

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characteristics of studied catalyst

The results from this research work are plotted and discussed in this chapter. The raw data for those results are summarized in Appendix A.

Combination of corona discharge and catalysis gives the feasibility of methane conversion at atmospheric conditions. The Cu/ZnO catalyst used in this research work was found to have a low BET surface area equal to $48 \text{ m}^2/\text{g}$. AAS was used to analyze the percentages of Cu to Zn in the catalyst equal to 11.4%. Figure 4.1 shows the XRD spectra for the fresh catalyst. This confirms that the CuO and ZnO crystalline phase exist on the catalyst.

4.2 Effect of oxygen partial pressure

4.2.1 Effect of oxygen partial pressure on conversions

Figure 4.2 shows the effect of oxygen partial pressure on methane and oxygen conversions at the total flow rate of 100 ml/min and applied voltage of 5000 V. The methane conversion increased almost linearly with increasing the oxygen partial pressure or oxygen concentration. The oxygen conversion was high especially in at low oxygen concentration. It was found that the maximum oxygen conversion appeared at the methane to oxygen ratio of 4:1. Oxygen plays an important role on the reaction rate because at even low concentration of methane in the feed, methane conversion is still high. It can also be explained that when the amount of oxygen present in the reaction increased, the active and excited species of oxygen such as O^\cdot and $\text{O}^{2\cdot-}$ from electron attachment would be increased. This large number of active oxygen ions can then further activate methane molecule.

