CHAPTER IV

RESULTS AND DISCUSSION

4. 1 Catalyst Characterization

4.1.1 Inductively Coupled Plasma (ICP)

In this work, all of catalysts were prepared by impregnation. The actual amounts of metal loading were determined by ICP. The results are shown in Tables 4.1 – 4.3.

Table 4.1 ICP results of various Ni loading

Catalysts	% Ni
3%Ni/KL	2.48
5%Ni/KL	5.33
7%Ni/KL	7.83
9%Ni/KL	8.52
11%Ni/KL	14.69
13%Ni/KL	21.58
15%Ni/KL	23.71

Table 4.1 shows ICP results of Ni/KL catalysts with various amounts of Ni loading. It seems that catalysts with 3%–9%Ni show not significantly difference from ICP results whereas the actual Ni loading from 11%–15%Ni show slightly higher Ni loading than the expected Ni loading. Tables 4.2 and 4.3 show ICP results of catalysts with adding Ca and Mg promoters. The results show that the actual amount of %Ni of all catalysts are slightly higher than 7 wt.%.

Table 4.2 ICP results of 7%Ni loading with various amounts of Mg loading

Catalysts	%Ni	%Mg
2%Mg-7%Ni/KL	7.54	2.01
3%Mg-7%Ni/KL	7.54	2.9
4%Mg-7%Ni/KL	7.39	3.78
5%Mg-7%Ni/KL	7.59	4.47

Table 4.3 ICP results of 7%Ni loading with various amounts of Ca loading

Catalysts	%Ni	%Ca
2%Ca-7%Ni/KL	7.26	2.5
3%Ca-7%Ni/KL	7.28	3.42
4%Ca-7%Ni/KL	8.07	4.41
5%Ca-7%Ni/KL	7.14	4.37

4.1.2 H_2 Pulse Chemisorption

The catalysts were characterized by H_2 pulse chemisorption to identify of metal dispersion. Table 4.4 shows the Ni dispersion which are calculated as the percentage of exposed Ni atoms per total number of Ni content of the sample, assuming a stoichiometry Ni:H = 1:1.

It can be clearly seen that the catalysts with high percent Ni loading tend to decrease the metal dispersion. This results can be concluded that high amount of Ni loading is the cause of metal sintering. In same results, Nimwattanakul (2004) studied the effect of Ni contents to the Ni dispersion of Ni/clinoptilolite catalyst. She found that Ni dispersion decrease with the amount of Ni loading (5%Ni/clio, 1.95% Ni dispersion; 8%Ni/clio, 1.02% Ni dispersion; 10%Ni/clio, 0.30% Ni dispersion). So, Ni sintering occurred during CO_2 reforming reaction.

For catalysts with adding Ca promoter, it found that Ni dispersion trend to decrease with adding Ca promoter. The 5%Ca-7%Ni/KL shows lower Ni dispersion than 2%Ca-7%Ni/KL as show in Table 4.4.

Many researchers studied the effect of adding Ca and Mg promoters on the Ni dispersion. Quincoces *et al.* (2001) found that Ni dispersion increases about 2% when adding 3%Ca but Ni dispersion slightly decreases when adding 5%Ca. Xu *et al.* (1999) found that Ni dispersion increase about 3% when adding Mg promoter. In general, Ni dispersion is effect to Ni surface area. Horiuchi *et al.* (1996) found that amounts of basic metal oxide (K_2O, Na_2O, MgO, CaO) are effect to the Ni surface area. They reported that adding small amount of basic metal oxide resulted in decrease the Ni surface area but increase in the amount of the added basic metal oxide resulted in an increase in the Ni surface area.

Table 4.4 Ni dispersion of the catalysts with various amounts of Ni loading

Catalysts	% Ni Dispersion
3%Ni/KL	4.615
5%Ni/KL	1.401
7%Ni/KL	1.262
9%Ni/KL	1.182
11%Ni/KL	0.814
13%Ni/KL	0.835
2%Ca-7%Ni/KL	0.751
5%Ca-7%Ni/KL	0.506

4.1.3 X-Ray Diffraction (XRD)

The X-Ray diffraction patterns of fresh catalysts before reduction are shown in Figure 4.1. The spectra exhibited different NiO diffraction lines corresponding to the NiO (111) at $2\theta = 37.3^\circ$, NiO (200) at $2\theta = 43.3^\circ$ and at the 2θ value of 63°. The peaks intensity of NiO are increased with increasing the Ni content due to higher NiO concentration while the other peaks were attributed to KL zeolite. However, with the Ni/KL catalysts a much stronger decrease in intensity of XRD patterns of zeolite structure was observed. The Ni crystallite size was calculated from the Scherrer equation and the results are shown in Table 4.5.

From this table it is found that the high amounts of Ni loadings show higher metal crystallite sizes than the small amounts of Ni loading. Large Ni crystallite size resulting in lower Ni dispersion, which is confirmed by H_2 pulse chemisorption.

After catalytic activity testing on CO_2 reforming, the XRD patterns of spent catalysts are presented in Figure 4.2. The Ni crystallite sizes of spent catalysts are shown in Table 4.4. The result shows that after the reaction, the peaks attributed to NiO are disappeared and the Ni peaks, attributed to Ni (111) at 44.5° and the (200) at 51.8°, were recorded. The diffraction peaks for metallic Ni were sharp and strong in the XRD patterns. It seems that high amounts of Ni loadings show higher metal crystallite sizes than the small amounts of Ni loading which might be the result of metal sintering.

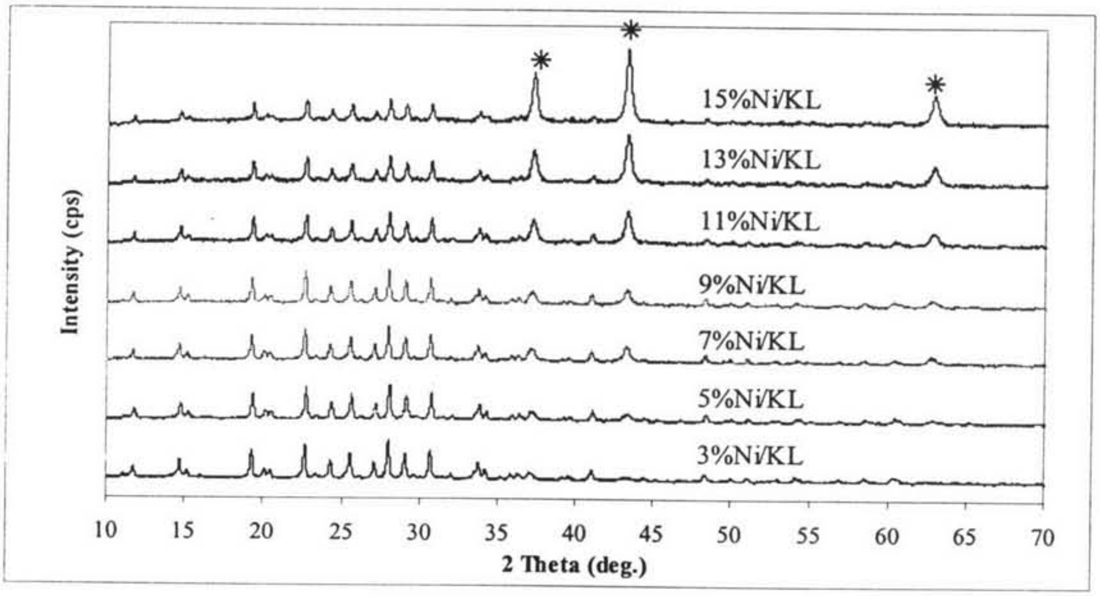

Figure 4.1 XRD patterns of fresh catalysts with different Ni loadings

(✳ = NiO peaks).

Table 4.5 Metal crystallite sizes of fresh catalysts with various amounts of Ni loadings

Catalyst	NiO (2θ =37.2°)	NiO (2θ =43.2°)	NiO (2θ =62.8°)
3%Ni/KL	8.34	18.62	-
5%Ni/KL	13.66	19.81	18.62
7%Ni/KL	18.12	19.00	18.61
8%Ni/KL	17.8	19.53	14.89
11%Ni/KL	17.44	19.72	15.52
13%Ni/KL	17.09	18.44	17.46
15%Ni/KL	20.1	22.77	18.34

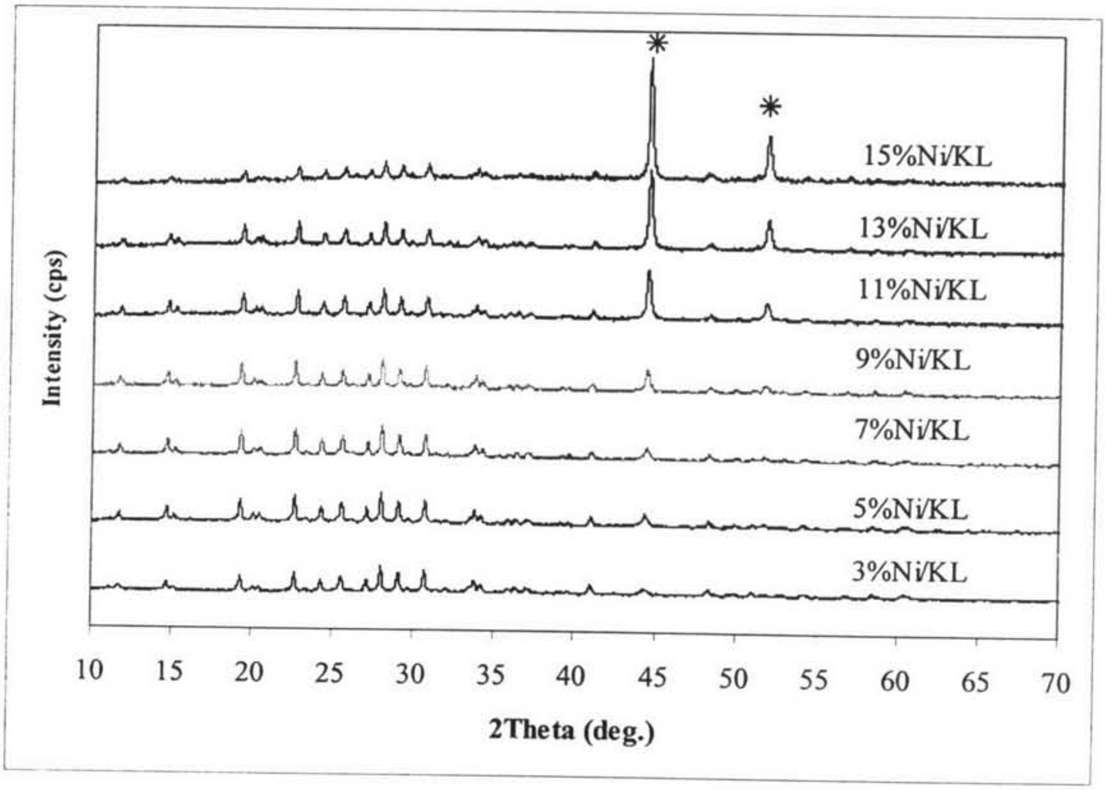

Figure 4.2 XRD patterns of the catalysts with different Ni loading after 5 hour of reaction (✳ = Ni peaks).

