the plasma system with catalyst always is lower than the one without catalyst. Consequently, methane and carbon dioxide conversions are lower than in the sole plasma system.

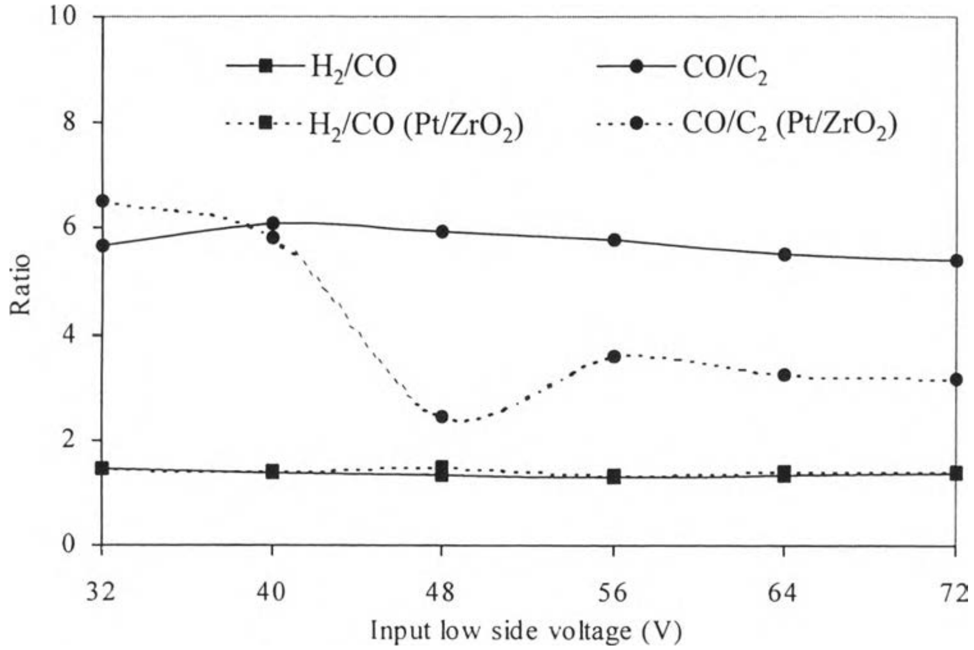

Figure 4.10 Effects of input low side voltage on H_2/CO and CO/C_2. (overall flowrate, 50 sccm; applied frequency, 600 Hz; input low side voltage, 56 V; gap width, 1.3 cm; $CH_4/CO_2/O_2$ feed mole ratio, 12:12:1; and with/without catalyst)

The methane and carbon dioxide conversions depend on the current since an increase in current will give more available electrons to initiate the reactions. Unfortunately, the conversion cannot reach 100 % by increasing input low side voltage because the discharge becomes unstable due to carbon formation on both electrodes as well as the quartz tube wall (reaction 4.7).

$$CO + e^- \rightarrow C + O + e^- \qquad (4.7)$$

From these results, it can be concluded that both carbon atoms from methane and carbon dioxide favor formation of carbon monoxide more than C_2 hydrocarbons at low current since carbon monoxide formation is easier than the coupling reaction of methane. At high currents, carbon monoxide can react further to form carbon leading to decreasing carbon monoxide and CO/C_2 ratio as well as carbon formation. The hydrogen atoms (or OH) tend to form H_2O more than hydrogen, so hydrogen decreases at higher voltage and lower frequency. The hydrogen and carbon monoxide both decrease at the same rate with increasing current so the H_2/CO is almost constant.

4.5 Conclusions

Pt/ZrO_2 has high activity for carbon dioxide reforming with methane, but only at very high temperatures. Catalyst deactivation and high operating temperature become a major drawback of Pt/ZrO_2. Therefore, operating this process at milder reaction conditions is of great interest. In this work, a corona discharge reactor was used to facilitate this reaction at lower temperatures. This study shows that the plasma favors low temperature, in contrast to Pt/ZrO_2 catalyst. The presence of Pt/ZrO_2 in discharge reactor did not show any synergetic effect on methane and carbon dioxide conversions. Moreover, conversions of methane and carbon dioxide in the presence Pt/ZrO_2 usually were lower than in the absence of Pt/ZrO_2 while oxygen conversion was higher because oxygen was activated by Pt/ZrO_2 at a much lower temperature than methane and carbon dioxide. C_2 hydrocarbons could not be found in the presence of Pt/ZrO_2. The oxidative coupling of methane and further dehydrogenation of ethane to produce ethylene, acetylene and hydrogen could be formed by plasma. Consequently, the H_2/CO ratio was higher than H_2/CO stoichiometric ratio of 1 when activated by carbon dioxide reforming with methane in this corona discharge, while H_2/CO ratios close to 1 were obtained when only Pt/ZrO_2 was used to activate this reaction.

4.6 Acknowledgements

The Thailand Research Fund is gratefully acknowledged for supporting this research work as well as providing a scholarship for the first author.

4.7 References

Bradford, M. C. J., and M. A. Vannice, "The Role of Metal-Support Interactions in CO_2 Reforming of CH_4," *Catal. Today*, **50**, 87 (1999).