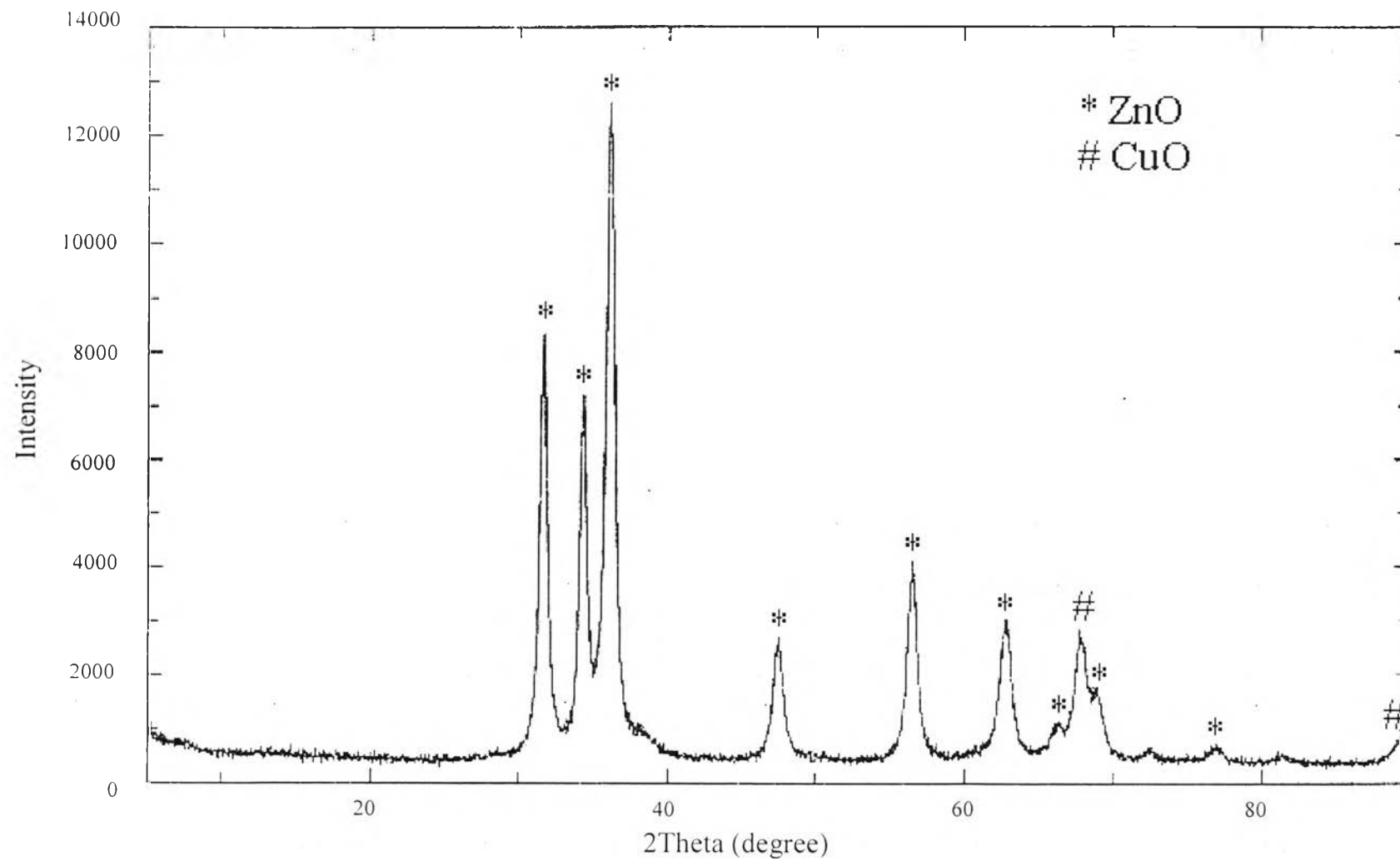


Figure 4.1 XRD spectra of the studied catalyst

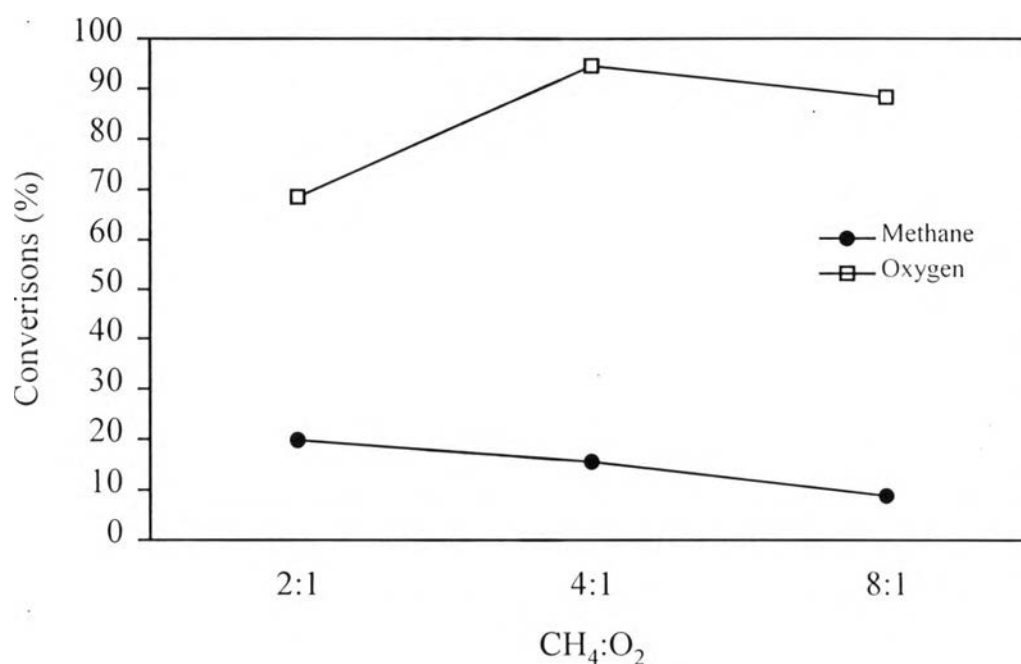


Figure 4.2 Effect of oxygen partial pressure on conversions of methane and oxygen at total flow rate = 100 ml/min and applied voltage = 5,000 V

