CHAPTER 5
RESULTS AND DISCUSSION

Figure 5.1 shows the catalytic performance of the catalyst system of alumina supported Mg-Li at differenct temperatures. At CH_4/O_2 = 1 and space velocity of 2000 h^{-1}, Mg/Al/Li gave higher methane conversion and C_2 selectivity at higher temperature. At 750^0C, up to 8.74% of methane conversion and 14.32 wt.% of product of ethylene were obtained.

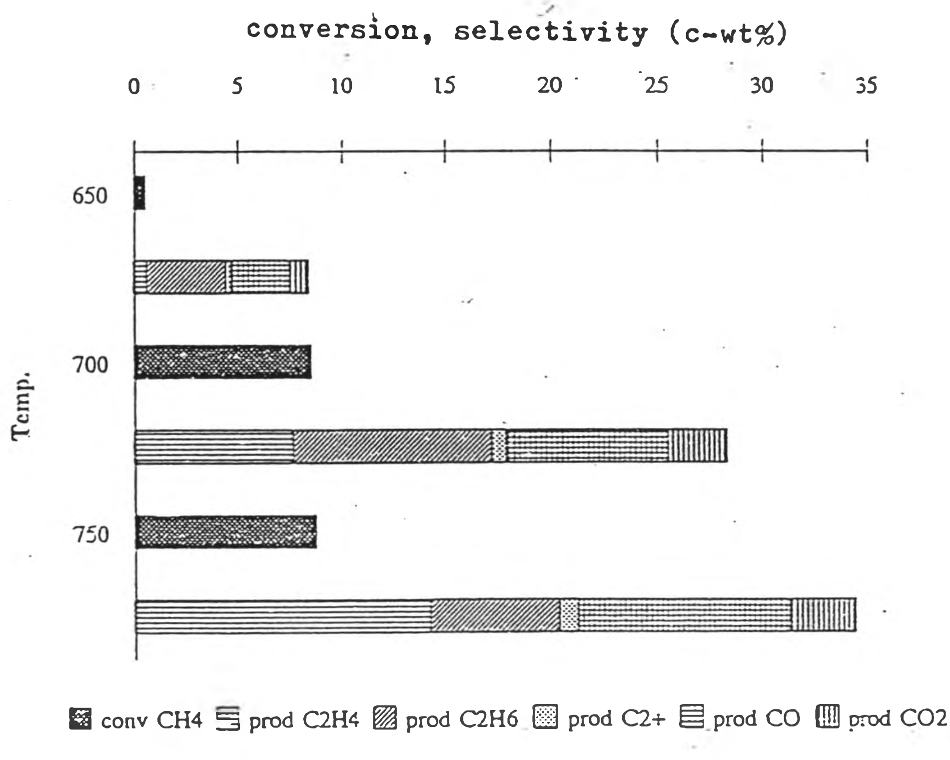

Fig.5.1 Effect of temperature on Mg/Al/Li at 2000 h^{-1} and CH_4/O_2 ratio of 1

The effect of CH_4/O_2 ratios on OCM over Mg/Al/Li at 2000h^{-1} and 750^0C is shown in Fig 5.2. It has been found that at the molar ratio of CH_4/O_2 of 2, methane conversion of 11.69 wt.% and ethylene product of 16.91 wt.% were obtained. Ethane amount was higher and CO amount was less when compares to the results of Fig. 5.1.

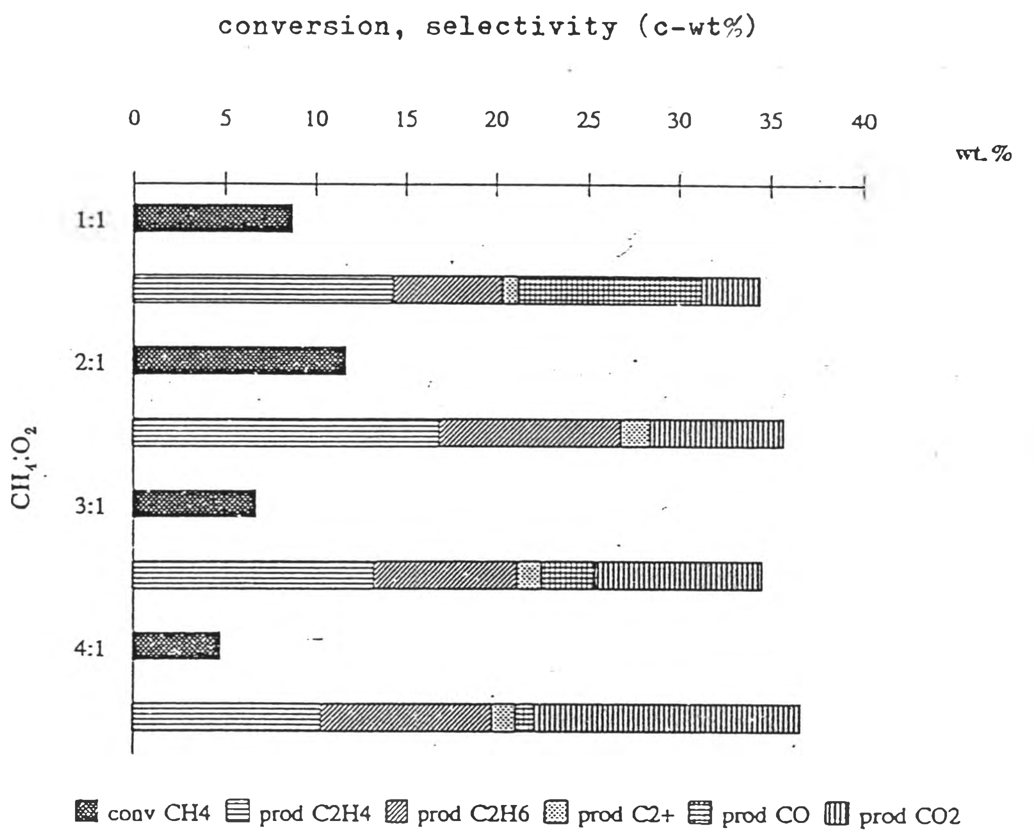

Fig.5.2 Effect of molar ratios of CH_4/O_2 on Mg/Al/Li at space velocity = 2000 h^{-1} and 750^{0}C.

In order to study, MnO_2 was concerned as the catalyst for the oxidative coupling of methane. To compare the performance of Mn and Mg with the pressure of lanthanide promoters, the catalyst systems as shown in Fig. 5.3 were studied. It has been found that Mg was far more effective than Mn. Of all the catalyst systems. ve

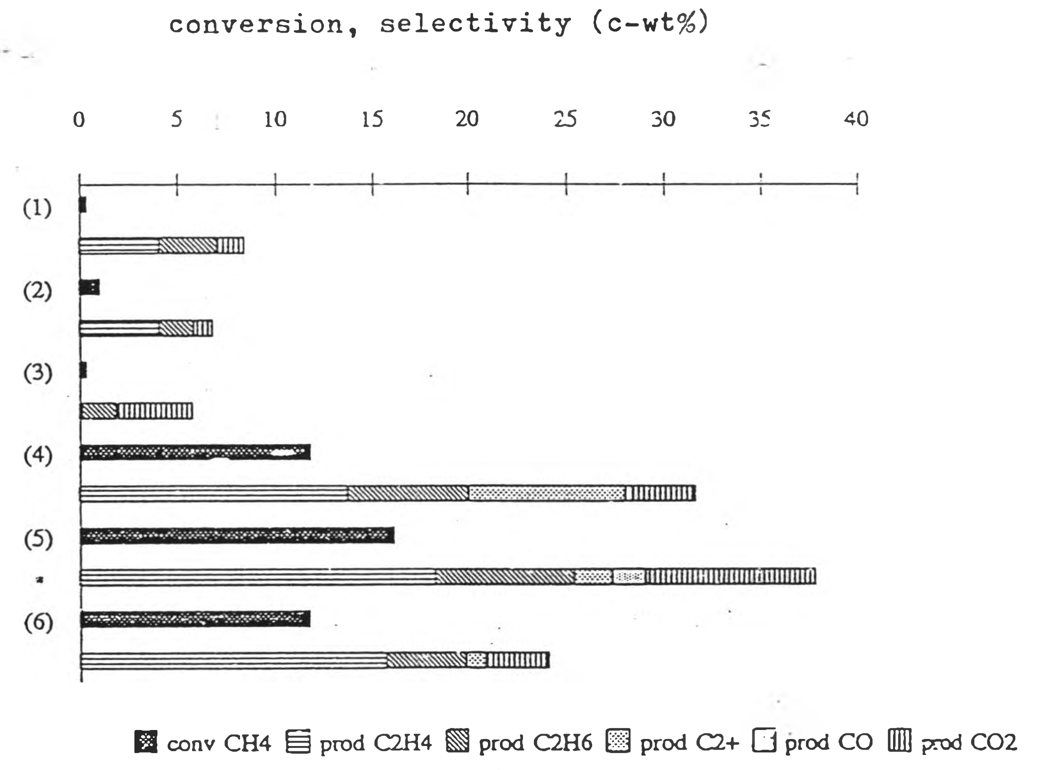

Fig. 5.3 Effect of Mg, Mn, on catalyst systems at CH_4/O_2 = 1, 750^{0}C, and space velocity = 2000h^{-1}