Table 4.6 Metal crystallite sizes of catalysts with various Ni loading after 5 hours of reaction

Catalysts	Ni ($2\theta = 44.5^{o}$)	Ni ($2\theta = 52^{o}$)
3%Ni/KL	-	-
5%Ni/KL	18.72	22.07.
7%Ni/KL	24.3	23.54
8%Ni/KL	24.51	25.23
11%Ni/KL	26.15	30.09
13%Ni/KL	27.03	28.3
15%Ni/KL	30.75	32.6

In order to improve the catalyst activity and stability of Ni/KL catalysts, Mg and Ca were used to study. The XRD patterns of catalysts with various amounts of Mg are presented in Figure 4.3. The NiO peaks occur at 2θ is 37.2, 43.2, and 62.8 degree. Catalysts with adding Mg give smaller and broader of Ni peaks and KL peaks than catalyst without Mg. This results can be implied that some part of NiO and KL zeolite might be covered by Mg promoter. In addition, the results show no Mg phase is detected. This indicates that Mg particles were formed in Ni-Mg/KL catalyst.

After catalytic activity testing for CO_2 reforming, the XRD patterns of spent catalysts with various percent of Mg loading are presented in Figure 4.4. The result shows that after the reaction, the peaks attributed to NiO are changed to Ni peaks which occurred at 2θ are 44.5 and 52 degree. It found that Ni peaks of used catalysts not change from NiO peaks of fresh catalysts. This results can be concluded that using Mg as a catalyst promoter might be prevent the metal sintering.

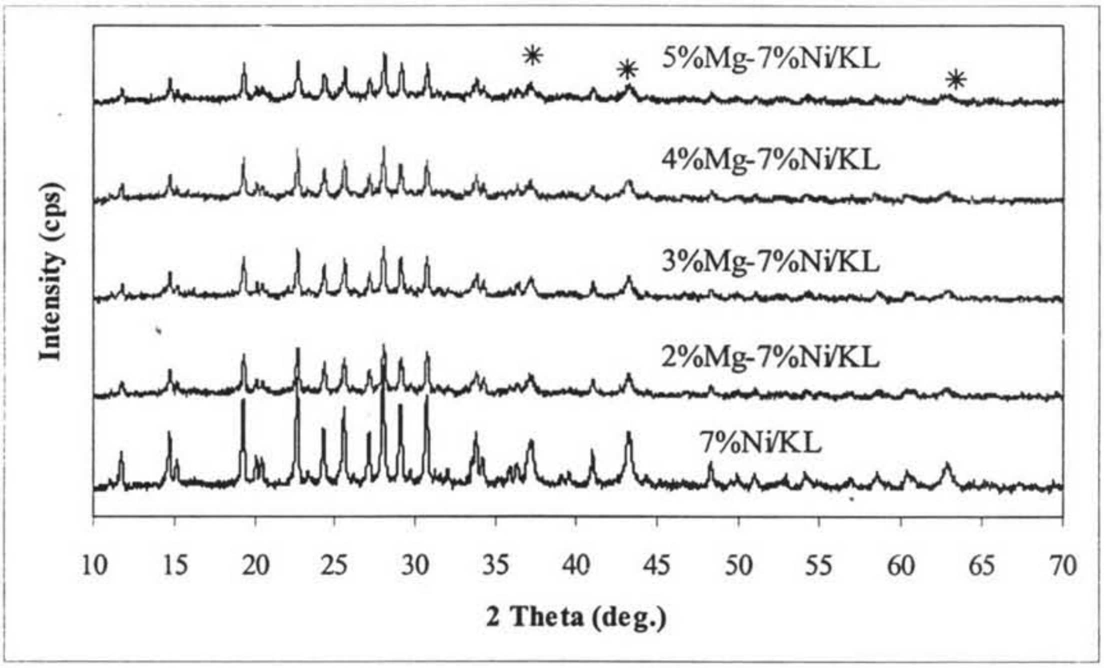

Figure 4.3 XRD patterns of 7%Ni with various amounts of Mg loading (✳ =NiO peaks).

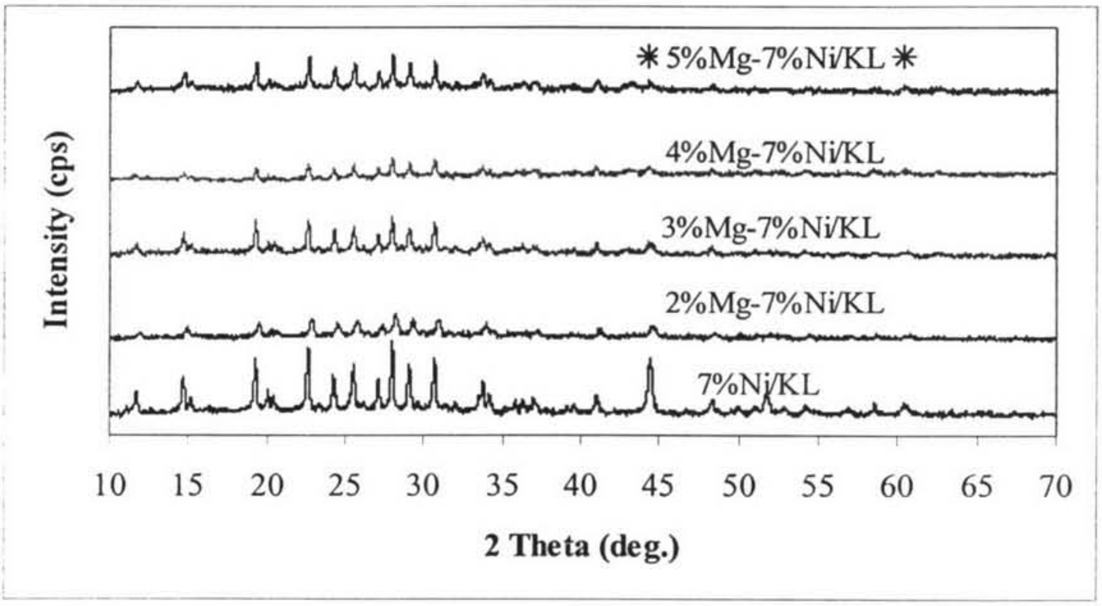

Figure 4.4 XRD patterns of 7%Ni with various amounts of Mg loading after 5 hours of reaction (✳ = Ni peaks).

The XRD patterns of catalysts with various amounts of Ca are presented in Figure 4.5. The NiO peaks occur at 2θ is 37.2, 43.2, and 62.8 degree. The results show that no Ca phase is detected, implying that Ca phase is probably presented in an amorphous-like or micro-crystallite state in the catalysts. From XRD peaks, it is observed that NiO peaks and KL zeolite peaks decrease and broad with adding Ca promoter. This can be suggested that some part of NiO and KL zeolite might be covered by Ca promoter.

Several researchers have reported the effect of adding Ca promoter. Quincoces *et al.* (2001) found that no important modifications of the crystallite sizes were observed when adding Ca promoter. Horiuchi *et al.* (1996) found that crystallite size of Ni catalyst with the addition of CaO was almost the same as that for the catalysts with no additive oxide.

Figure 4.6 exhibits the XRD patterns of Ca promoted 7%Ni/KL zeolite catalysts after 5 hours of reaction. The results show that after the reaction, the peaks of NiO are disappeared and the Ni peaks attributed to Ni (111) at 44.5° and Ni (200) at 51.8° are recorded. It found that Ni peaks of used catalysts are almost the same size as NiO peaks of fresh catalysts. This results can be suggest that adding Ca promoter might be prevent the metal sintering.

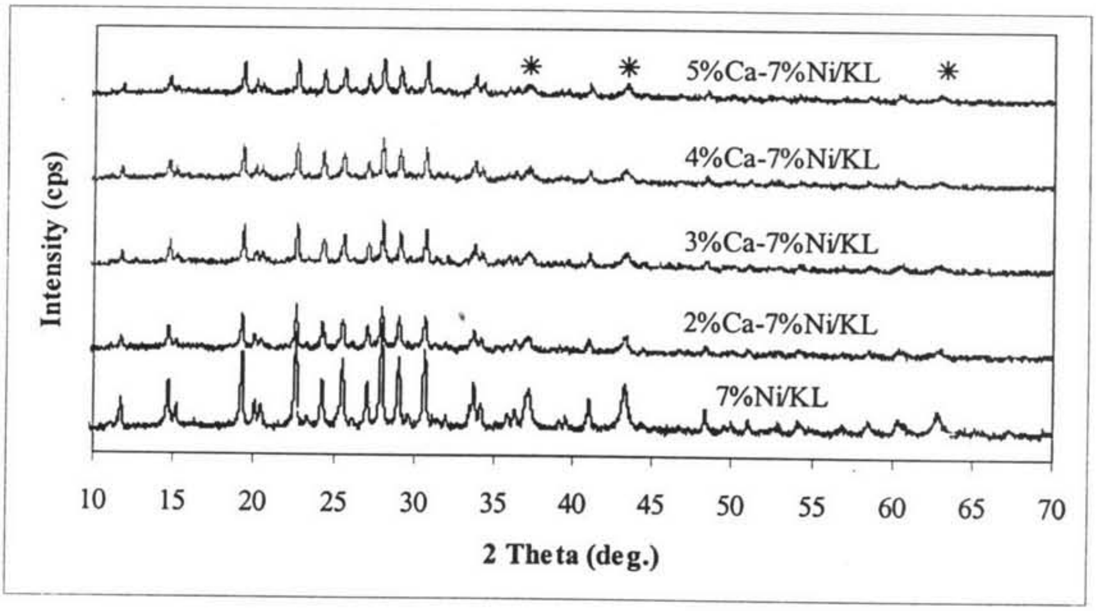

Figure 4.5 XRD patterns of 7%Ni with various amounts of Ca loading (✳ =NiO peaks).

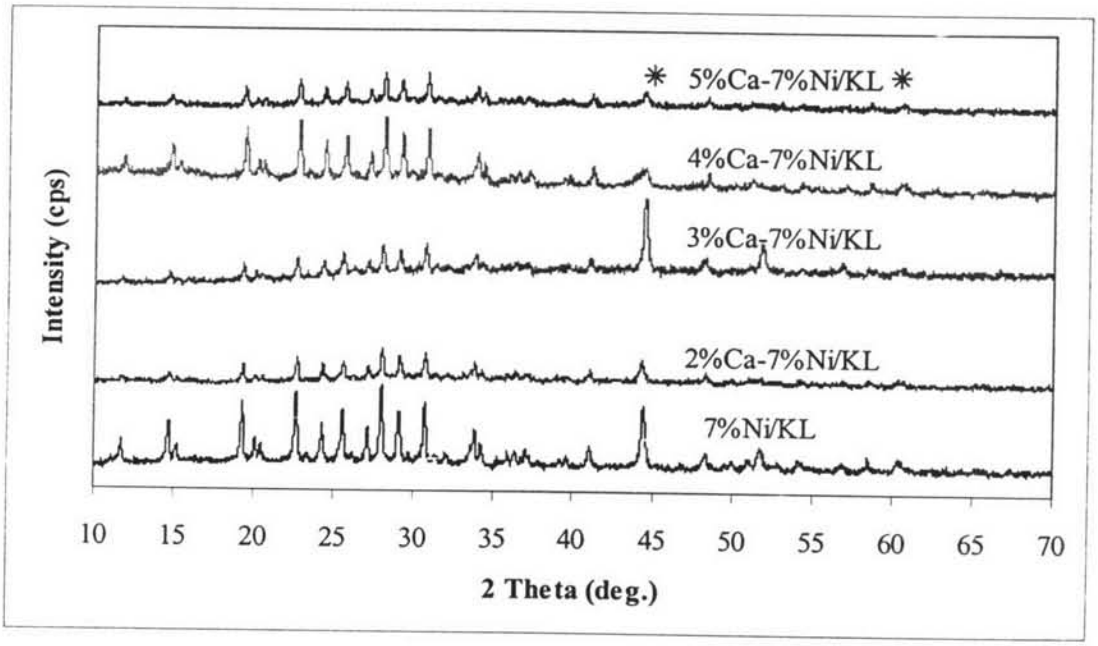

Figure 4.6 XRD patterns of 7%Ni with various amounts of Ca loading after 5 hours of reaction (✳ = Ni peaks).