4.2.2 Effect of oxygen partial pressure on products selectivities

According to Figure 4.3, all products selectivities except carbon dioxide significantly increased with decreasing the oxygen partial pressure. At high concentration of oxygen, methane conversion is high but all products selectivities are low, this can be explained that the products seem to be further oxidized to carbon dioxide. Methanol was found as only trace in the product stream. Another oxygenate product, formaldehyde, selectivity was improved from 4.6 to 13.5 by increasing CH₄:O₂ from 2:1 to 8:1. Although the first priority product, methanol, was produced in small quantity, the other useful product, synthesis gas, was produced substantially and its selectivity increased with decreasing the oxygen concentration in the feed. The highest selectivities of synthesis gas obtained from this experiment were 19.3% and 33.6% for CO and H₂ respectively. A significant amount of C₂ hydrocarbons was also found

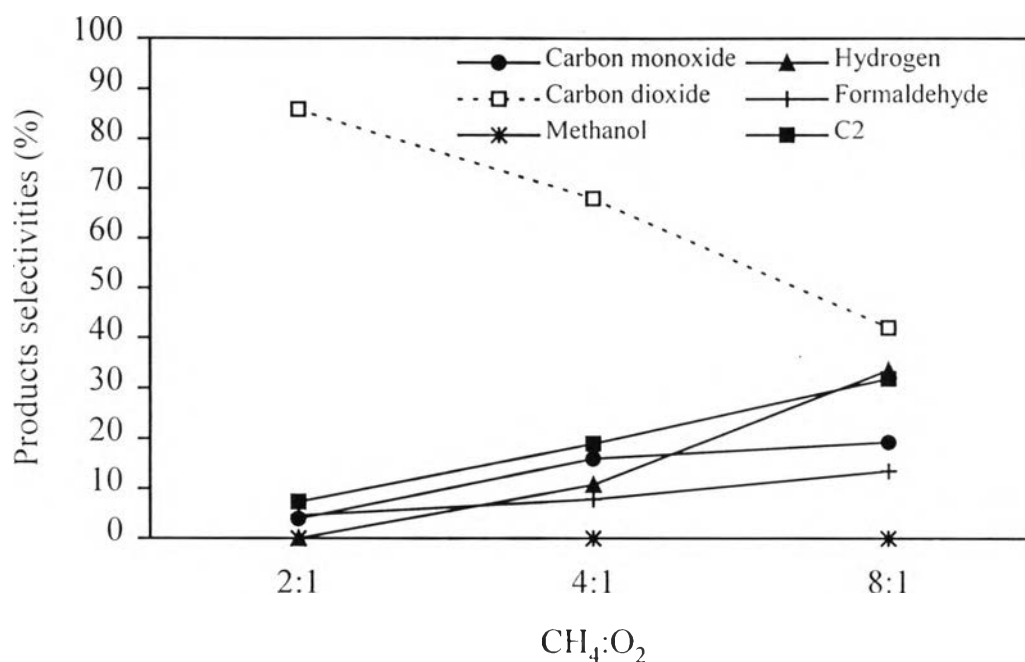


Figure 4.3 Effect of oxygen partial pressure on products selectivities at total flow rate = 100 ml/min and applied voltage = 5,000 V

in the product stream. Its selectivity increased with decreasing the oxygen partial pressure. Moreover, as the oxygen partial pressure decreases, the undesired product, CO₂, is sharply reduced.

4.3 Effect of applied voltage

4.3.1 Effect of applied voltage on conversions

The effect of applied voltage on both conversions of methane and oxygen is shown in Figure 4.4. At the beginning of increasing the applied voltage from 5,000 V to 6,000 V, the methane conversion increased significantly from 15.6% to 22.6%. However, beyond 6,000 V, methane conversion almost remained constant with increasing applied voltage. The reason that the methane conversion remains almost constant is insufficient of