(1) Mn/Al/Li/0.2Ce

(2) Mn/Al/Li/0.2Pr

(3) Mn/Al/Li/0.2Sm

(4) Mn/Al/Li/0.2Ce

(5) Mn/Al/Li/0.2Pr

(6) Mn/Al/Li/0.2Sm

Mg/Al/Li/0.2Pr exhibited as high as 16.13% of methane conversion and 18.25% of ethylene product at molar ratio of CH_4/O_2 = 1,750^{0}C and space velocity 2000h^{-1}.

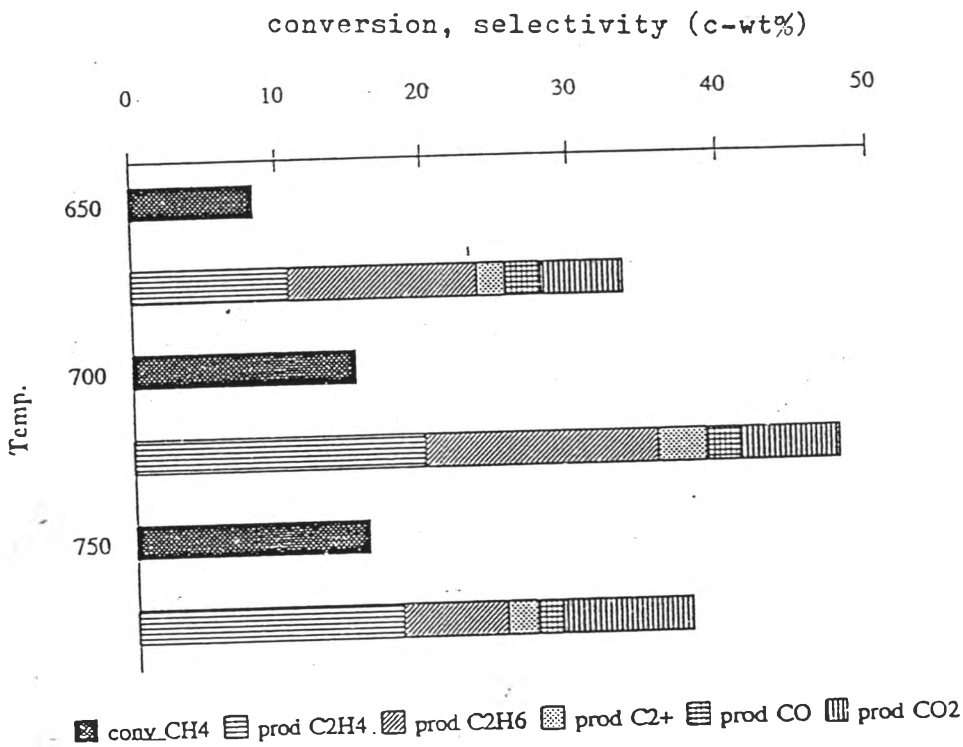

Fig 5.4 Effect of temperature on Mg/Al/Li/0.2Pr at CH_4/O_2 = 1 and space velocity = 2000 h^{-1}.

Fig. 5.4 shows the effect of temperature on OCM over Mg/Al Li/0.2Pr at CH_4/O_2 ratio of 1 and space vellocity of 2000 h^{-1}. The best ethylene yield was confirmed at 750^{0}C. As shown in Fig. 5.5, as high as 26.15 % of methane conversion and 20.53 % of ethylene were obtained at 4000 h^{-1}, 750^{0}C with CH_4/O_2 ratio of 1. The amount of CO and CO_2 formed at 4000 h^{-1} was also far less than that formed at 2000 h^{-1}.

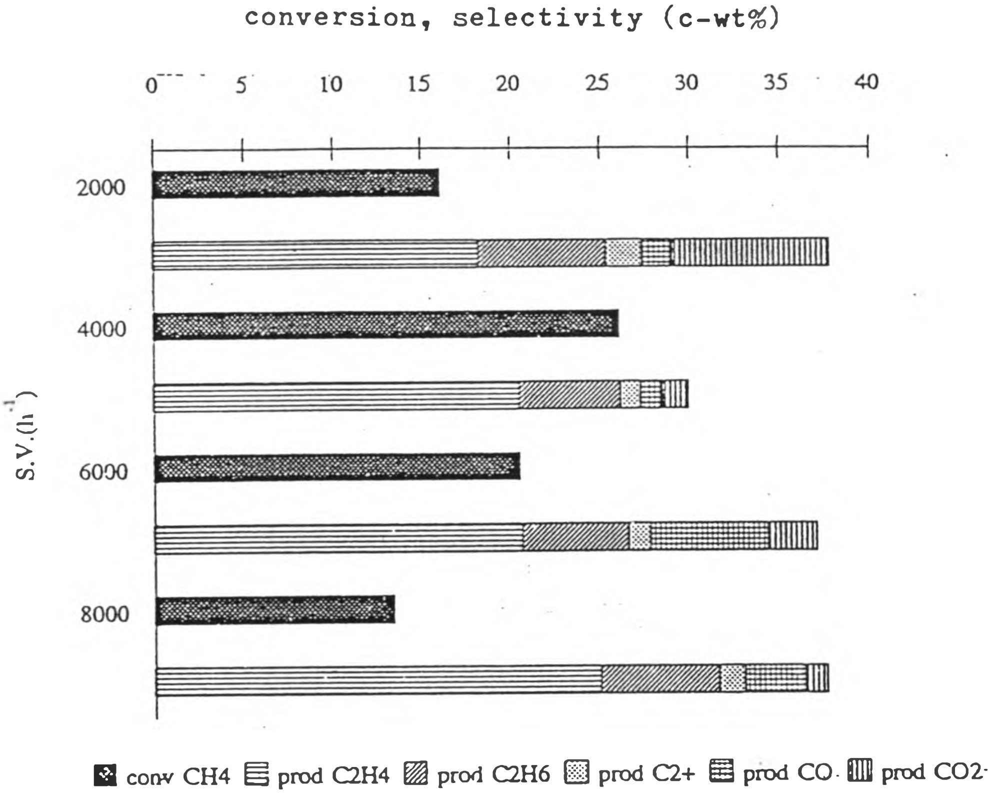

Fig. 5.5 Effect of space velocity on Mg/Al/Li/0.2Pr at CH_4/O_2 = 1 and 750^{0}C.