4.1.4 Thermogravimetric analysis (TGA)

Coke formation is the most important problem for CO_2 reforming of CH_4. In this work, the amount of coke formation on the catalysts was measured by TGA, which calculated from weight loss. The results are shown in Tables 4.8 and 4.9. A weight loss was observed in TGA experiments for all catalysts, indicating a significant amount of carbon deposition during 5 hours on stream. The deposition of inactive carbon during methane reforming can be originated from either methane decomposition or CO disproportionate which are thermodynamically favorable below 900°C.

For Mg promoted, coke formations are shown in Table 4.8. It is found that the amount of carbon deposition decreases with adding Mg promoter from 2 to 4 wt.%. But when amount of Mg is 5%, it showed the highest carbon deposition.

For Ca promoted, it is found that 2%Ca and 3%Ca show higher carbon formation than that of other weight percents, which can be suggested that the rate of CH_4 decomposition is higher than rate of CO_2 dissociation that makes carbon accumulation on the metal surface, resulting in rapid deactivation. The 4%Ca and 5%Ca show lower carbon formation, which make the catalysts show higher stability.

Table 4.7 Amounts of carbon deposited on Mg-promoted catalysts after 5 hours of reaction

Catalysts	% Coke
2%Mg-7%Ni/KL	7.16
3%Mg-7%Ni/KL	7.24
4%Mg-7%Ni/KL	7.87
5%Mg-7%Ni/KL	9.75
7%Ni/KL	7.89

Table 4.8 Amounts of carbon deposited on Ca-promoted catalysts after 5 hours of reaction

Catalysts	% Coke
2%Ca-7%Ni/KL	15.26
3%Ca-7%Ni/KL	11.88
4%Ca-7%Ni/KL	7.36
5%Ca-7%Ni/KL	7.82
7%Ni/KL	7.89

4.4.5 Temperature Program Oxidation (TPO)

Wang and Lu (1997) proposed that catalyst deactivation caused by carbon deposition depends on amount, type and location of carbon formed. In order to characterize the carbon species formed during the CO_2 reforming of CH_4, the samples were analyzed by TPO technique. Figure 4.7 shows TPO profiles of carbon deposition on the 7%Ni/KL catalyst and 7%Ni/KL catalysts with various amount of Mg loading after 5 hours of reaction. In TPO profiles, two peaks of oxidized carbon are observed. A first peak is observed at 270 – 400°C that may related with C_α as a superficial carbide. These species may be the reaction intermediate and their reactivity correlate with the catalytic activity (Swaan *et al.*, 1994). A second peak is observed around 480–720°C, identified as whisker-like filamentous carbon (Quincoces *et al.*, 2001). This species is produced by adsorbed carbon atom derived from CH_4 decomposition and CO dissociation. From the figure, it is seen that when increasing the amount of Mg, the area under the profiles tend to increase. This can be suggested that the higher Mg content, the higher amount of carbon is deposited. Carbon on 5%Mg-7%Ni/KL shows the maximum oxidation rate but carbon is more easy to be oxidized with the peak occurring around 580°C. For 7%Ni/KL, 3%Mg-7%Ni/KL, and 4%Mg-7%Ni/KL catalysts carbon is more difficult to be oxidized with the peak occurring around 620°C. Several researches have shown that there is a relationship between oxidation temperature and the distance between the coke on the support and the metal. Coke on the metal is burned at the lower temperature than the coke on the support because metal can catalyst the coke combustion by oxygen. For the 5%Mg-7%Ni/KL catalyst surface carbon deposit is close to Ni particle because Ni and carbon are all the surface. While Ni particles were more deposited in inner pores of 7%Ni/KL, 3%Mg-7%Ni/KL, and 4% Mg-7%Ni/KL catalysts during the impregnation resulting in longer distance between surface carbon and Ni particles so that the gasification of carbon on these catalysts become more difficult (Wang and Lu, 1997).

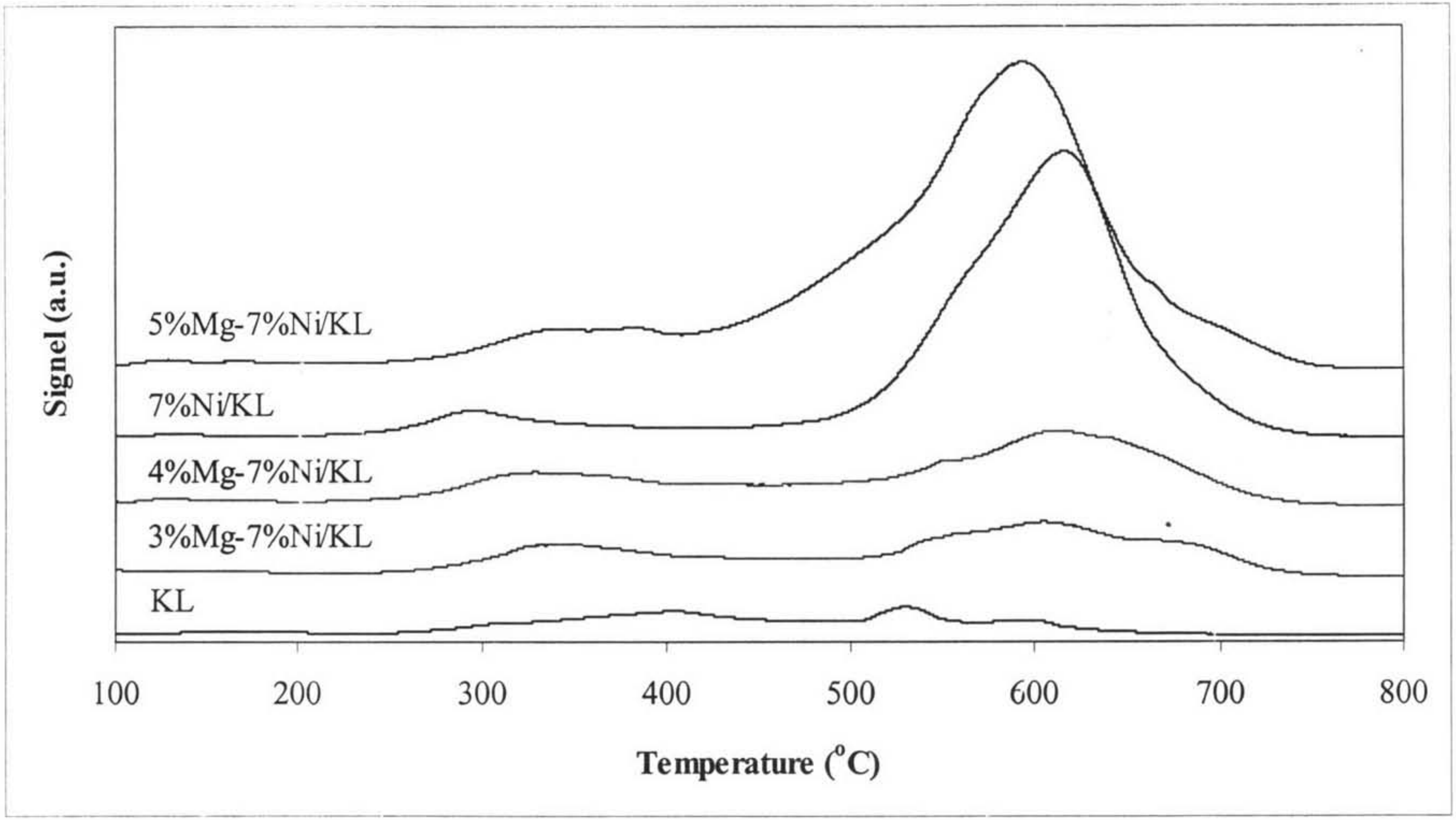

Figure 4.7 TPO profiles of the Mg-promoted catalysts after 5 hours of the reaction.

4.2 Activity Test

4.2.1 Effect of Ni Loading

A series of Ni/KL catalysts with various amounts of Ni loading from 3 to 15 wt% are tested for their activity. Before the activity test, the catalysts are reduced in a stainless steel the reactor with H_2 at 600 °C for 1 hour. Reactant gas composed of $CH_4 : CO_2 = 1$ and He as the balance gas are fed to the reactor. The activity tests are carried out at 700 °C for 5 hour. The catalytic activities of all catalysts are shown in Figures 4.8 to 4.11. Figure 4.8 shows the CH_4 conversion with time on stream of catalysts with various amounts of Ni loading. It seems that the CH_4 conversion increases with increasing amounts of Ni from 3 to 15 wt%. These results are not in agreement with Roh *et al.* (2002) work, which studied the effect of Ni loading over Ni/θ-Al_2O_3 catalysts. They found that the CH_4 conversion increased with increasing amount of Ni loading from 3 to 12 wt%. However, a gradual decrease in activity was observed when Ni loading is increased to more than 12%. They suggested that this is due to the effect of Ni sintering which eventually caused the catalyst deactivation. However, Ni sintering, resulting from high percent metal loading (Table 4.3), did not affect to the activity of the catalysts for the CO_2 reforming of CH_4 with Ni/KL catalyst.

It is clearly seen that when Ni loading is increased from 7 to 15 wt%, their CH_4 conversions show no significantly differences (around 95% CH_4 conversion at 5 hours of reaction time) whereas the CH_4 conversions of 3 and 5 %Ni show lower CH_4 conversion than those of 7 to 15 %Ni (89% CH_4 conversion for 3%Ni/KL catalyst and 92.5% CH_4 conversion for 5%Ni/KL catalyst after 5 hours of reaction time). So, it seems that the 7 wt.%Ni is the most suitable amount of Ni loading. However, the CH_4 conversions of all catalysts are slightly dropped about 2% after 5 hours of testing time. This is because the Ni particles gradually aggregated and sintered in the KL support.

Figure 4.9 shows CO_2 conversion of various amounts of Ni loading. It clearly seen that the CO_2 conversions are lower than the CH_4 conversions, which can be suggested that rate of CH_4 decomposition is higher than rate of CO_2 dissociation. Some of the CO_2 conversions show difference trends as CH_4 conversions, which might be the result of side reactions.