Chang, J.-S., P. A. Lawless, and T. Yamamoto, "Corona Discharge Process," *IEEE Trans. Plasma Sci.*, **19**, 1152 (1991).

Choudhary, V. R., B. S. Uphade, and A. S. Mamman, "Simultaneous Steam and CO_2 Reforming of Methane to Syngas Over NiO/MgO/SA-5205 in Presence and Absence of Oxygen," *Appl. Catal. A: Gen.*, **168**, 33 (1998).

Glocker, G., and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics, Wiley, Now York, 193 (1939).

Kogelschatz, U., L. M. Zhou, B. Xue, and B. Eliasson, "Production of Synthesis Gas Through Plasma – Assisted Reforming of Greenhouse Gases," *Proc. 4th Int. Conf. on Greenhouse Gas Control Technologies, Interlaken, Switzerland*, 385 (1998).

Larkin, D. W., T. A. Caldwell, L. L. Lobban, and R. G. Mallinson, "Oxygen Pathways and Carbon Dioxide Utilization in Methane Partial Oxidation in Ambient Temperature Electric Discharges," *Energy and Fuels*, **12**, 740 (1998a).

Larkin, D.W., M. Leethochawalit, S. Chavadej, T. A. Caldwell, L.L. Lobban, and R. G. Mallinson, "Carbon Pathways, CO_2 Utilization, and In Situ Production Removal in Low Temperature Plasma Methane Conversion to Methanol," *Proc. 4th Int. Conf. on Greenhouse Gas Control Technologies, Interlaken, Switzerland*, 397 (1998b).

Larkin, D.W., L. L. Lobban, and R. G. Mallinson, "Production of Organic Oxygenates in the Partial Oxidation of Methane in a Silent Electric Discharge Reactor," *Ind. Eng. Chem. Res.*, **40**, 1594 (2001).

Lesueur, H., A. Czernichowski, and J. Chapelle, "Electrically Assisted Partial Oxidation of Methane," *Int. J. Hydrogen Energy*, **19**, 139 (1994).

Liu, C., A. Marafee, B. Hill, G. Xu, R. Mallinson, and L. Lobban, "Oxidative Coupling of Methane with ac and dc Corona Discharge," *Ind. Eng. Chem. Res.*, **35**, 3295 (1996).

Lowke, J.J., and R. Morrow, "Theory of Electric Corona Including the Role of Plasma Chemistry," *Pure&Appl. Chem*, **66**, 1287 (1994).

Marafee, A., C. Liu, G. Xu, R. Mallinson, and L. Lobban, "An Experimental Study on the Oxidative Coupling of Methane in a Direct Current Corona Discharge Reactor over Sr/La_2O_3 Catalyst," *Ind. Eng. Chem. Res.*, **36**, 632(1997).

Mutaf-Yardimci, O., A. V. Saveliev, A. A. Fridman, and L. A. Kennedy, "Employing Plasma as Catalyst in Hydrogen Production," *Int. J. Hydrogen Energy*, **23**, 1109 (1998).

O'Connor, M. A., and Julian R. H. Ross, "The Effect of O_2 Addition on the Carbon Dioxide Reforming of Methane Over Pt/ZrO_2 Catalysts," *Catal. Today*, **46**, 203 (1998).

Savinov, S. Y., H. Lee, H. K. Song, and B.-K. Na, "Decomposition of Methane and Carbon Dioxide in a Radio-Frequency Discharge," *Ind. Eng. Chem. Res.*, **38**, 2540 (1999).

Stagg-Williams, S. M., F. B. Noronha, G. Fendley, and D. E. Resasco, "CO_2 Reforming of CH_4 over Pt/ZrO_2 Catalysts Promoted with La and Ce Oxides," *J. Catal.*, **194**, 240 (2000).

Thanyachotpaiboon, K., S. Chavadej, T. A. Caldwell, L. L. Lobban, and R. G. Mallinson, "Conversion of Methane to Higher Hydrocarbons in AC Nonequilibrium Plasmas," *AIChE J.*, **44**, 2252 (1998).

Wang, S., and G. Q. Ju, "Reforming of Methane with Carbon Dioxide over Ni/Al_2O_3 Catalysts: Effect of Nickel Precursor," *Appl. Catal. A: Gen.*, **169**, 271 (1998).

Yao, S. L., T. Takemoto, F. Ouyang, A. Nakayama, and E. Suzuki, "Selective Oxidation of Methane Using a Non-Thermal Pulsed Plasma," *Energy & Fuels*, **14**, 459 (2000).

Zhou, L. M., B. Xue, U. Kogelschatz, and B. Eliasson, "Nonequilibrium Plasma Reforming of Greenhouse Gases to Synthesis gas," *Energy & Fuels*, **12**, 1191 (1998a).

Zhou, L. M., B. Xue, U. Kogelschatz, and B. Eliasson, "Partial Oxidation of Methane to Methanol with Oxygen or Air in a Non-equilibrium Discharge Plasma," *Plasma Chem. Plasma Processing*, **18**, 375 (1998b).