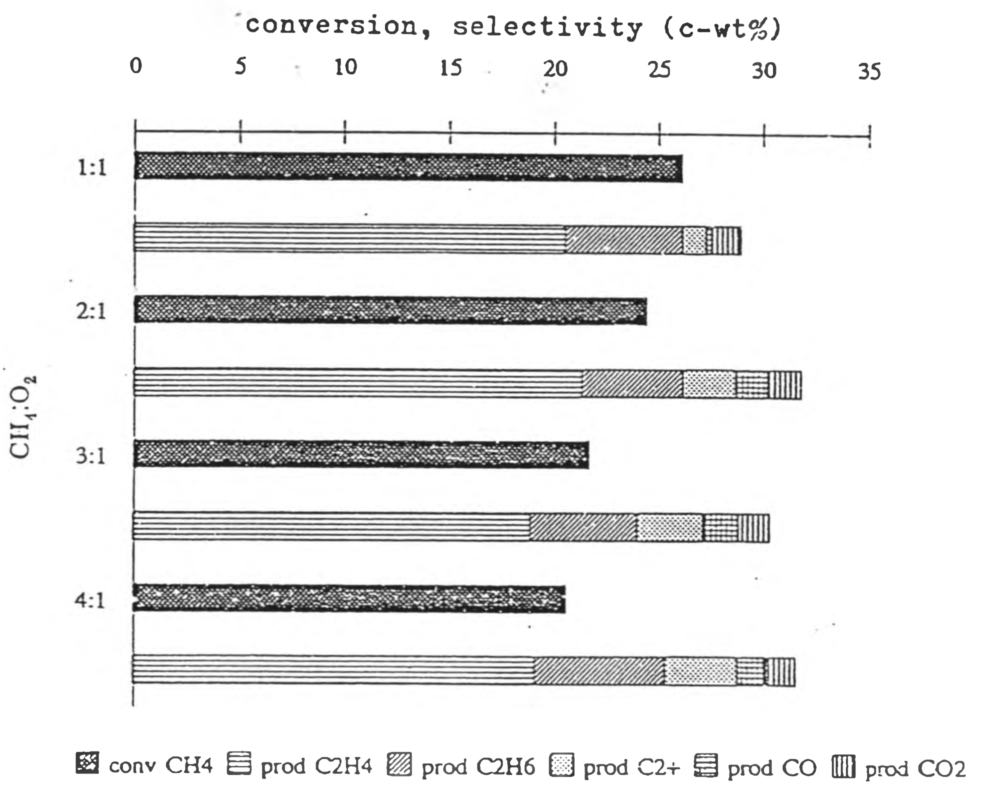

Fig. 5.6 Effect of molar ratios of CH_4/O_2 on Mg/Al/Li/0.2Pr at 750^{0}C and space velocity = 4000 h^{-1}.

The effect of molar ratios of CH_4/O_2 on OCM over Mg/Al/Li/0.2Pr was then investigated at 750^{0}C and space velocity of 4000 h^{-1}. As shown in Fig. 5.6, the optimum ethylene was confirmed at CH_4/O_2 ratio of 1.

Regarding to Ce promoter, the effect of temperature on OCM over Mg/Al/Li/0.2Ce was in vestigated at CH_4/O_2 ratio of 1 and space velocity of 2000 h^{-1}. As shown in Fig.5.7, both methane conversion and C_2 selectivity increased at higher temperature.

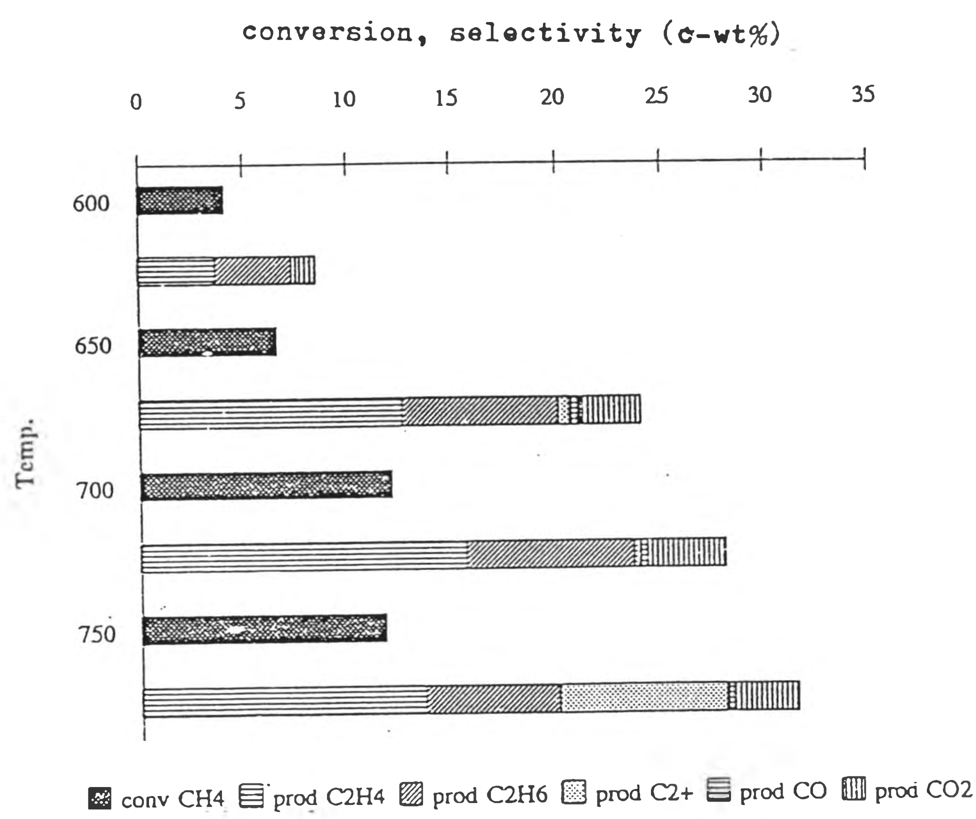

Fig. 5.7 Effect of temperature on Mg/Al/Li/0.2Ce at CH_4/O_2 = 1 and velocity = 2000 h^{-1}

At 700 C , as high as 12.15% of methane conversion and 15.3% of ethylene were obtained.

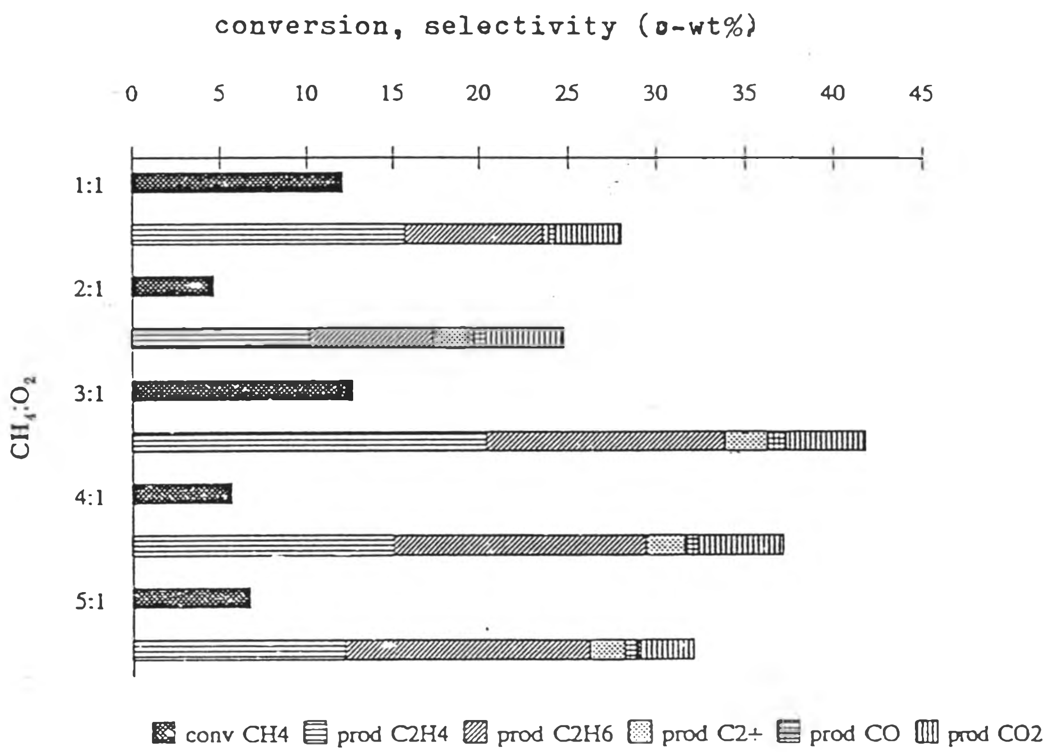

Fig.5.8 Effect of molar ratios of CH_4/O_2 on Mg/Al/Li/0.2Ce at 700 C and space velocity = 2000 h^{-1}

The effect of CH_4/O_2 ratio on OCM over Mg/Al/Li/0.2Ce was then investigated at 700 C and space velocity of 2000 h^{-1}. As shown in Fig. 5.8 , at CH_4/O_2 ratio of 3, up to 12.73% of methane conversion and 20.047% of ehtylene were obtained.