The H_2 selectivity and H_2 production in terms of mol/g-catalyst are shown in Figures 4.10 and 4.11. Figure 4.10 shows H_2 selectivity of various amounts of Ni loading. It is found that H_2 selectivity is above 50%. This result can be suggested that the rate of CH_4 decomposition is higher than rate of CO_2 dissociation. Figure 4.11 shows H_2 production of different amounts of Ni. It is found that 3 and 5 wt.%Ni show lower H_2 production than others wt% of Ni loading. The 7 to 15 wt.% Ni give the H_2 production about 92×10^{-2} mol/g-catalyst. However, H_2 productions of these catalysts are decreased to 90×10^{-2} mol/g-catalyst within 5 hour of reaction.

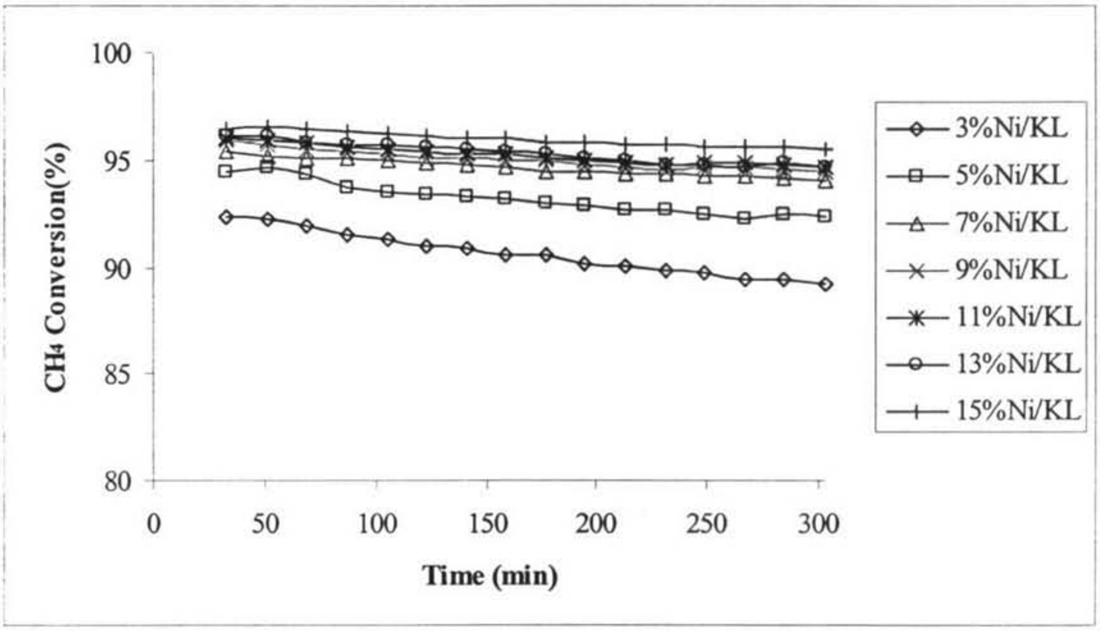

Figure 4.8 CH_4 conversions of the catalysts with various amounts Ni loadings at 700°C.

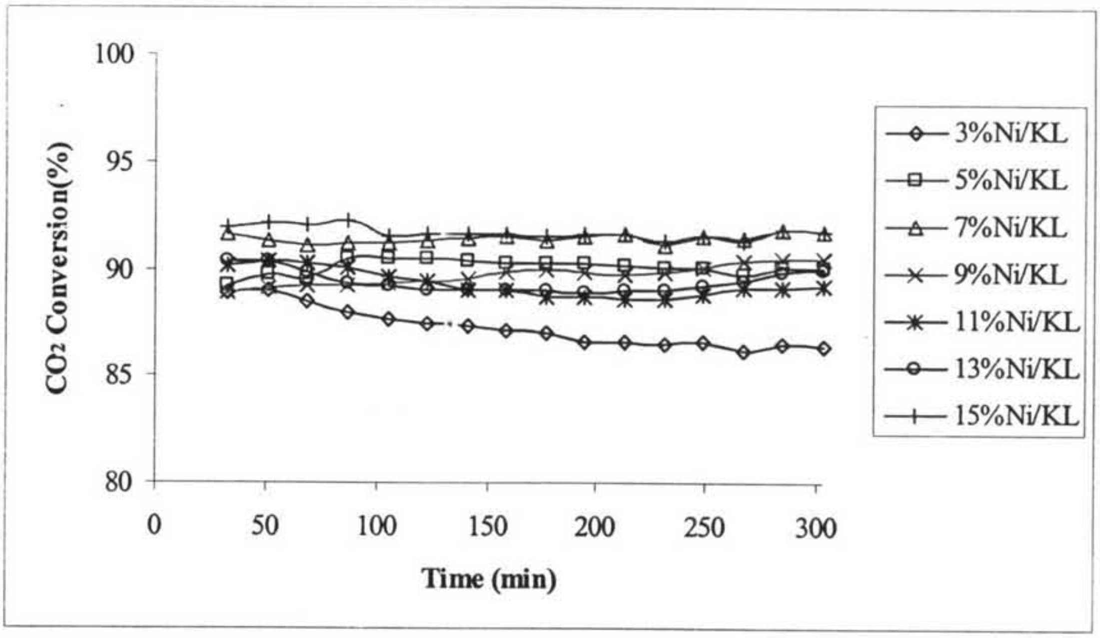

Figure 4.9 CO_2 conversions of the catalysts with various amounts of Ni loadings at 700°C.

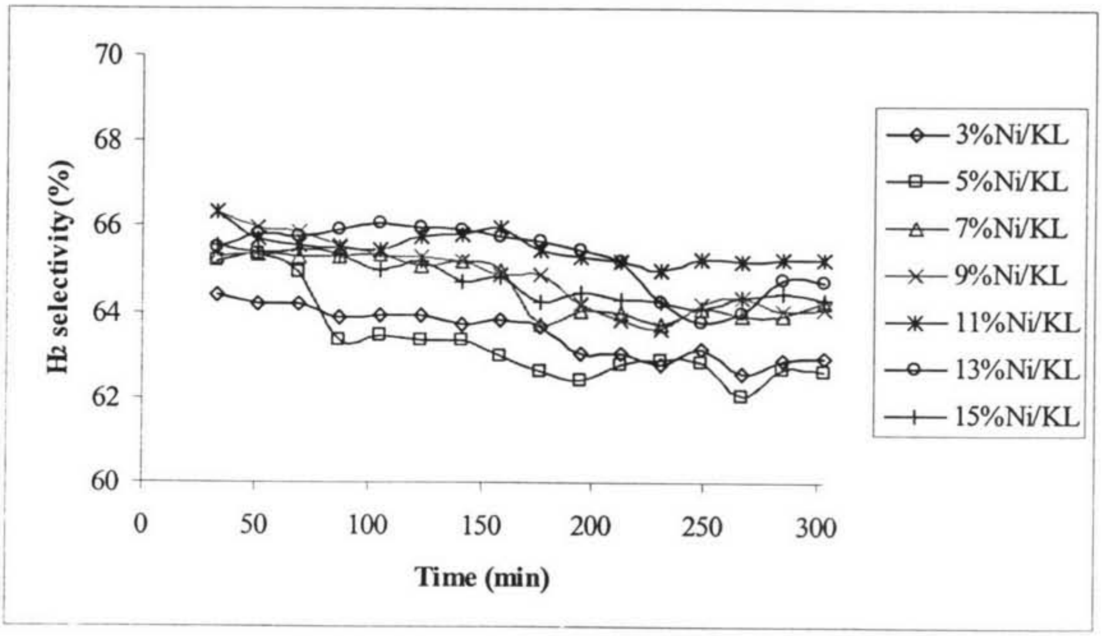

Figure 4.10 H_2 selectivity of the catalysts with various amount of Ni loadings at 700°C.

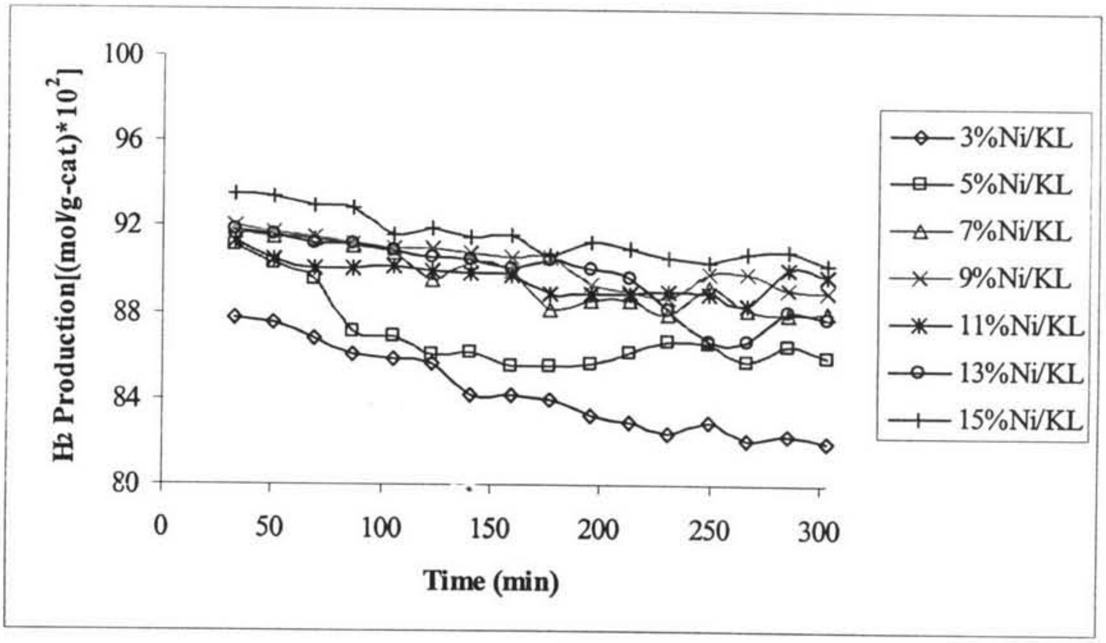

Figure 4.11 H_2 productions of the catalysts with various amounts of Ni loadings at 700°C.

It seems that 7 wt.%Ni is the suitable amount of Ni loading. Figure 4.12 shows CH_4 and CO_2 conversion of 7 wt.%Ni. The result is clearly seen that CH_4 conversion drop from 95.3% to 94%. The CH_4 conversion of this catalyst is higher than CO_2 conversion about 3%. Effect of Ni loading on the catalytic performance of Ni/KL catalysts for the CH_4 reforming with CO_2 is summarized in Table 4.10. CH_4 and CO_2 conversions, H_2 selectivity, H_2 production and H_2/CO ratio over Ni/KL are presented. The trends of CO_2 conversion are lower than CH_4 conversion. The relation between CO_2 conversion and H_2/CO ratio indicates the strong influence of the water gas shift reaction (WGS). For Ni/KL catalysts, the H_2/CO ratio are much higher compared to those for many catalysts reported in the literature, suggesting that the influence of reverse water gas shift reaction (RWGS) minimized. This results are not in agreement with Roh *et al.* (2002), which studied the effect of Ni content. They found that rate of CO_2 conversion is higher than rate of CH_4 conversion. Besides, H_2 yield is slightly lower than CH_4 conversion. They suggested that there is reverse water gas shift reaction ($H_2 + CO_2 \rightarrow H_2O + CO$) during CO_2 reforming reaction. Thus, H_2/CO ratio is lower than unity.