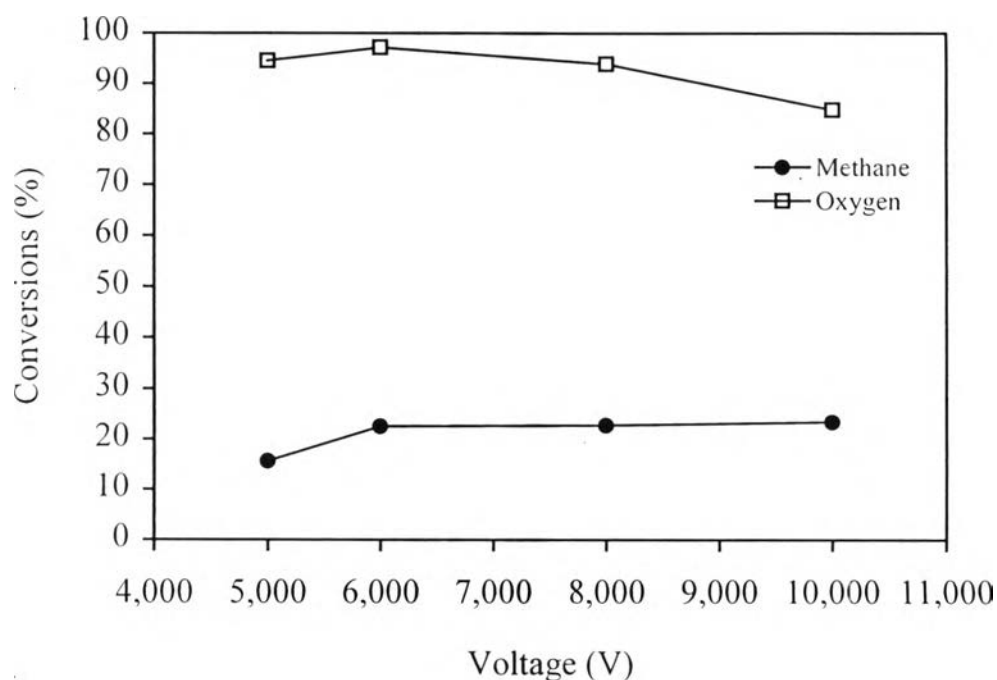


Figure 4.4 Effect of applied voltage on conversions of methane and oxygen at total flow rate = 100 ml/min and $\text{CH}_4:\text{O}_2 = 4:1$

oxygen in the reaction. Under the studied condition, oxygen conversion was very high, greater than 90%, and it indicates that the oxygen supplied from the feed was not enough for further increasing methane conversion when increasing the applied voltage. Therefore, oxygen is limiting the reaction and this is supported by the results of the previous experiment where at low oxygen concentration the methane conversion was also low.

4.3.2 Effect of applied voltage on products selectivities

Figure 4.5 illustrates the effect of applied voltage on products selectivities. A amount of methanol produced in this experimental condition was very low. The selectivity of formaldehyde slightly decreased with increasing the applied voltage. C_2 hydrocarbons selectivity improved significantly by increasing the applied voltage from 5,000 V to 6,000 V but stayed almost the same at about 35% beyond 6,000 V. A significant quantity