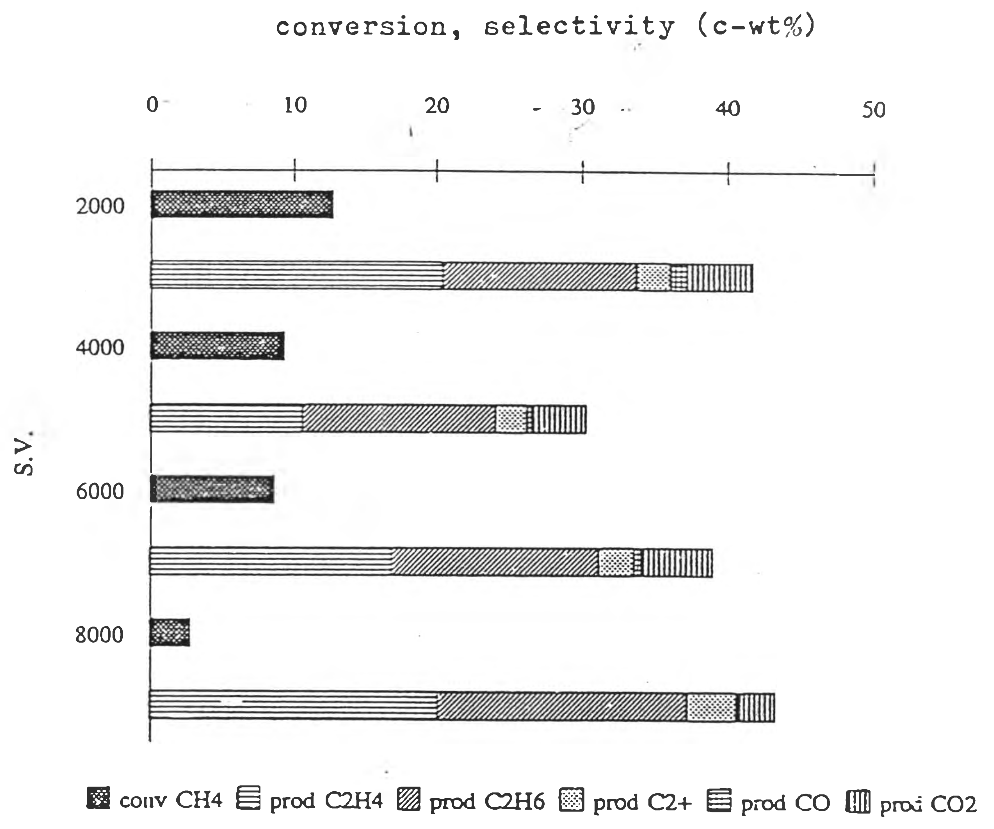

Fig. 5.9 Effect of space velocity on Mg/Al/Li/0.2Ce at CH_4/O_2 = 3 and 700° C

At CH_4/O_2 ratio of 3 and 700°C , the effect of space velocity was observed as shown in Fig. 5.9. The conversion of methane decreased with the increasing space velocity. The best ethylene yield was confirmed at 2000 h^{-1}.

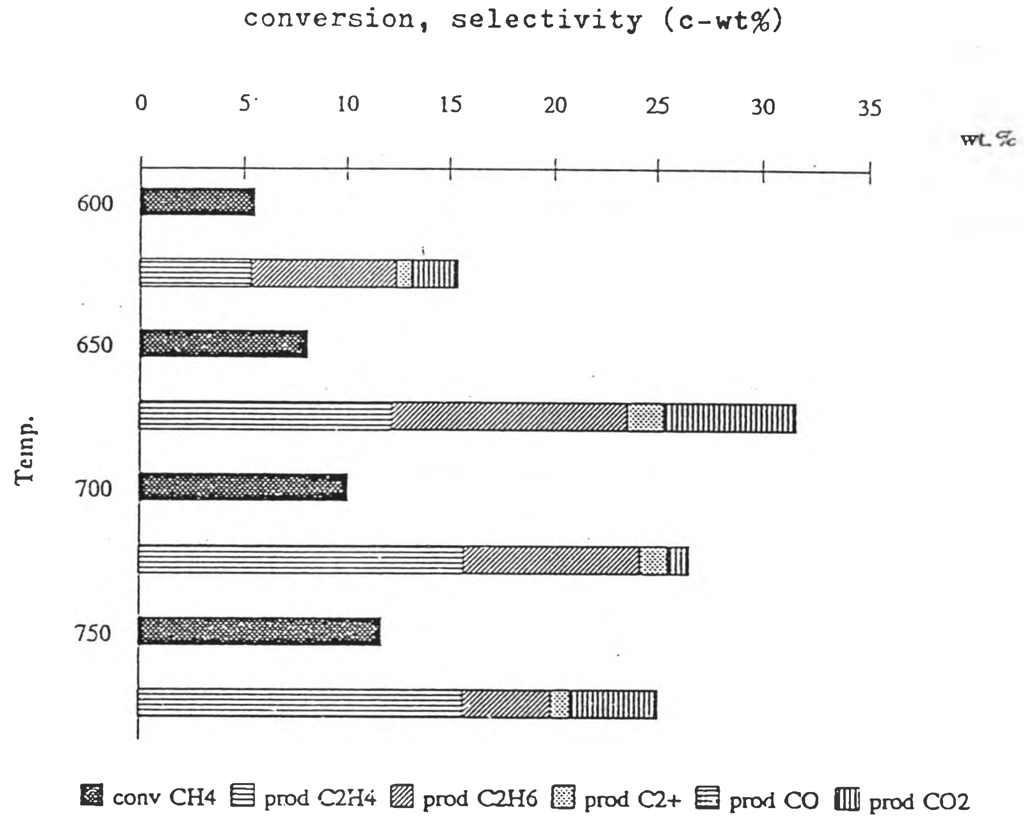

Fig. 5.10 Effect of temperature on Mg/Al/Li/0.2Sm at CH_4/O_2 = 1 and space velocity = 2000 h^{-1}

As for Sm promoter, the effect of temperature on OCM over Mg/Al/Li/0.2Sm was investigated at CH_4/O_2 ratio of 1 and space velocity of 2000 h^{-1}. Both methane conversion and C_2 selectivity increased with the higher temperature. At 700 °C, up to 10.12 % methane conversion and 15.76 % of ethylene were obatained.

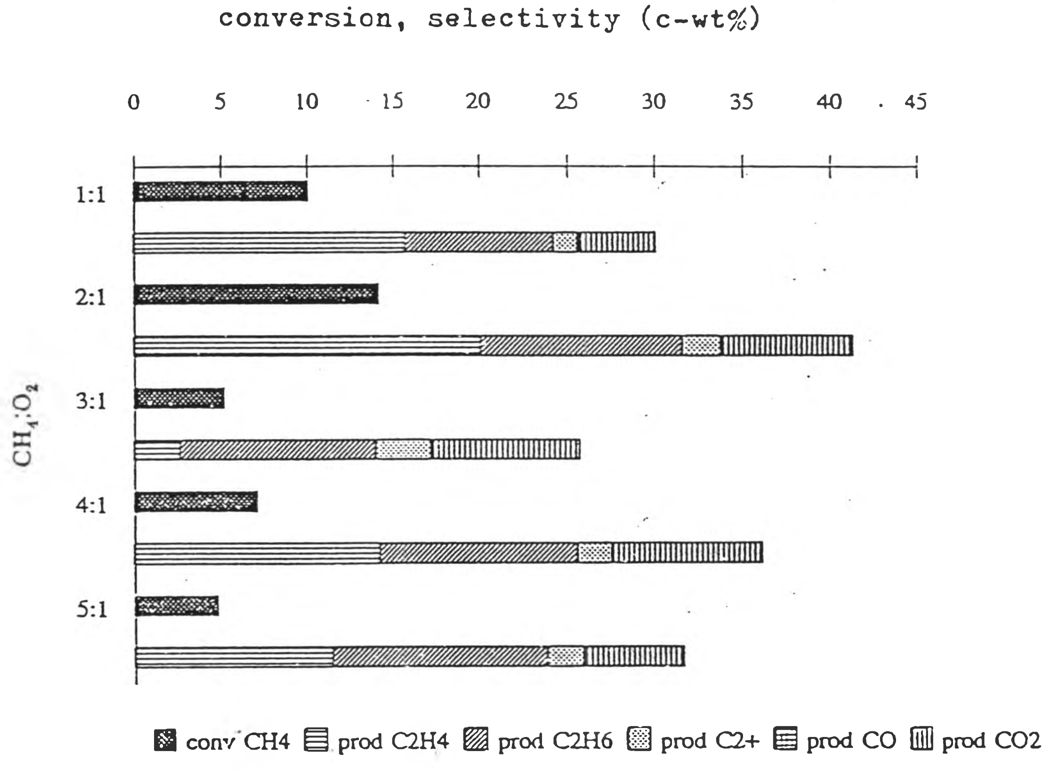

Fig. 5.11 Effect of molar ratios of CH_4/O_2 on Mg/Al/Li/0.2Sm at 700 °C and space velocity = 2000 h^{-1}

The effect of CH_4/O_2 ratio was then investigated at 700 °C and space velocity of 2000 h^{-1}. As shown in Fig.5.11, up to 14.18% of methane conversion and 20.11% of ethylene were obtained at CH_4/O_2 ratio of 2.