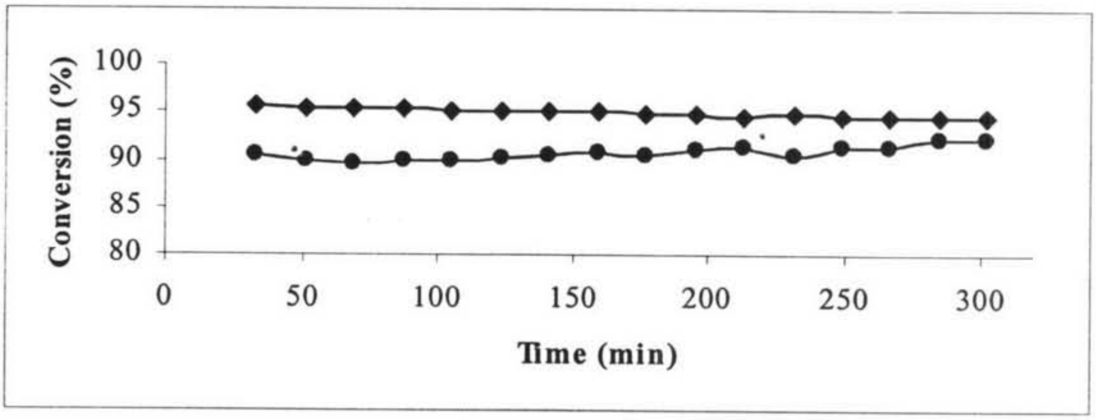

Figure 4.12 (◆) CH_4 and (●) CO_2 conversions of 7%Ni/KL catalyst at 700°C.

Table 4.9 Effect of Ni content on CH_4 conversion, CO_2 conversion, H_2 selectivity, H_2 production, and H_2/CO ratio after 5 h of reaction

Ni content (%)	X_{CH4} (%)	X_{CO2} (%)	S_{H2} (%)	H_2 prod. (mol/g-cat) x10^2	H_2/CO ratio
3	89.23	86.34	62.91	81.97	1.70
5	91.93	89.33	62.56	85.88	1.68
7	94.08	91.76	64.22	88.06	1.80
9	94.41	90.50	64.11	88.99	1.79
11	94.71	89.18	65.21	89.70	1.81
13	94.68	89.96	64.69	87.78	1.83
15	95.20	91.68	64.31	90.22	1.80

4.2.2 Effect of Promoters

4.2.2.1 Effect of Mg Loading

In order to improve the catalytic activity and stability of Ni/KL catalysts, Mg was used to study. Ni contents were fixed at 7 wt%. The results of CH_4 and CO_2 conversions of Mg promoted catalysts are shown in Figures 4.13 and 4.14. A decrease in the CH_4 and CO_2 conversions with the amount of Mg in the catalysts is observed and the catalytic performance of Mg promoted catalysts decreases with adding Mg. The 3%Mg-7%Ni/KL shows the highest CH_4 conversion whereas 5%Mg-7%Ni/KL shows the lowest CH_4 conversion. The CH_4 conversion observed over the Mg promoted catalysts was maintained for 5 hours of reforming, however, was significantly lower than that observed over unpromoted catalysts. This indicated that the MgO doped was favorable for the improvement of stability. Because adding Mg can reduce the coke formation on the catalyst. The 5%Mg-7%Ni/KL shows the highest stability which might be from carbon on this catalyst is easy gasification as see from TPO result.

The CO_2 conversions are lower than CH_4 conversion of all catalysts. The CO_2 conversion of unpromoted catalyst is higher than CO_2 conversions of promoted catalysts. For the results of H_2 selectivity and H_2 production in terms of mol/g-catalyst of 7%Ni with various amounts of Mg loading are shown in Figures 4.15 and 4.16. Figure 4.15 shows the H_2 selectivity of catalysts with different amounts of Mg. The H_2 selectivity of 3%Mg-7%Ni/KL and 4%Mg-7%Ni/KL catalysts are above 50% which can be suggested that the rate of CO_2 dissociation is lower than rate of CH_4 decomposition or from the side reactions. Whereas the H_2 selectivity of 2%Mg-7%Ni/KL and 5%Mg-7%Ni/KL catalysts are lower than 50% which might be the effect of side reactions. In addition, the H_2 selectivity of catalysts with adding Mg are much lower than catalyst without Mg. Among the catalyst examined 7%Ni-3%Mg shows the highest H_2 selectivity and constant at 55% along 5 hours of testing time.

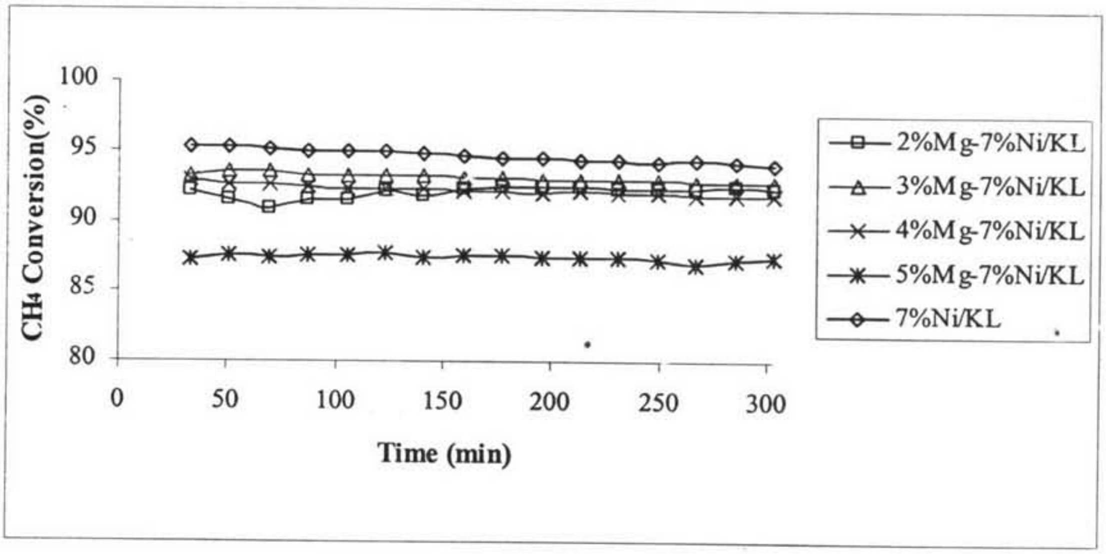

Figure 4.13 CH_4 conversion of 7%Ni with various amounts of Mg loadings at 700°C.

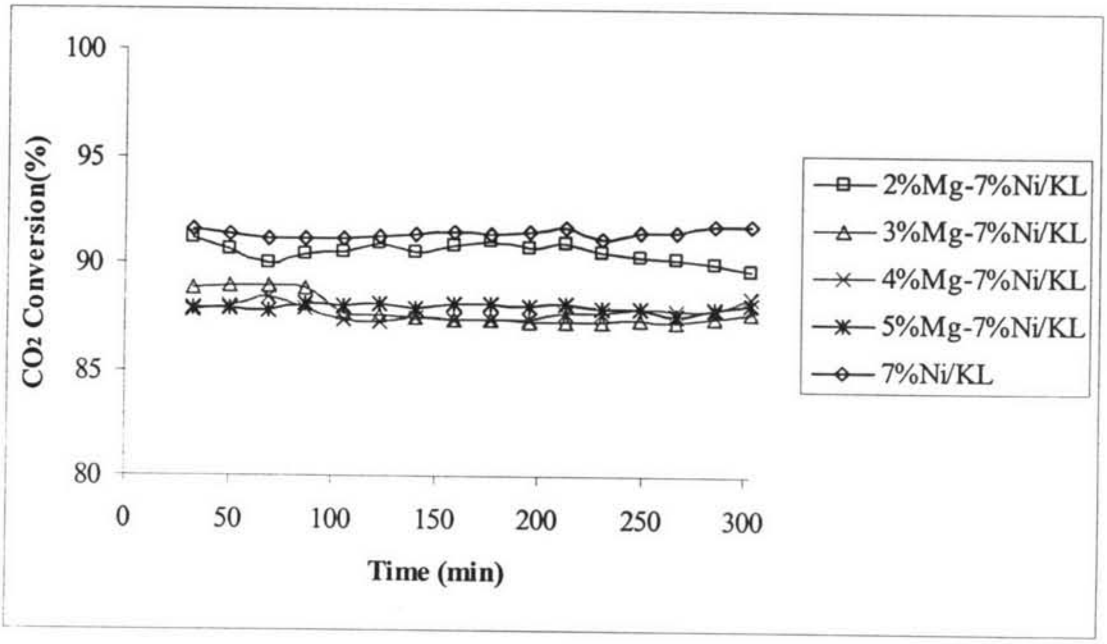

Figure 4.14 CO_2 conversion of 7%Ni with various amounts of Mg loadings at 700°C.

The results of H_2 production are shown in Figure 4.16. This results show the same trend as CH_4 conversions which adding Mg can not improve the H_2 production within 5 hours of reaction time. The 7%Ni-3%Mg shows the highest H_2 production when compare to other wt.%Mg. However, in term of stability adding Mg can improve the stability of the catalysts. From this figure, H_2 production of catalyst without Mg trend to drop more than H_2 production of catalysts with adding Mg within 5 hours of testing time.

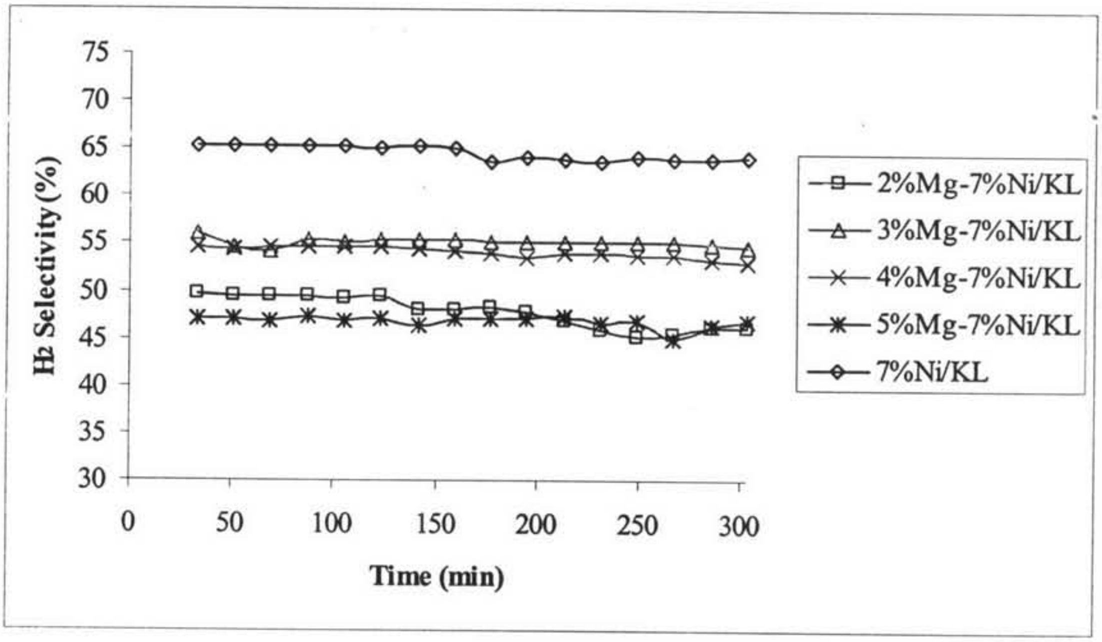

Figure 4.15 H_2 selectivity of 7%Ni with various amounts of Mg loadings at 700°C.