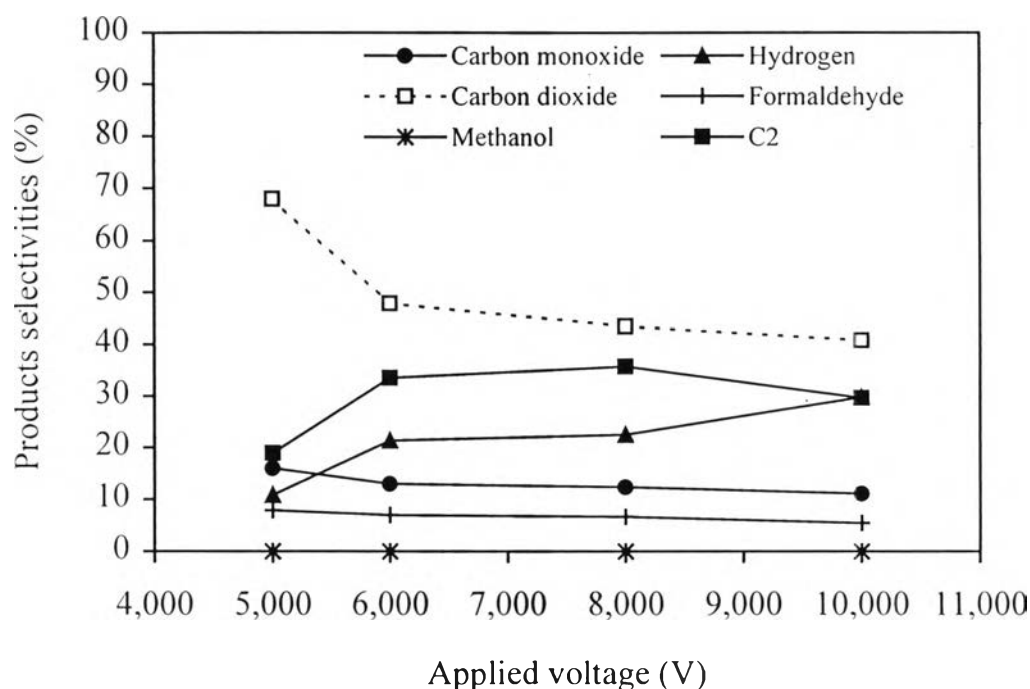


Figure 4.5 Effect of applied voltage on products selectivities at total flow rate = 100 ml/min and $\text{CH}_4:\text{O}_2 = 4:1$

of synthesis gas was also found in the product stream. As the applied voltage increased, CO selectivity decreased from 16.0% to 11.1%. The hydrogen gas selectivity dramatically increased from 10.8% to 29.8% while the applied voltage increased from 5,000 V to 6,000 V. This hydrogen gas produced may be from the reaction of the products because the conversion of methane is almost the same in this voltage range. As the applied voltage increased, the degree of over oxidation reduced and CO_2 produced from the reactor reduced. It is very interesting to point out that an increase of the coupling reaction of methane to C_2 formation appears with increasing applied voltage.

4.4 Effect of total flow rate

4.4.1 Effect of total flow rate on conversions of methane and oxygen

Figure 4.6 shows both methane and oxygen conversions with respect to changing total flow rate or residence time. An increasing the total

