

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterizations

This section shows the catalyst characterization results of Ni supported KL zeolite, which are the BET surface area, X-ray Diffraction (XRD) and Temperature Programmed Reduction (TPR).

4.1.1 Surface Area Measurement

BET surface area analysis was performed to determine the surface area and pore volume of the catalysts. The surface areas of KL zeolite with different Ni loading catalysts (3, 5, 7, 10 and 15 % by weight of Ni on KL zeolite) were measured by multiple point BET method. The BET characterization results are shown in Table 4.1.

Table 4.1 BET characterization results

% Ni loading on KL zeolite	Surface area (m ² /g)	Pore volume (cc/g)
0	322	0.25
3	228	0.19
5	217	0.17
7	214	0.13
10	178	0.14
15	166	0.14

Since the surface area of the KL zeolite without impregnated Ni, blank KL zeolite, was much higher than those surface areas of supported catalysts, as shown in Table 4.1, the metal loading can reasonably cause a decline in BET surface area. KL zeolite was covered by nickel metal and hence overall surface area decreased. The effect of Ni loading on pore volume is also illustrated in Table 4.1. The addition of

Ni decreased the pore volume of catalysts. These results can be explained by the Ni particles deposited into the active pore of catalysts.

4.1.2 X-Ray Diffraction (XRD)

Thermal stability testings of KL zeolite catalyst support were performed by using XRD characterization to ensure that KL zeolite can tolerate at high temperatures. The XRD patterns of KL zeolites calcined at different temperatures (750, 800, 850, 900 and 1000°C) are shown in Figure 4.1. The result showed that KL zeolites calcined at the temperature range of 750 to 850°C have XRD patterns as same as uncalcined KL zeolite but KL zeolite calcined at 900°C shows lower intensity of diffraction peak than uncalcined KL zeolite. And KL zeolite calcined at 1000 °C does not show the XRD pattern of KL zeolite. In conclusion, KL zeolite can tolerate the maximum temperature around 850°C.

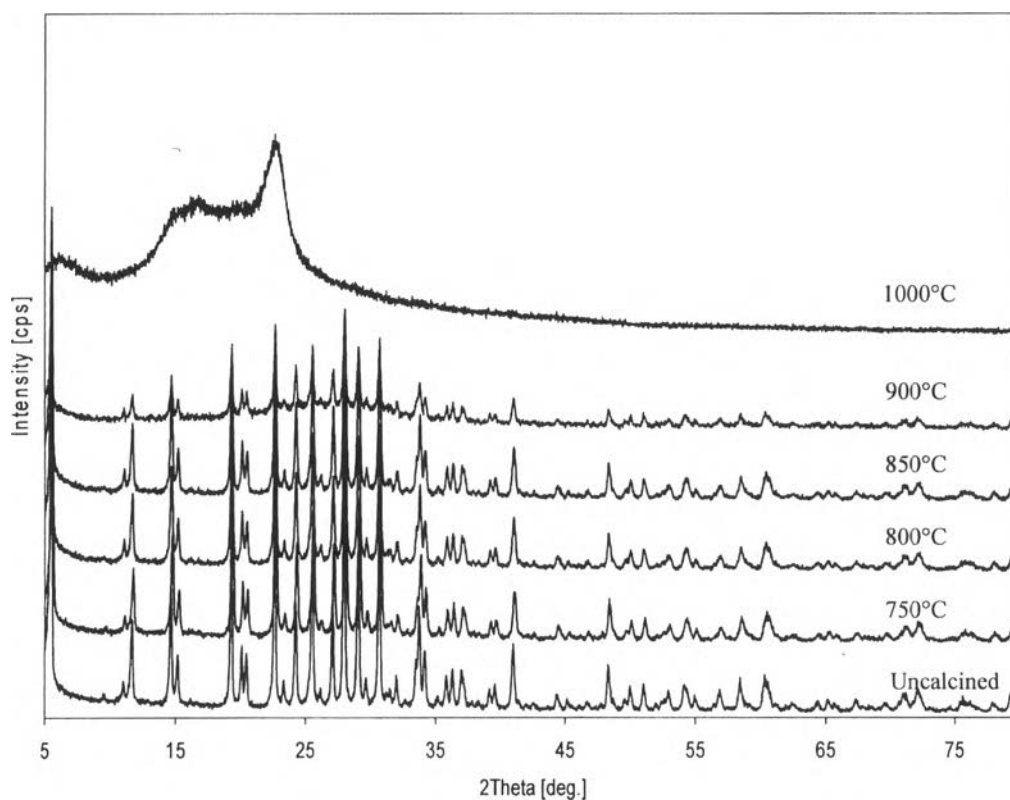


Figure 4.1 XRD patterns of KL zeolite and calcined KL zeolites at various temperatures.