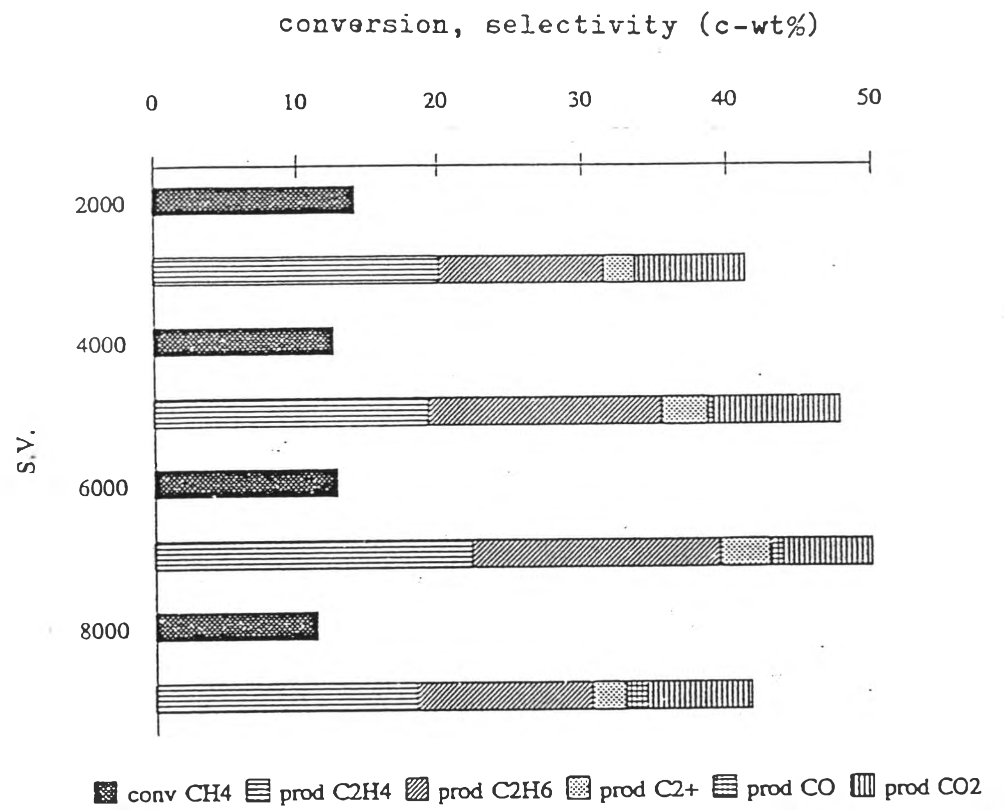

Fig.5.12 Effect of space velocityon Mg/Al/Li/0.2Sm at 700 °C and $CH_4/O_2 = 2$

The effect of space velocity was then observed at 700 °C and CH_4/O_2 ratio of 2. As shown in Fig 5.12, as high as 12.87% of methane conversion and 22.37% of ethylene were obtained at 6000 h^{-1}.

When compared the performance of Ce, Sm, and Pr promoters, it has been shown in Table 5.1 that Mg/Al/Li/0.2Pr was the most proper catalyst.

Table 5.1 Catalyst performance of different catalyt systems on OCM

System	CH_4 conversion(%)	C_2H_4 product(%)
Mg/Al/Li/0.2Ce	12.73	20.47
Mg/Al/Li/0.2Pr	26.15	20.53
Mg/Al/Li/0.2Sm	12.87	22.37

From the above conclusion, Pr system was thus selected to further study. The detailed study was made to find out the optimum amount of Pr that should be contained in the catalyst system of Mg/Al/Li/Pr. The effects of temperature, CH_4/O_2 ratio and space velocity were also investigated as the previous preliminary investigation.

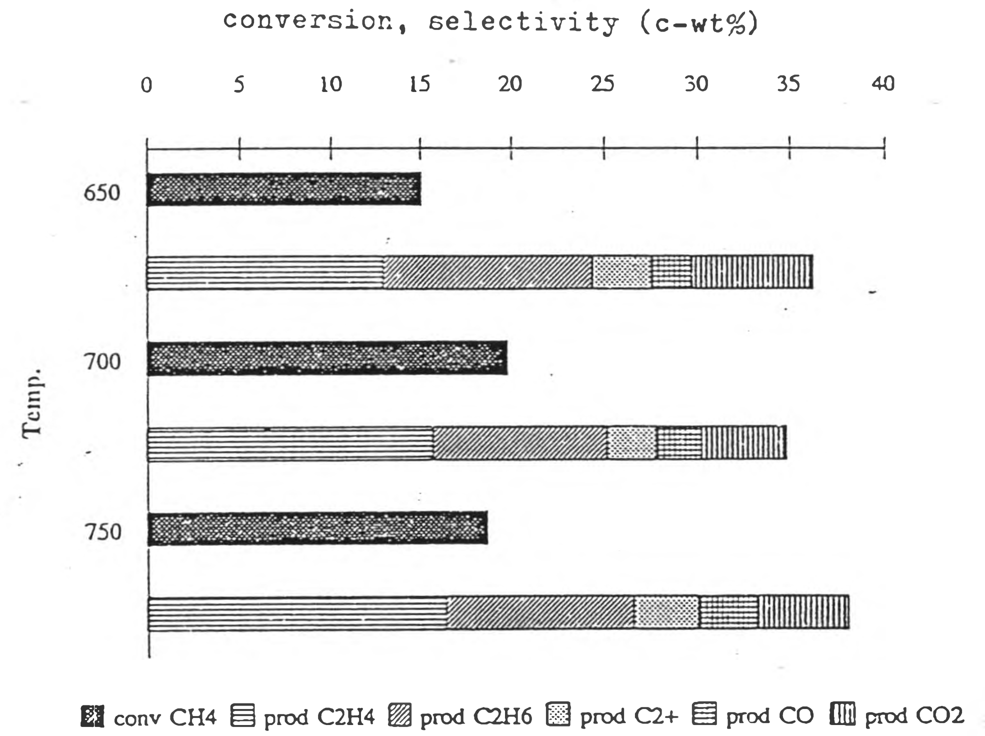

Fig.5.13 Effect of temperature on Mg/Al/Li/0.05Pr at CH_4/O_2 = 1 and space velocity= 2000 h^{-1}

According to Fig. 5.13 to Fig.5.15, it has been concluded that the catalyst system of Mg/Al/Li/0.05Pr exhibited its best performance at 700 °C, 4000 h^{-1}, and CH_4/O_2 ratio of 2. As high as 25.15% of methane conversion and 22.64% of ethylene were obtained at the conditions indicated above.