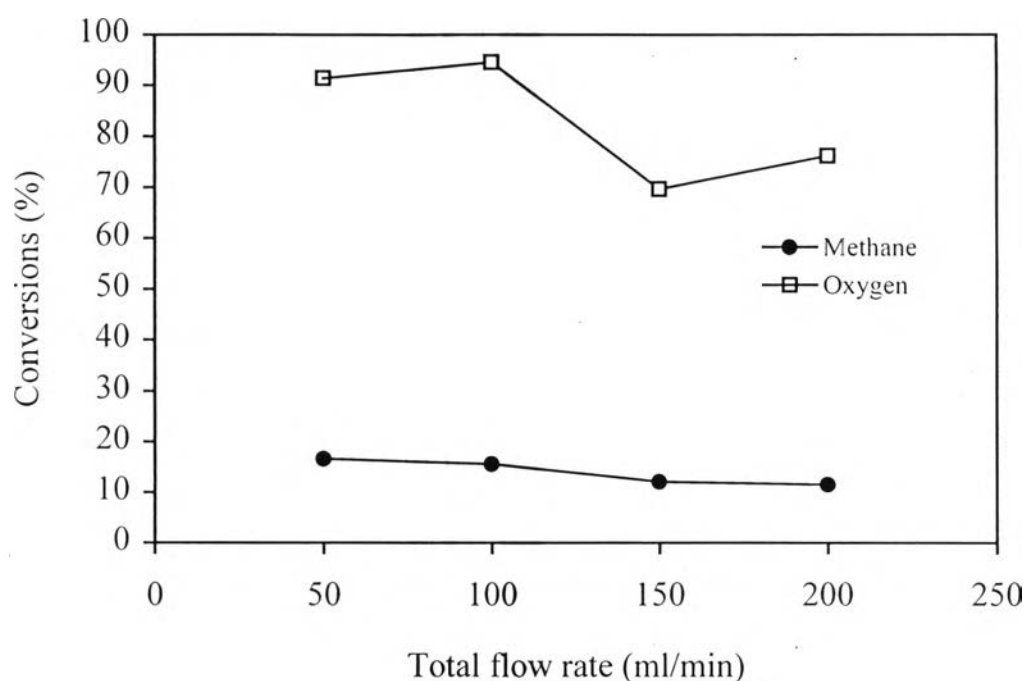


Figure 4.6 Effect of total flow rate on conversions of methane and oxygen at $\text{CH}_4:\text{O}_2 = 4:1$ and applied voltage = 5,000 V

flow rate corresponds to the residence time. Both methane and oxygen conversions slightly decreased with increasing the total flow rate of the feed gas from 50 to 200 ml/min. At the total flow rate of 50 ml/min, the system gave highest methane conversion of 16.6% while oxygen conversion was about 90%.

4.4.2 Effect of total flow rate on products selectivities

The effect of total flow rate on products selectivities is showed in Figure 4.7. All of the products selectivities except CO_2 increased with decreasing the total flow rate. At a total flow rate of 50 ml/min, formaldehyde selectivity was equal to 10.9%, C_2 hydrocarbons selectivity was about 33.4%, CO selectivity was 17.0% and H_2 selectivity was 33.9%. This indicates that the longer reaction time leads to get higher products selectivities.

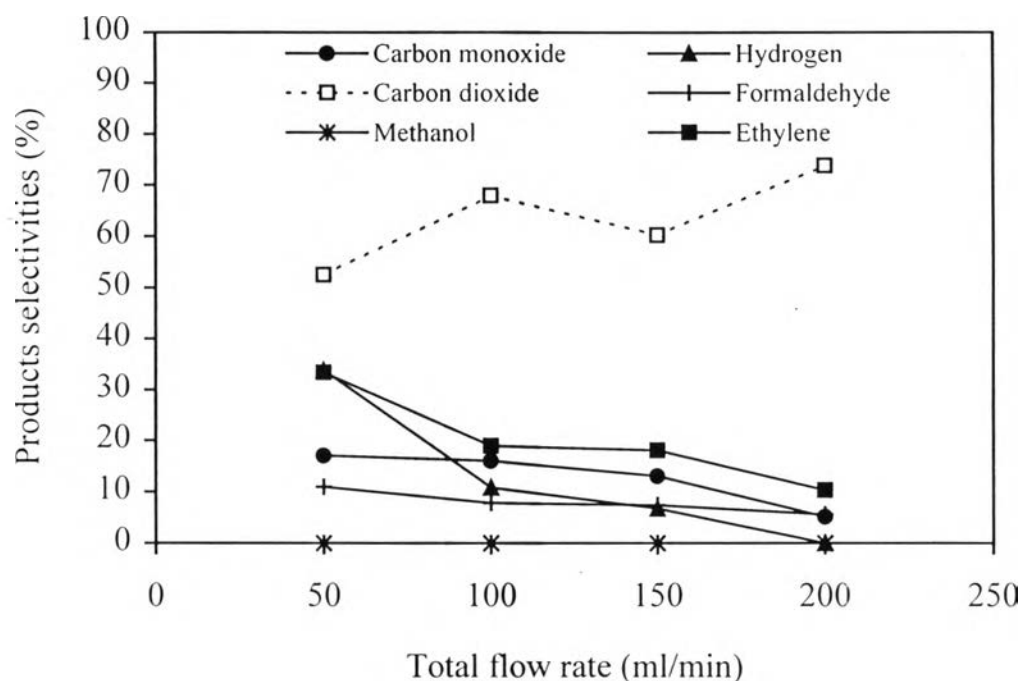


Figure 4.7 Effect of total flow rate on products selectivities at $\text{CH}_4:\text{O}_2 = 4:1$ and applied voltage = 5,000 V

However, the undesired product, CO_2 , did not decrease with increasing the total flow rate.