The XRD patterns of catalysts with different Ni loadings are illustrated in Figure 4.2. Two major XRD peaks, attributed to NiO (111) at 37.3° , NiO (200) at 43.3° (Matsumura and Nakamori, 2004) and at the 2θ value of 63.0° (Oh *et al.*, 2003), were observed resulting from nickel nitrate decomposition after calcinations, while the other peaks were attributed to KL zeolite. The peak intensity of nickel oxide was increased with the increase in the nickel content due to the higher nickel oxide concentration.

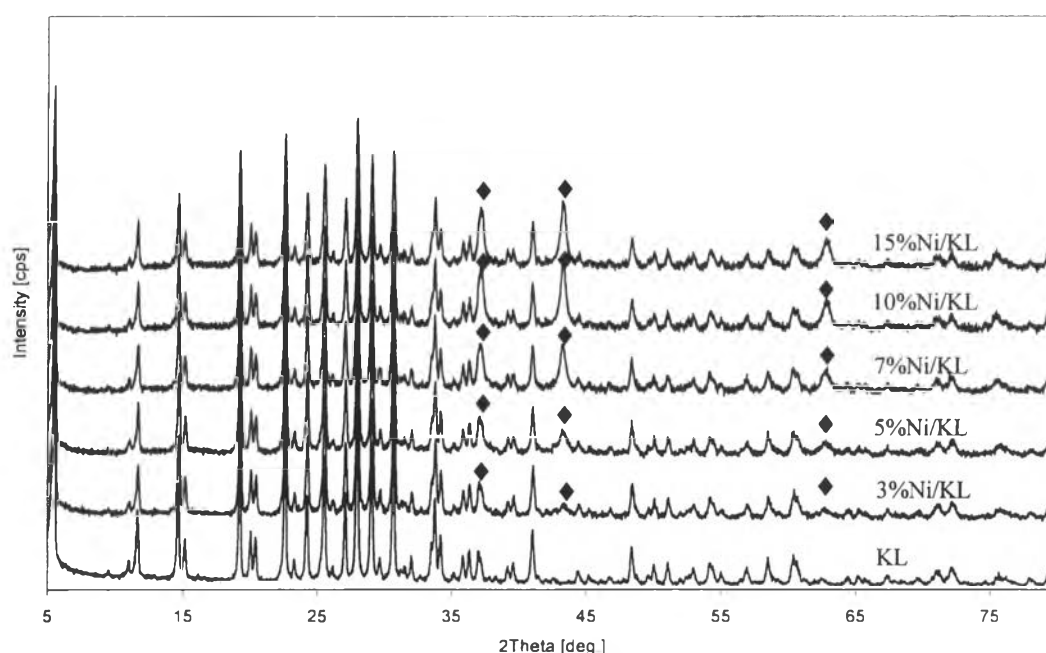


Figure 4.2 XRD patterns of KL zeolite and nickel supported on KL zeolite catalysts calcined at 700°C for 4 hours; (◆), nickel oxide phase.

The XRD patterns of 7%Ni/KL zeolite catalysts with different ceria content are very similar to those of the samples without ceria and illustrated in Figure 4.3. The result shows that no ceria phase was detected, implying that ceria phase is probably present in an amorphous-like or micro-crystallite state in the catalysts. Ni is present in nickel oxide phase at about 37.3° and 43.3° resulting from after calcination nickel nitrate was decomposed to nickel oxide. The higher content of ceria, the lower nickel oxide peak intensity were observed. It indicated that ceria greatly promoted surface Ni dispersion.