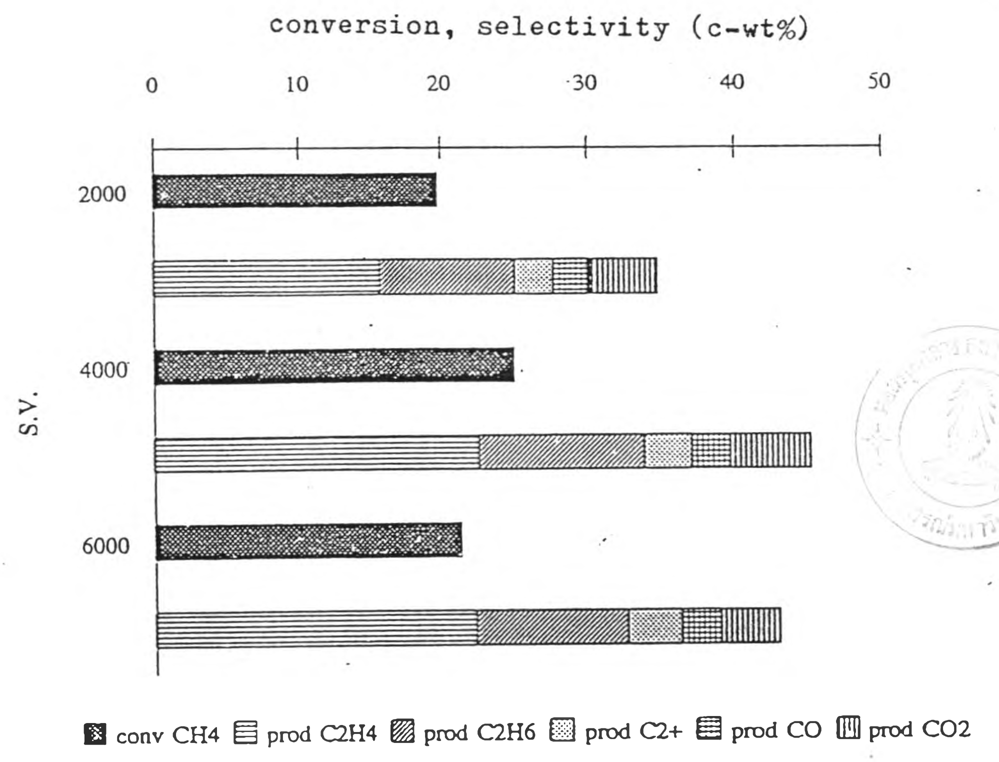

Fig.5.14 Effect of space velocity on Mg/Al/Li/0.05Pr at CH_4/O_2 = 1, and 700 °C

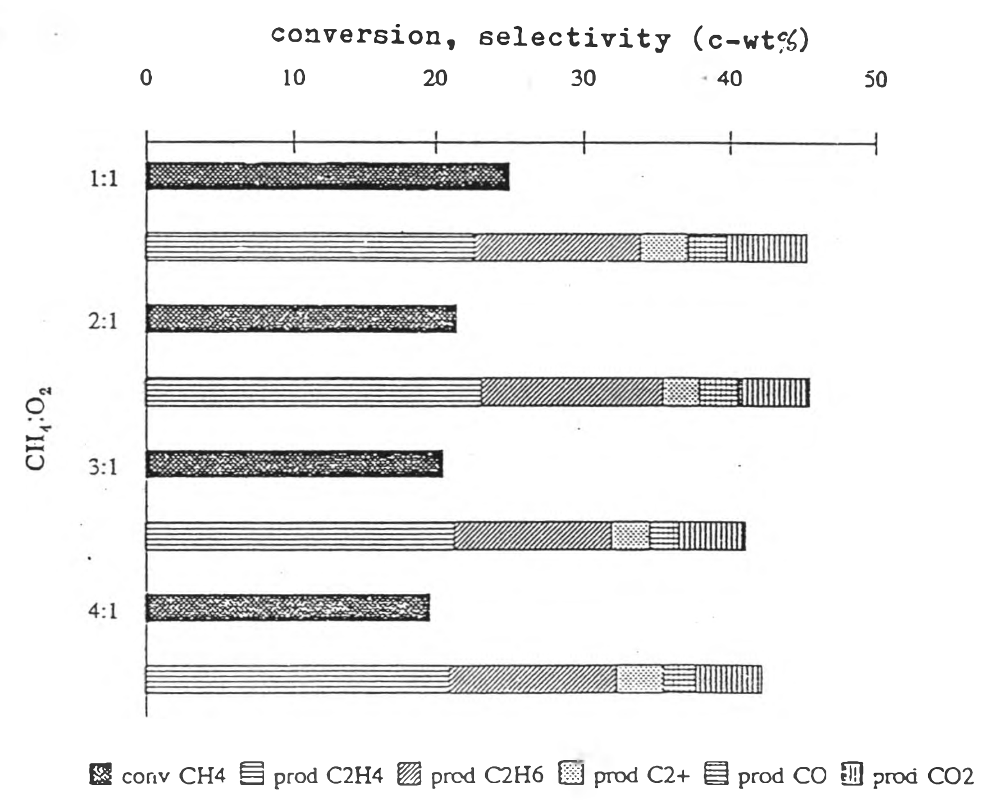

Fig.5.15 Effect of molar ratios of CH_4/O_2 on Mg/Al/Li/0.05Pr at 700 °C and space velocity = 2000 h^{-1}

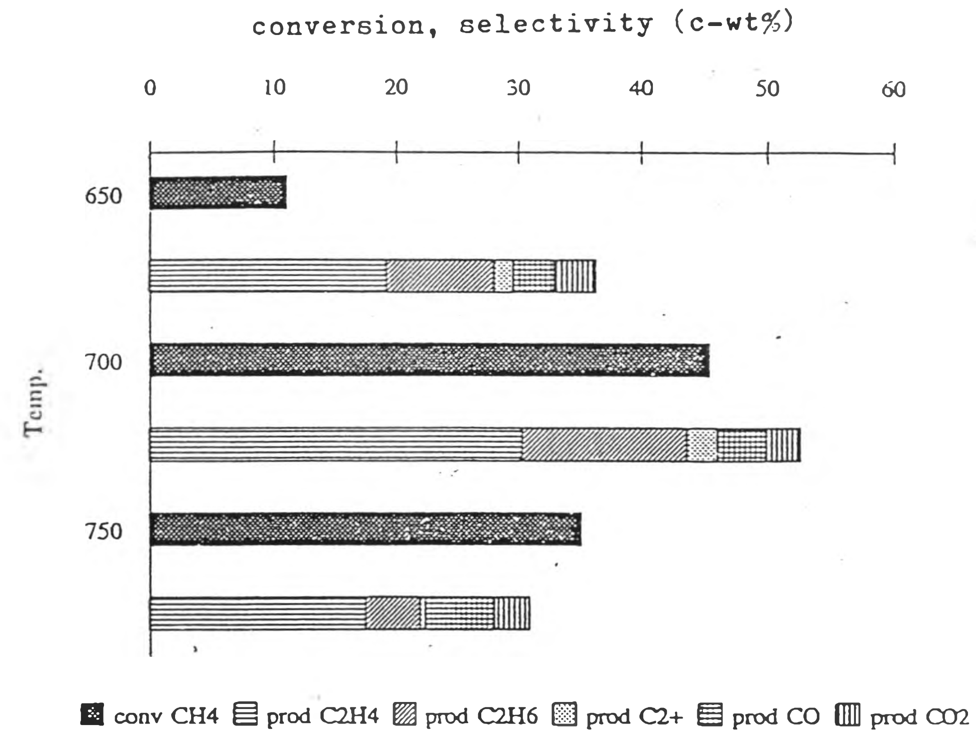

Fig.5.16 Effect of temperature on Mg/Al/Li/0.1Pr at space velocity = 2000 h^{-1} and $CH_4/O_2 = 1$

As shown in Figs. 5.16-5.18, Mg/Al/Li/0.1 Pr exerted as high as 45.48 % of methane conversion and 30.38 % of ethylene at 700 °C, 2000 h^{-1} with CH_4/O_2 ratio of 1.