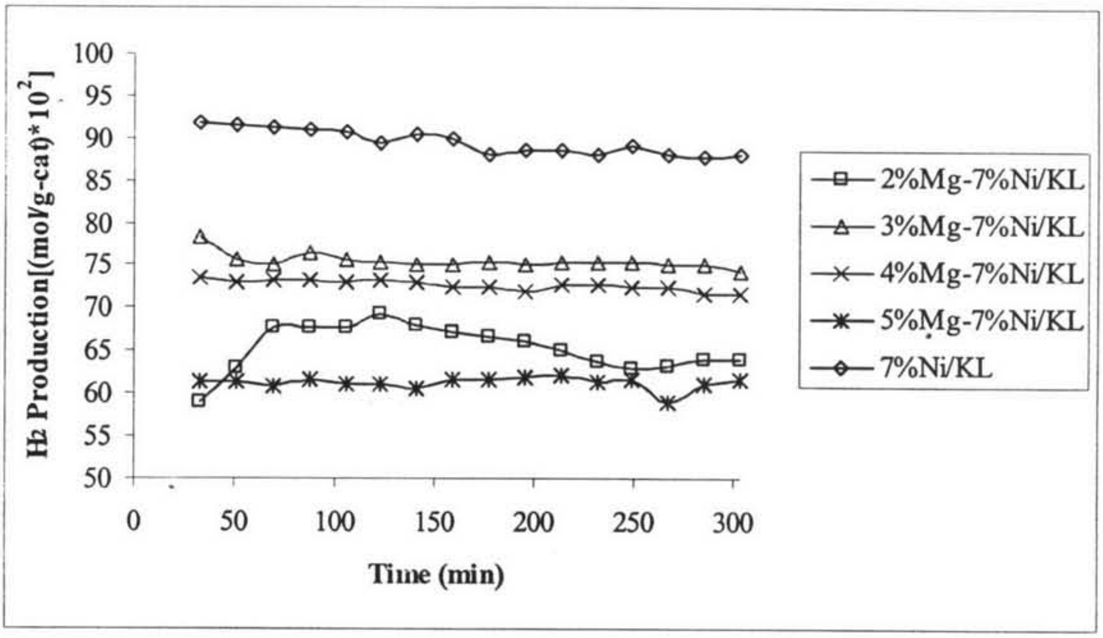

Figure 4.16 H_2 production of 7%Ni with various amounts of Mg loadings at 700°C.

There are many researchers studied the effect of adding Mg promoted on the catalytic activity and stability. The appropriate amount of Mg can enhance stability of the catalysts. Based on two-path mechanism proposed by Stagg *et al.* (1998), the stability of the catalysts depends on the balancing between the rate of carbon deposition and the rate of carbon removal. If the rate of carbon deposition is higher than the rate of carbon removal, the active sites of the catalysts are blocked by carbon deposition, inhibiting the methane decomposition. However, this carbon can be removed out by cleaning mechanism, which are the reaction of deposite carbon and O_{ads} forming CO. The basicity support can favor the CO_2 adsorption. The CO_2 adsorption promotes the inverse of the Boudouard reaction, ($CO_2 + C \leftrightarrow 2\ CO$) decreasing the amount of carbon deposition (Quincoces *et al.*, 2001).

In this work, adding Mg might increase the basicity of support. It is noticeable that the addition of Mg to the Ni/KL catalyst remarkably stabilized the catalytic performance. The lower catalytic activity in this reforming might be the cause of portion of Ni particles was covered with Mg, which is revealed by XRD line broadening when Mg was added. Horiuchi *et al.*, (1996) found that adding basic metal oxide can reduce the catalytic activity. They believed that basic metal oxide cover a part of the Ni surface.

4.2.2.2 Effect of Ca loading

The 7%Ni with 2-5%Ca/KL catalysts were tested for their activity at 700°C. Figure 4.10 shows the CH_4 conversions of 7%Ni over KL zeolite with 2-5%Ca. The results show that the catalyst with adding Ca also give lower conversion than the unpromoted catalyst which caused by Ca promoter cover some part of Ni active site as shown from XRD results. Adding 5 %Ca presents the highest stability along the 5 hours of reaction time. However, the conversions of promoted catalysts are lower than the conversion of unpromoted catalyst. The CO_2 conversions of catalyst with various amounts of Ca are shown in Figure 4.18. The CO_2 conversions of Ca promoted catalysts are lower than unpromoted catalyst except for 4%Ca.

The H_2 selectivity of the catalysts with various amounts of Ca (2-5 wt.%) are shown in Figure 4.12. It is found that the H_2 selectivity of catalysts with adding Ca are lower than the catalyst without Ca. The H_2 selectivity of these catalysts are above 50% which can be suggested that the rate of CH_4 decomposition is higher than the rate of CO_2 dissociation.

The H_2 productions in term of mol per gram catalyst of the catalysts are shown in Figure 4.13. It is found that the catalyst without adding Ca show the best H_2 production. It give H_2 production more than 90% even though a slightly decrease with the time on stream is occurred. Adding 5 wt.%Ca shows the best performance in term of stability. It presents about 0.70 mol/g-cat. along 5 hours of reaction.

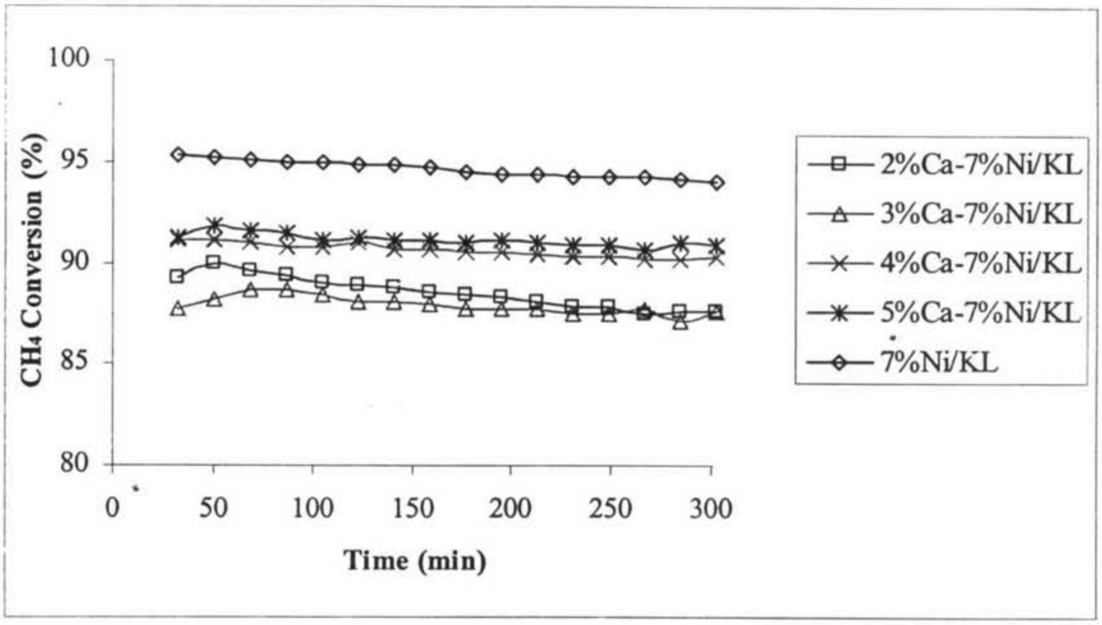

Figure 4.17 CH_4 conversion of 7%Ni with various amounts of Ca loadings at 700°C.

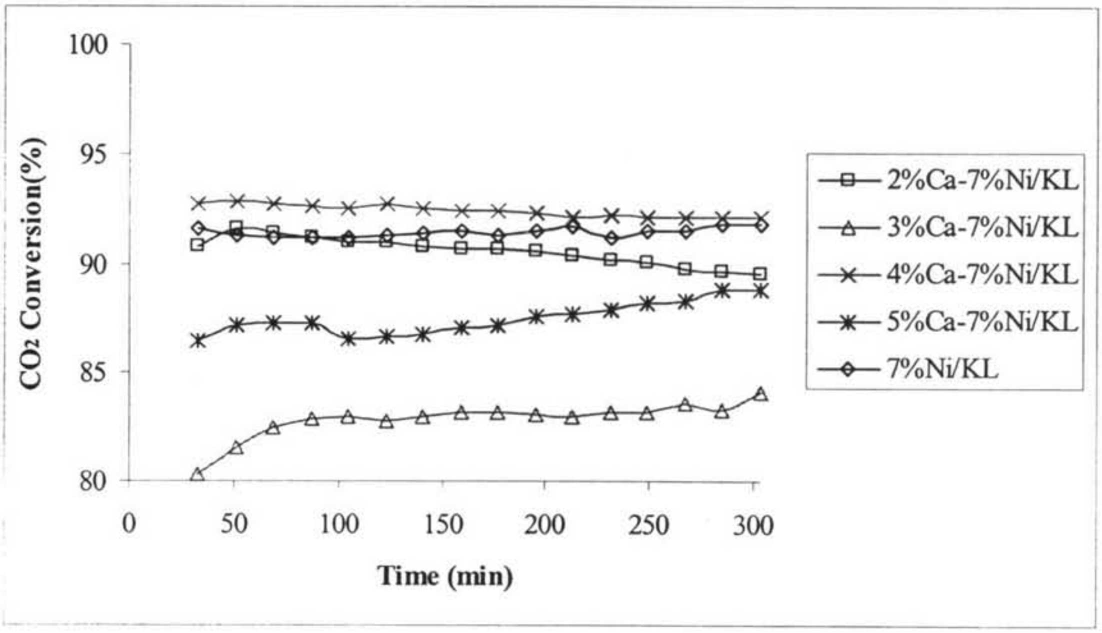

Figure 4.18 CO_2 conversion of 7%Ni with various amounts of Ca loadings at 700°C.