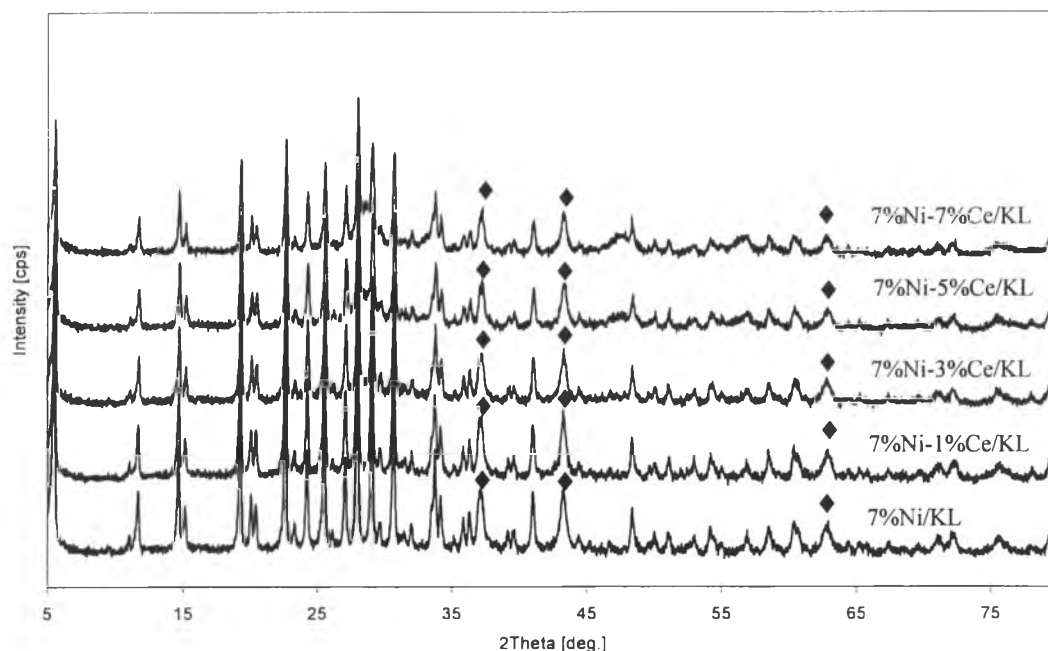


Figure 4.3 XRD patterns of ceria promoted Ni/KL zeolites calcined at 700°C for 4 hours; (◆), nickel oxide phase.

After catalytic activity testing on steam reforming of methane was accomplished, 7%Ni/KL zeolite catalyst was found to be the best catalyst. Hence, 7%Ni/KL zeolite was chosen to study the XRD pattern after 5 hours of reaction. Figure 4.4 exhibits the XRD patterns of calcined and spent 7%Ni/KL zeolite. The result shows that after the reaction, the peaks attributed to nickel oxide were disappeared and the Ni peaks, attributed to Ni (111) at 44.5° and to Ni (200) at 51.8°, were recorded, showing that the nickel particles were completely reduced during the reaction (Matsumura and Nakamori, 2004, Zhang *et al.*, 2003 and Roh *et al.*, 2003). The Ni crystallite size of the spent catalyst is 28 nm (from XRD results), which is bigger than the result reported by Roh *et al.* (2003).

Figure 4.5 exhibits the XRD patterns of ceria promoted 7%Ni/KL zeolite catalyst after 5 hours of reaction. It was observed that the peak intensity of Ni metal tends to decrease and broad with increasing of ceria content. This can be suggested that the catalysts with high ceria content have higher Ni dispersion than the catalysts with low ceria content.