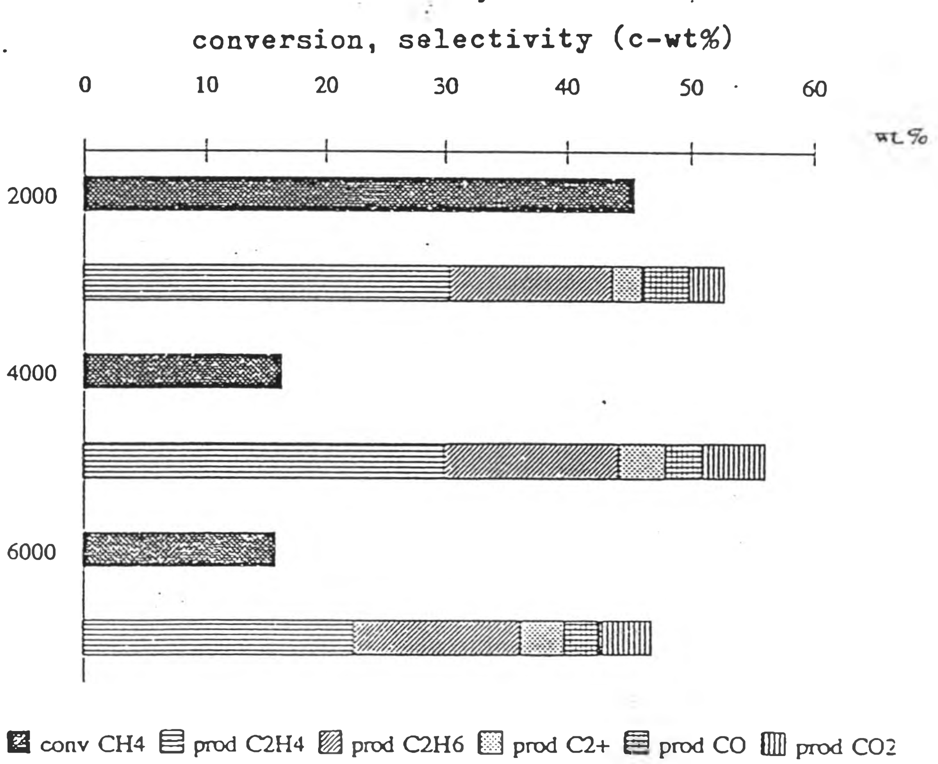

Fig.5.17 Effect of space velocity on Mg/Al/Li/0.1Pr at $CH_4/O_2 = 1$ and 700 °C

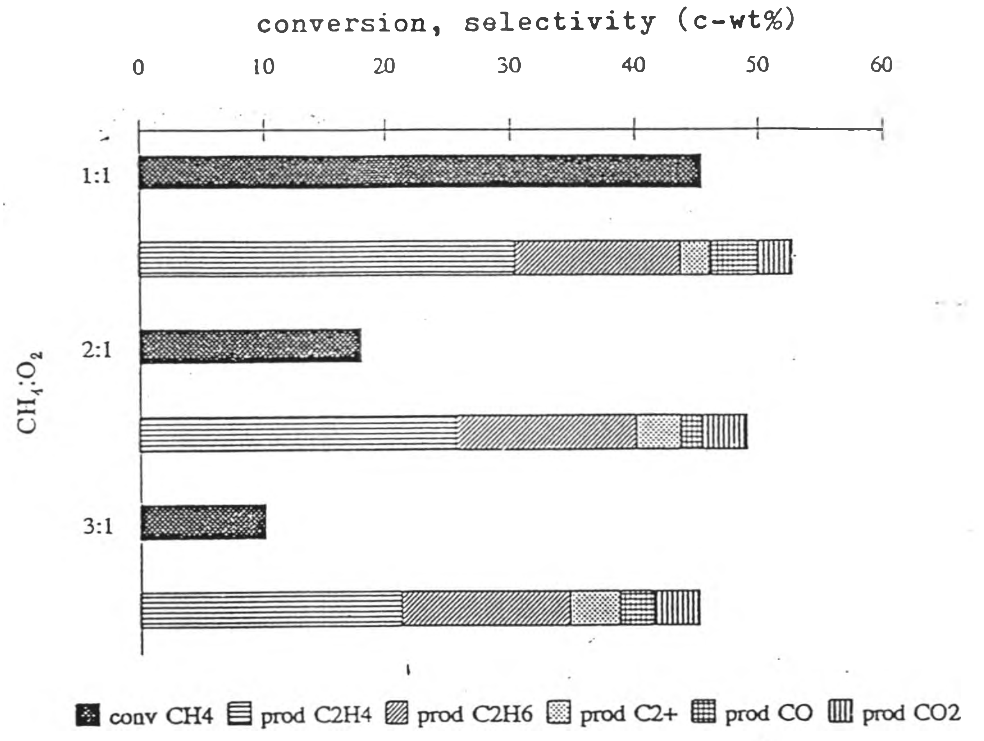

Fig.5.18 Effect of molar ratios of CH_4/O_2 on Mg/Al/Li/0.1Pr at space velocity = 2000 h^{-1} and 700 °C

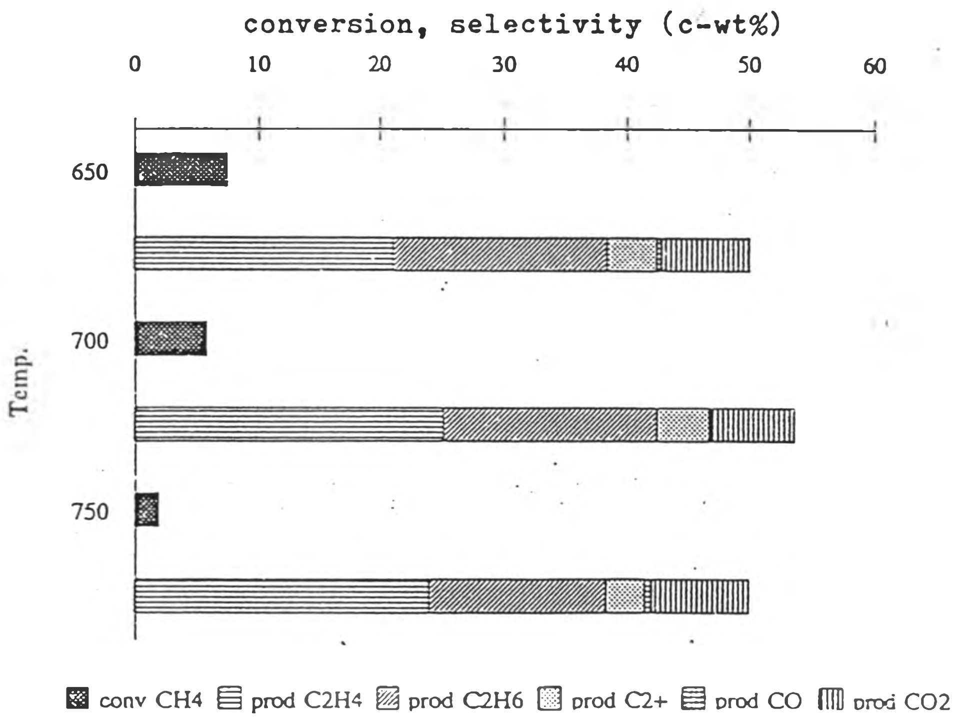

Fig.5.19 Effect of temperature on Mg/Al/Li/0.3Pr at space velocity = 2000 h^{-1} and CH_4/O_2 = 1

According to Figs. 5.19 to 5.21, Mg/Al/Li/0.3 Pr exhibited its best performance at 700 oC, 4000h^{-1}, and CH4/O2 ratio of 1. Up to 22.24 % of methane conversion and 32.71 % of ethylene were obtained at the above-mentioned conditions.