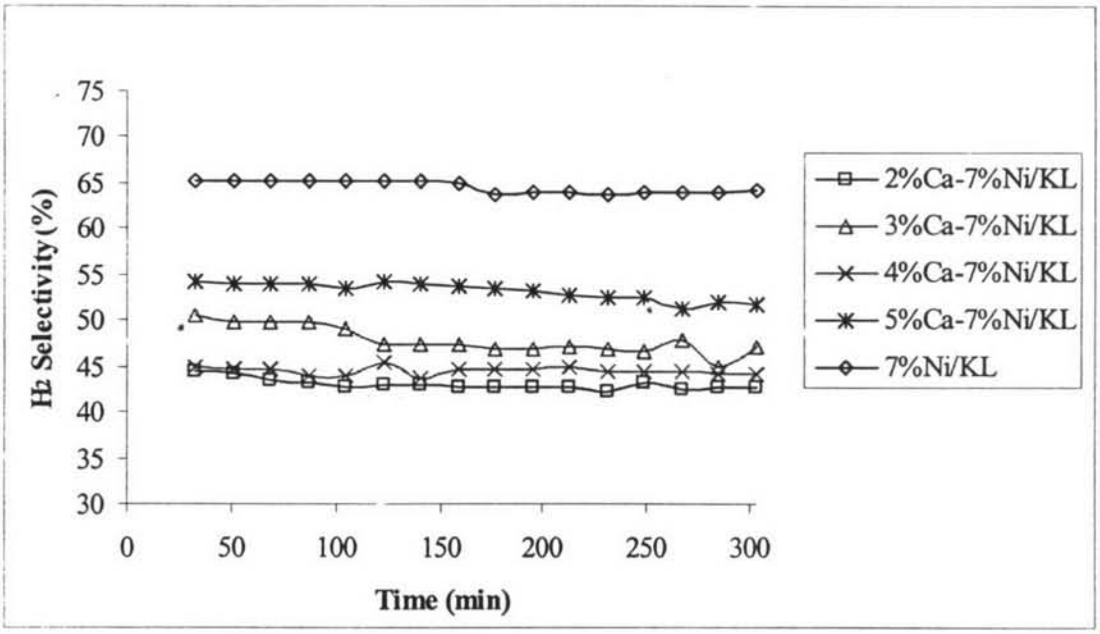

Figure 4.19 H_2 selectivity of 7%Ni with various amounts of Ca loadings at 700 °C.

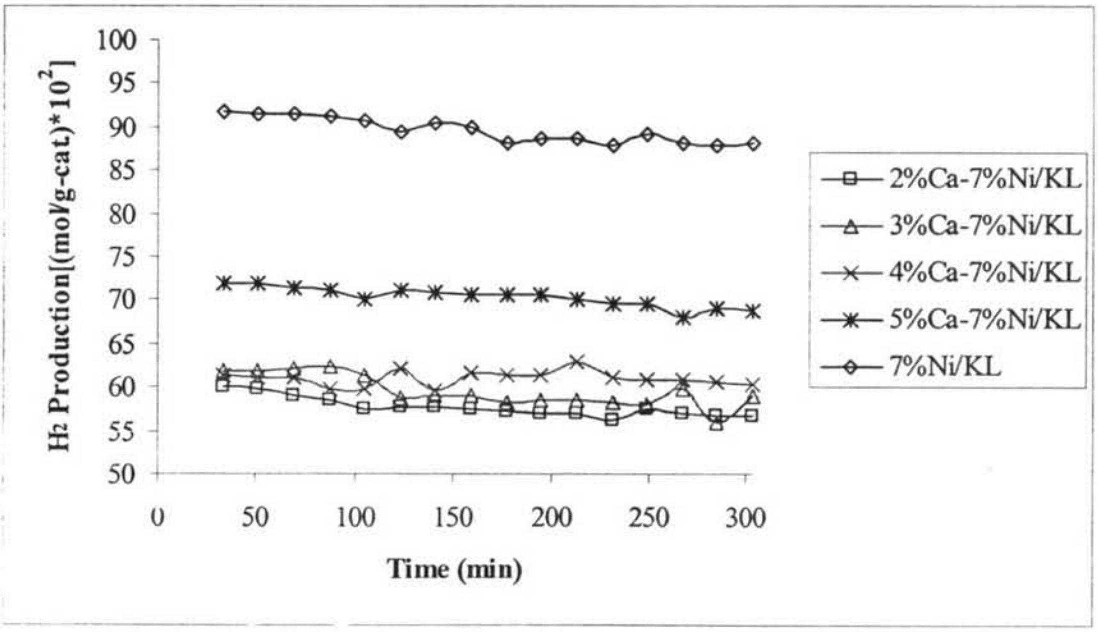

Figure 4.20 H_2 production of 7%Ni with various amounts of Ca loadings at 700 °C.

4.3 KH Zeolite Synthesis and Characterization

From previous work (Kangsilalai, 2005), KH zeolite was successful synthesized by sol-gel process using synthesis Silatrane and Alumatrane as precursors. However, using synthesis Silatrane and Alumatrane as the precursors is a difficult method. Because it is hard to control properties of each batch of synthesized precursors. So that, KH zeolite from each batch could give different properties such as different morphology which might affect to the catalyst activity and coke formation.

In this work, KH zeolite was initially attended as the catalyst support, prepared by sol-gel process using Silatrane and Alumatrane. Therefore, synthesis of KH zeolite was improved by using Ludox HS-40 colloidal silica and Aluminium Isopropoxide as the precursors. KH zeolite was synthesized by sol-gel process with a fixed molar ratio of SiO_2 : $0.1Al_2O_3$: 4 K_2O : $410H_2O$. The Ludox HS-40 colloidal silica and Aluminium Isopropoxide were mixed together with KOH. After that the gel mixture was aged for 50 hours before undergoing hydrothermal microwave treatment at 150°C for 5 hours. Even when the reaction mixture is fixed, a large number of variables can impact on zeolite crystallization. Of these variables, the mixing speed and time employed are the most obvious parameter and the conditions are present in Appendix B.

From XRD result, it was indicated that KH zeolite can be synthesized by using Ludox HS-40 colloidal silica and Aluminium Isopropoxide as the precursors, which is an easy way to produce this zeolite. The XRD pattern of synthesize KH zeolite is shown in Figure 4.21. It is apparent that the XRD pattern consists of 15 main reflections corresponding to (111), (022), (141), (142), (321), (143) planes. The XRD pattern of this zeolite closely matches that of KH zeolite (SiO_2 : $0.1Al_2O_3$: $3K_2O$: $410H_2O$) reported by Kaengsilalai (2006).

The activity of KH zeolite is shown in Figure 4.22. It is found that 7%Ni/KH catalyst shows high CH_4 conversion and constant along 5 hours of reaction time. The high stability for this catalyst might be a result of basicity of the KH zeolite, which can increase the cleaning mechanism rate and decrease the carbon deposition. From this figure, the CH_4 conversion is higher than CO_2, which is indicated that rate of CH_4 deconposition to H_2 and C more than rate of CO_2 dissociation.

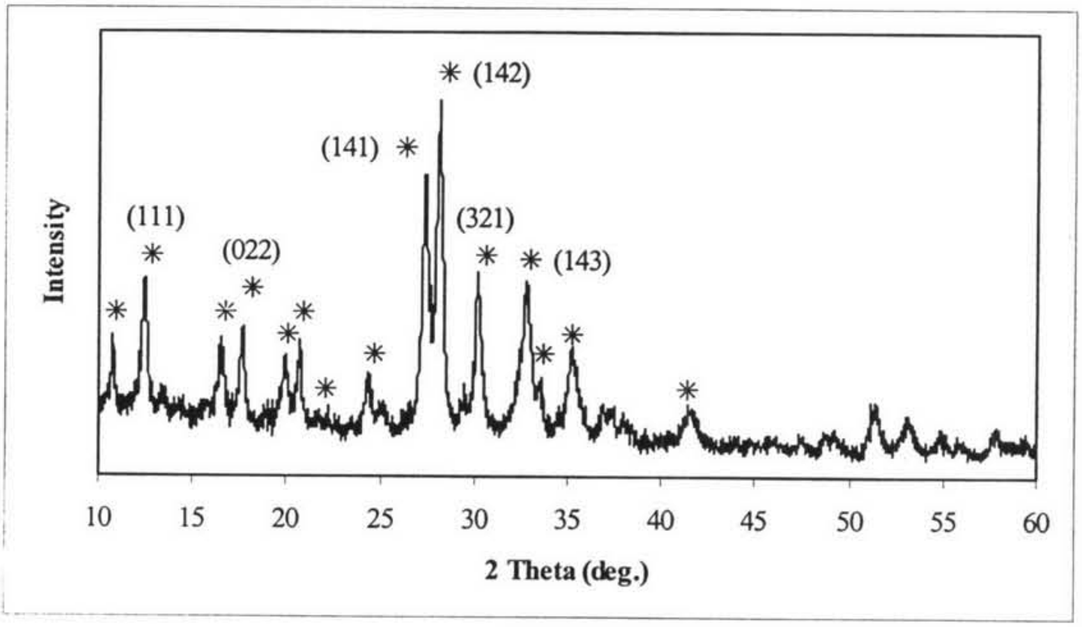

Figure 4.21 XRD pattern of synthesis KH zeolite.

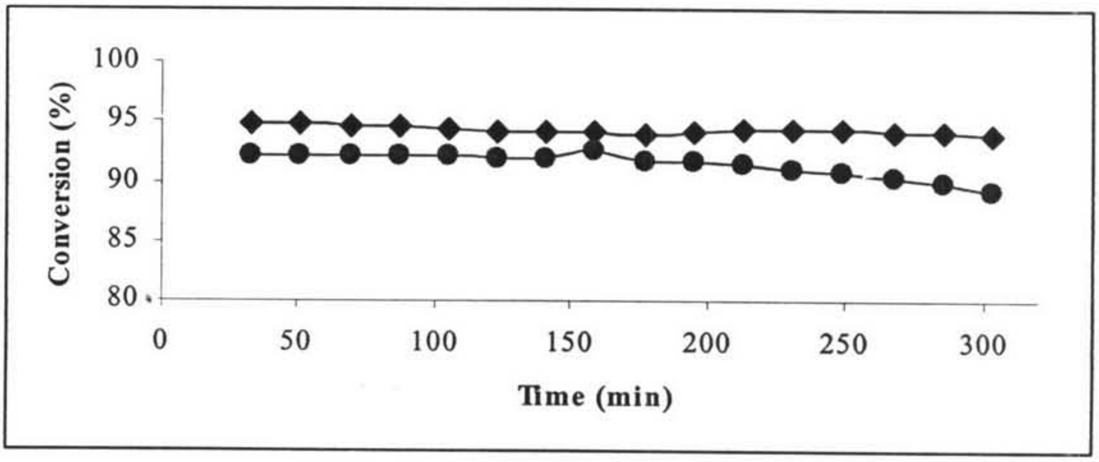

Figure 4.22 (♦) CH_4 and (●) CO_2 conversion of 7%Ni/KH catalyst at 700°C.

For comparison the effect of support KH zeolite in this work and KL zeolite with 7%Ni loading and KH zeolite which is synthesized from Silatrane and Alumatrane (Kaengsilalai, 2006) with 8% Ni loading were also compared. Figures 4.23-4.26 show all activity of three employed Ni supported catalysts, which notations are: KH_1 = KH zeolite synthesized by using Ludox HS-40 colloidal silica and Aluminium Isopropoxide as the precursors, KH_2 = KH zeolite synthesized by using Silatrane synthesis and Alumatrane synthesis as the precursors (Kangsilalai, 2006). It was found that Ni supported on KL zeolite and both KH zeolite provided a similarly excellent activity on both CH_4 and CO_2 conversions. However, the activity of Ni/KL and Ni/KH_1 tended to slightly decrease along testing time, which might be the effect of coke formation. It seem that Ni supported on KH_2 zeolite catalyst show higher stability of the catalyst compared to others.