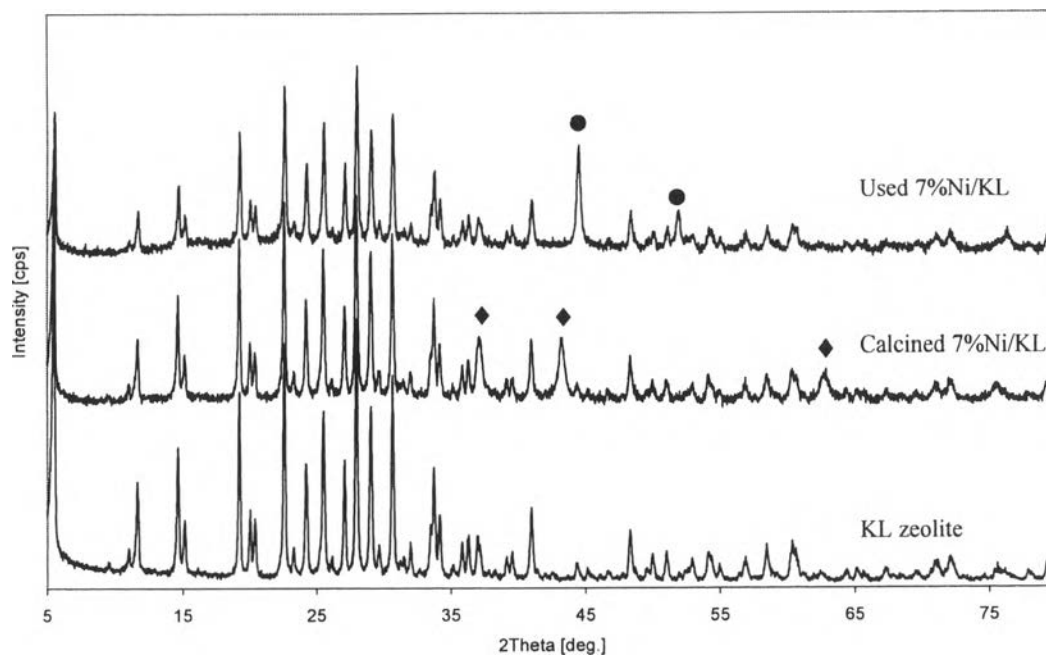


Figure 4.4 XRD patterns of KL zeolite, fresh and used (5 hours of reaction) 7%Ni/KL zeolite catalyst; (◆), nickel oxide phase (●), nickel metal phase.

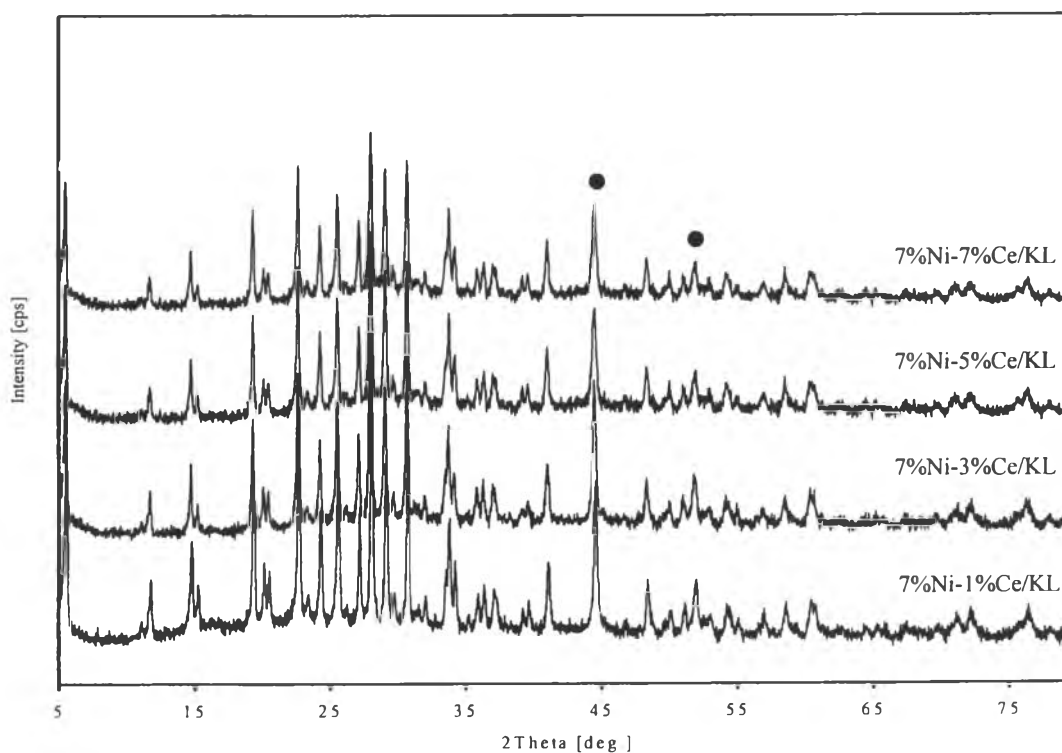


Figure 4.5 XRD patterns of used ceria promoted 7%Ni/KL zeolite catalyst (5 hours of reaction); (●), nickel metal phase.