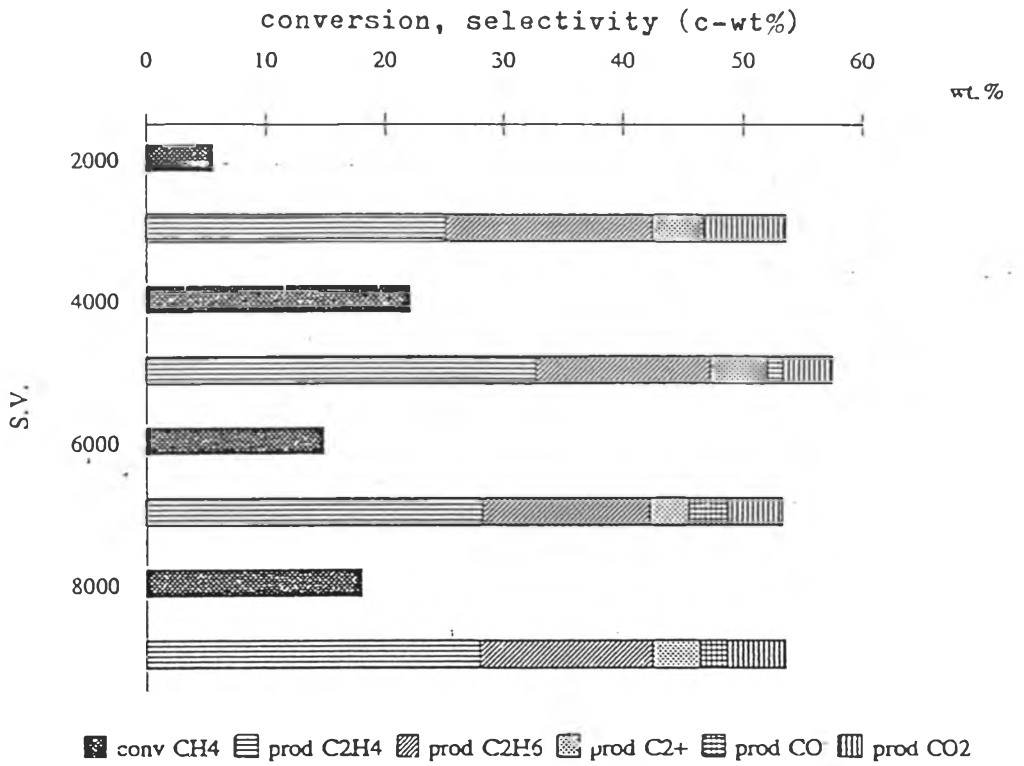

Fig.5.20 Effect of space velocity on Mg/Al/Li/0.3Pr at CH_4/O_2 = 1 and 700 °C

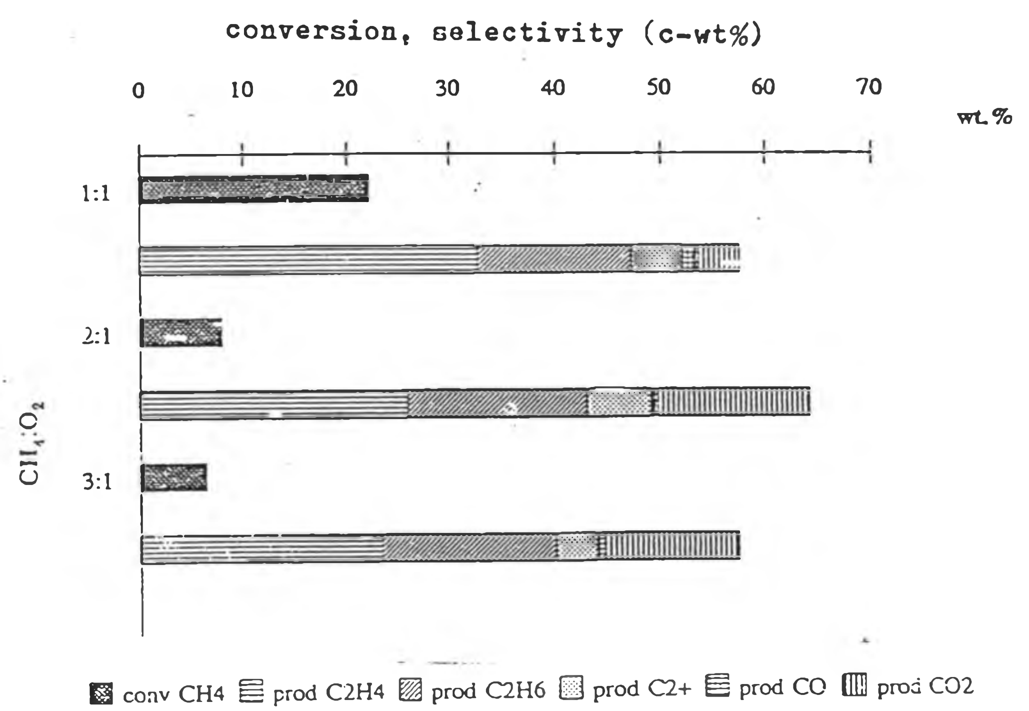

Fig.5.21 Effect of molar ratios of CH_4/O_2 on Mg/Al/Li/0.3Pr at 700 °C and space velocity = 4000 h^{-1}

Table 5.2 Catalytic performance of Mg/Al/Li/Pr in different amount of Pr on OCM

	0.05Pr	0.1Pr	0.2Pr	0.3Pr
conversion of methane (wt.%)	25.25	45.48	26.15	22.24
product of ethylene (wt.%)	22.67	30.38	20.53	32.71
product of ethane (wt.%)	11.25	13.33	5.67	14.64
YPP*(wt.%)	5.72	13.81	5.39	7.27

YPP*(yield per pass) was defined by the multiplication of conversion and ethylene selectivity

When taken the performance of Mg/Al/Li/Pr with different amount of Pr on OCM at each best condition into consideration, it has been found that Mg/Al/Li 0.1Pr was the most optimum catalyst as shown in Table 5.2.

Discussion

1. Effect of MgO on the catalyst systems

From this study, Mg/Al/Li added with 0.2Ce, 0.2Pr and 0.2Sm were far more effective than Mn/Al/Li added with those lanthanides. This should be discussed in term of the basicity of MgO. From the principle of chemistry, the oxides of metals on the left (and especially the lower left) of Periodic Table is more basicity than the right side of the Periodic Table. From the study of A.A. Davydov et. al[ ]. they mentioned the basic sites on the oxide surface caused the methane coupling. They used Sm_2O_3 for increasing the basic sites on MgO surface. From Lewis's definition, base is the electron donor. MgO is more basic than MnO_2, thus it donates electrons to the active center of Li^+O^-. The electrons then are so densed to activate Li^+O^- to form C_2 reaction and other products.

2. Effect of Pr on the catalyst systems

Many lanthanum metal oxides was used as the promoter for the OCM reaction. Pr in this study was more effective than Ce and Sm. It was difficult to understand why Pr^{3+} was more effective ; however, it might be related to the value of the magnetic moment of Pr^{3+} which is higher than those of Ce^{3+} and Sm^{3+}

	(in B.M.)
$Ce^{3+}(4f^1)$	2.3 - 2.5
$Pr^{3+}(4f^2)$	3.4 - 3.6
$Sm^{3+}(4f^5)$	1.5 - 1.6

3. Effect of Al_2O_3 on the catalyst systems

Generally Al_2O_3 influences the yields because of its pore volume and pore size. The alumina increase the pore size and pore volume as following comparison:

	Pr	Al/Pr
area	6.1482	27.3521
pore volume (cc/g)	0.0129	0.1382
pore size (A)	83.9261	197.1733

For Mg/Li/O/0.1Pr, it gave 5.73 wt.% of methane convarsion and 17.65 wt.% of ethylene product, while Mg//Al/Li/0.1Pr gave 35.14 wt.% of methane conversion, and 17.55 wt.% of ethylene product at the same conduction.

4. Effect of molar ratios of CH_4/O_2

Generlly, other studies on the OCM with catalysts were mentioned that at low partial pressure of oxygen would produce a high yield. It could be seen that oxygen was used in the following reactions:

1. To form the active centers $[Li^+O^-]$

$Li_2O + 1/2\ O_2 \rightarrow 2Li^+O^{2-}$

$2Li^+O^{2-} + 1/2\ O_2 \longrightarrow 2Li^+O^- + O^{2-}$

$Li^+O^- + CH_4 \longrightarrow LiOH + CH_3$

2. To form O^- at the surface of catalysts for activation of methane

$O_2 + O_2^{2-} \rightleftharpoons 2O_2^-$

For lanthanide, the radicals $CH_3^{\cdot}$ were formed when oxygen was present in the reactant stream.

3. To react with $^{\cdot}CH_3$ and C_2H_5 raddicals

$^{\cdot}CH_3 + O_2 \longrightarrow {}^{\cdot}CH_3O_2$

$^{\cdot}CH_3O_2 + C_2H_6 \longrightarrow CH_3O_2H + {}^{\cdot}C_2H_5$

$^{\cdot}C_2H_5 + O_2 \longrightarrow C_2H_4 + {}^{\cdot}HO_2$

From these reactions oxygen was used in many steps, thus the sufficient amount of oxygen is necessary. In this study CH_4/O_2 ratio of 1 was appropriate for the catalyst system of Mg/Al/Li/0.1Pr.

5. The effect of temperature

Temperature influences the collision of gas, then the collision influences the rate of reaction. it is concluded the temperature influence the rate of reaction. From Arrhenius, the rate constant ' k' depends on the temperature. Then the conversion would increase at the temperature increases. While temperature gradually increases to a certain level for the specific catalyst system, the amount of gas physically adsorbed decreases rapidly with increasing temperature. It is well known for catalysis that the reaction depend on adsorbed gas on the catalyst, thus the decrease of desired yield when temperature rises to 750^0C was found for the certain catalyst system. For example Mg/Al/Li/0.1Pr, at 2000 h^{-1} and CH_4/O_2 ratio of 1, exerted 45.48% of methane conversion and 30.38% of ethylene product at 700^0C gave methane conversion of 35.14% and 17.55% of product of ethylene at 750^oC