4.5 Effect of catalyst

4.5.1 Effect of catalyst on conversions of methane and oxygen

Table 4.1 shows the conversion of reactant gases in the catalytic and non-catalytic systems. As the partial pressure of oxygen in the feed gas increased, methane conversion of both systems increased. The non-catalytic system gave higher methane conversion than the catalytic system. In contrast, oxygen conversion in the catalytic system was much higher than the non-catalytic system. This may lead to a conclusion that under the presence of catalyst, the system can have a better utilization of oxygen to form an oxygenate products.

4.5.2 Effect of catalyst on products selectivities

Table 4.2 illustrates the comparison of the catalytic and non-catalytic systems on products selectivities. The non-catalytic system produced a large amount of C₂ hydrocarbons which consisted of ethane, ethylene and acetylene as shown in Table 4.3. Only ethylene was found in the catalytic system. The results indicate that under the presence of catalyst, an increase of oxygen conversion result in higher CO₂ formation and less the C₂ selectivity.

Table 4.1 Comparison of catalytic and non-catalytic systems on conversions at total flow rate = 100 ml/min and applied voltage = 5,000 V

CH ₄ :O ₂	CH ₄ conversion (%)		O ₂ conversion (%)	
	With catalyst	no catalyst	with catalyst	no catalyst
2:1	19.8	48.6	68.5	46.9
4:1	15.6	35.4	94.5	56.6
8:1	8.9	27.3	88.2	53.0

Table 4.2 Comparison of catalytic and non-catalytic systems on products selectivities at total flow rate = 100 ml/min and applied voltage = 5,000 V

CH ₄ :O ₂	Selectivity (%) For HCOH		selectivity (%) for CO/H ₂		selectivity (%) for C ₂		Selectivity (%) for CO ₂	
	With catalyst	no catalyst	with catalyst	no catalyst	with catalyst	no catalyst	with catalyst	no catalyst
2:1	4.6	2.2	4.0/0.0	34.5/52.6	7.4	58.3	85.9	9.9
4:1	7.8	4.6	16.0/10.8	26.6/59.0	19.0	59.9	68.0	9.9
8:1	13.5	5.9	33.6/19.3	11.2/55.1	31.9	53.9	42.0	12.4

Table 4.3 Summation of C₂ selectivity at total flow rate = 100 ml/min and applied voltage = 5,000 V

CH ₄ :O ₂	selectivity (%) for ethane		Selectivity (%) for ethylene		selectivity (%) for acetylene	
	with catalyst	no catalyst	With catalyst	No catalyst	with catalyst	no catalyst
2:1	0	37.2	7.4	11.9	0	9.1
4:1	0	30.8	19.0	18.7	0	10.4
8:1	0	19.3	31.9	22.5	0	12.2

Eventhough the catalytic system gives higher yields of oxygenate products but methanol found in the product stream was still a trace in both systems. The non-catalytic system also gives a possibility of synthesis gas production, but hydrogen gas, which is found in large quantities, may come from the oxidative coupling of methane reaction. The catalytic system produces a high CO/H₂ ratio while the non-catalytic system produces low CO/H₂. For the undesired product CO₂, the non-catalytic system shows the CO₂ selectivity at only about 10% while the catalytic system has a CO₂ selectivity in range of 40% to 85%. This indicates that the non-catalytic system is very preferable for the production of C₂ hydrocarbons.

The temperature of the reactor wall while the reaction was running was observed to be oscillating in the range of 250 to 300°C. And it should be clarified that the total flow rate of 50, 100, 150 and 200 ml/min are equivalent to the residence time of 0.12, 0.06, 0.04 and 0.03 second respectively.