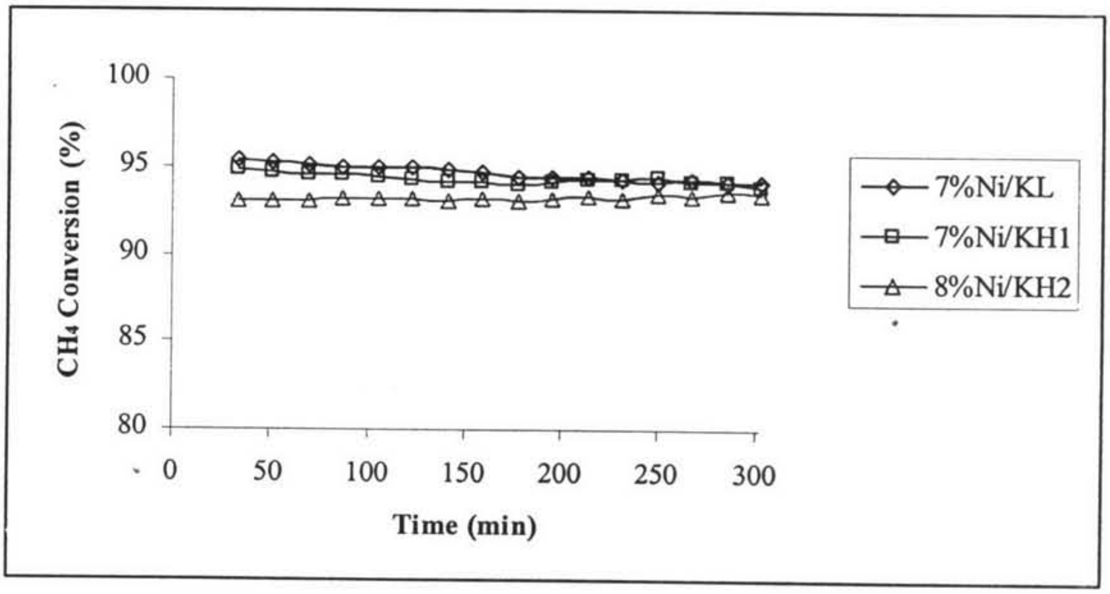

Figure 4.23 CH_4 conversions of Ni over KL, KH_1 (KH zeolite synthesize from Ludox HS-40 colloidal silica and Aluminium Isopropoxide) and KH_2 (KH zeolite synthesize from Silatrane synthesis and Alumatrane synthesis) catalysts.

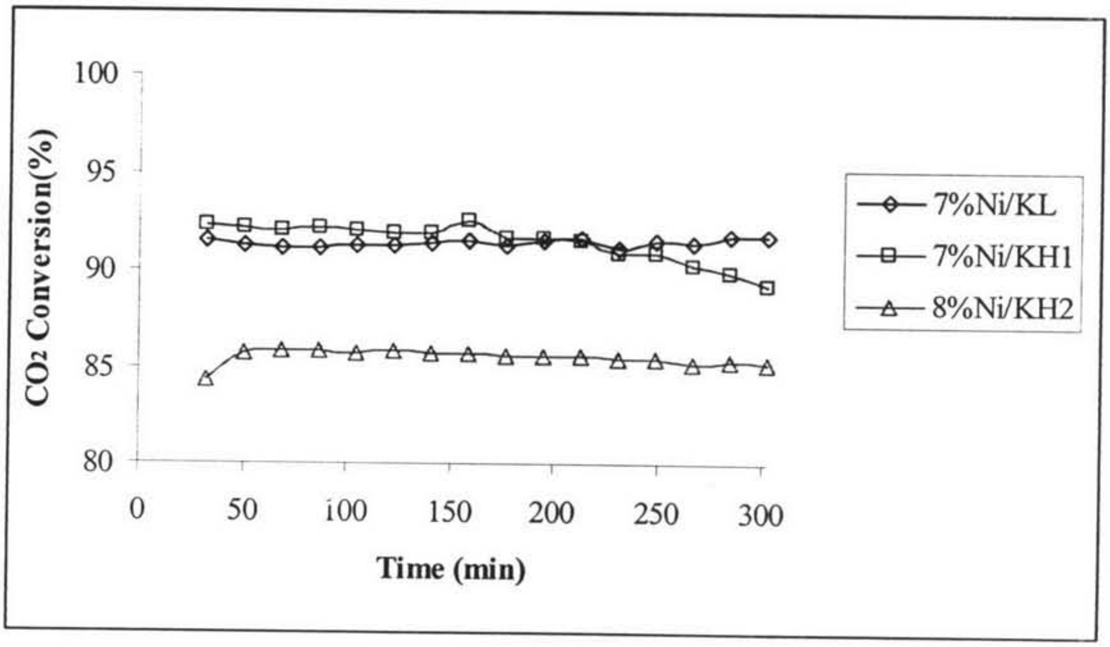

Figure 4.24 CO_2 conversions of Ni over KL, KH_1 (KH zeolite synthesize from Ludox HS-40 colloidal silica and Aluminium Isopropoxide) and KH_2 (KH zeolite synthesize from Silatrane synthesis and Alumatrane synthesis) catalysts.

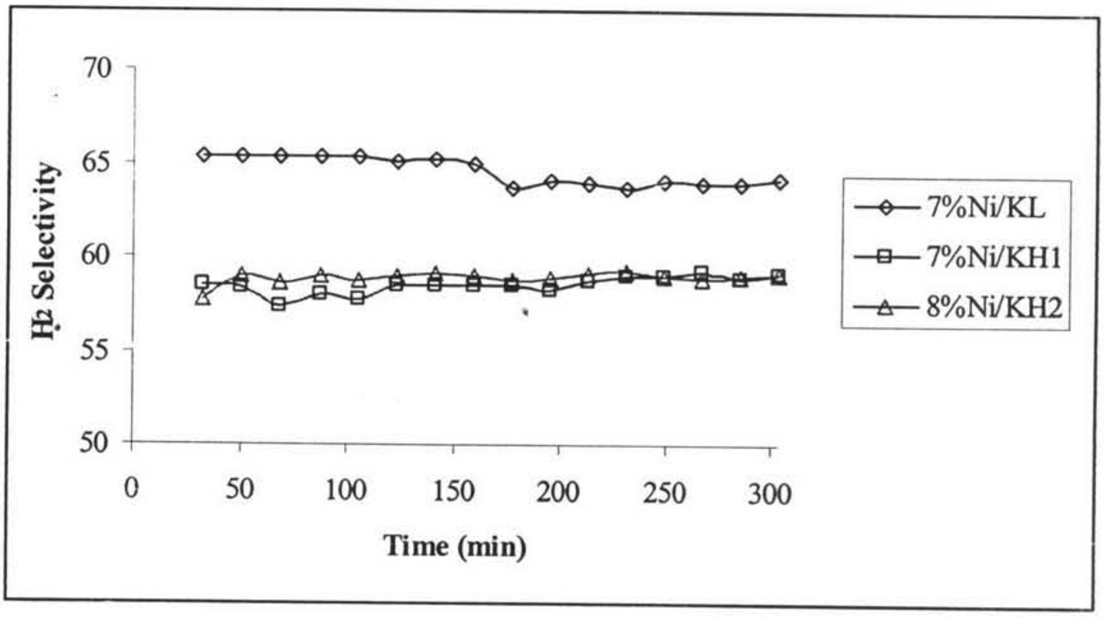

Figure 4.25 H_2 selectivity of Ni over KL, KH_1 (KH zeolite synthesize from Ludox HS-40 colloidal silica and Aluminium Isopropoxide) and KH_2 (KH zeolite synthesize from Silatrane synthesis and Alumatrane synthesis) catalysts.

For H_2 selectivity and H_2 production, it seems that using KL zeolite shows the highest H_2 selectivity and H_2 production. The different in catalytic activity of these catalysts might be come from the effect of morphology. Kaengsilalai (2006) studied the effect of morphology to catalytic activity for CO_2 reforming of CH_4. She studied three morphology of KH zeolite, which are flower-shape, dog-bone, and disorder. Her results showed that the morphology can affect to CH_4 reforming activity and flower-shape or dog-bone were suggested to be the suitable supports for this reaction, since it can give the higher CH_4 conversion and H_2 production.

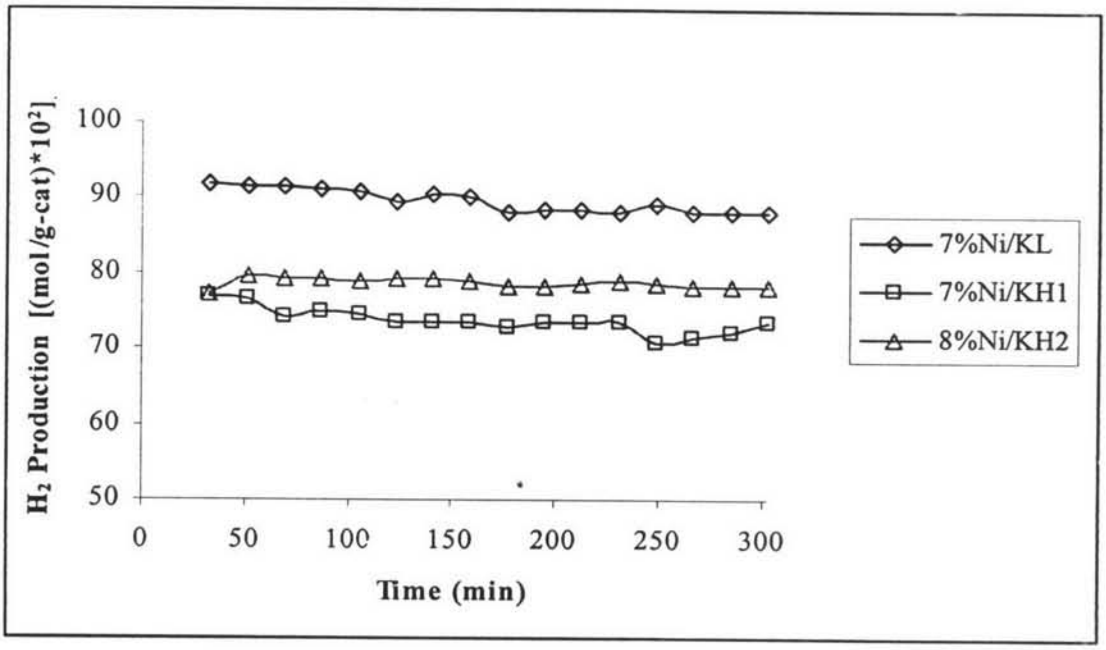

Figure 4.26 H_2 production of Ni over KL, KH_1 (KH zeolite synthesize from Ludox HS-40 colloidal silica and Aluminium Isopropoxide) and KH_2 (KH zeolite synthesize from Silatrane synthesis and Alumatrane synthesis) catalysts.