4.1.3 Temperature Programmed Reduction (TPR)

TPR curves of Ni/KL zeolite catalysts with various Ni loadings (0, 3, 5, 7, 10 and 15 wt%) are presented in Figure 4.6. The KL zeolite shows no peak along the whole temperature range. For Ni/KL catalysts, a broaden peak appears in the range from 300 to 620°C. With the increase of Ni content, TPR profiles show a reduction peak with a maximum at 450°C, followed by a hump at about 620°C. According to Dong *et al.* (2001) and Dong *et al.* (2002), pure nickel oxide shows a reduction peak at about 420°C. The area under the peak is attributed to the H₂ consumption for reducing NiO to metallic Ni. The increasing of Ni contents results in higher area under the peak. Based on the analysis, the reduction peak at 450°C for the catalysts corresponds to bulk nickel oxide with small interaction with support. Dong *et al.* (2002) suggested that the reduction degree of nickel oxide in the catalysts increased with the increasing of nickel loading. Therefore, the catalyst with low content of Ni resulted in the strong interaction between support and metal. A hump (at 620°C) can be assigned to the complex NiO_x species, which has a strong interaction with support (Roh *et al.*, 2003). NiO_x shoulders can be seen over the catalysts having more than 10% Ni content.

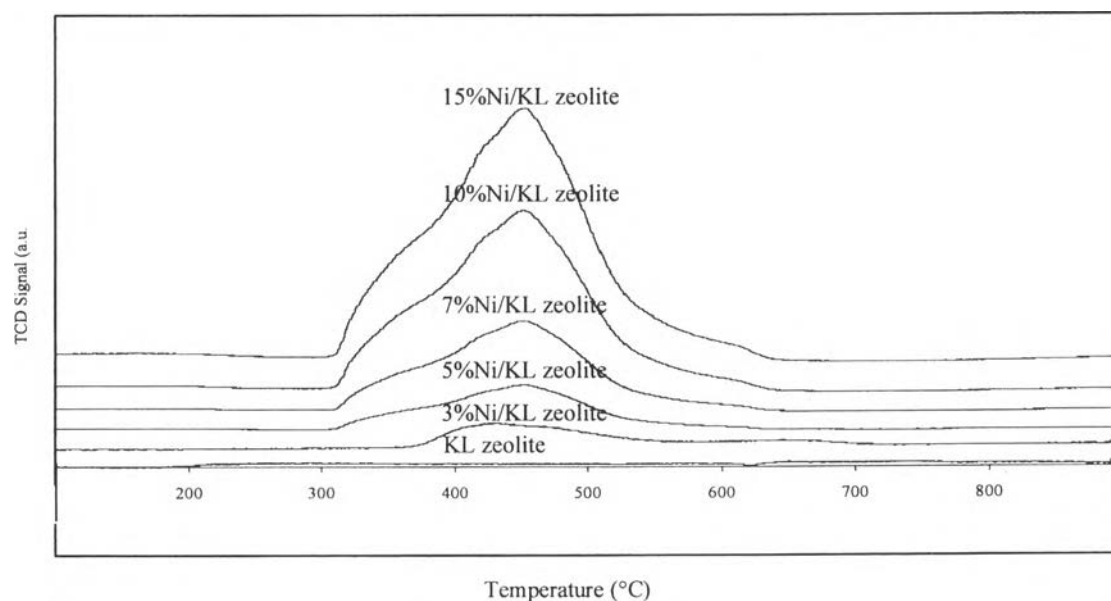


Figure 4.6 TPR patterns of Ni/KL zeolite catalysts with different Ni loadings.

TPR curves for ceria promoted Ni/KL zeolite catalysts (7wt% of Ni with ceria contents of 1, 3, 5 and 7 wt%) are presented in Figure 4.7. The 7%Ni/KL zeolite catalyst shows a maximum peak at 450°C corresponding to high uniformity of nickel oxide. The promoted catalysts showed a broader main reduction peak at higher temperatures than that for the 7%Ni/KL zeolite. In the case of ceria promoted catalysts, hydrogen consumption was observed from 200 to 300°C. The width of the reduction peak suggests a broad particle size distribution (Montaya *et al.*, 2000), concluding that it is associated to a more dispersed nickel oxide exhibiting a strong interaction with the support. The reduction peak shifts to a higher maximum temperature as the ceria content increases. This is associated to larger nickel oxide particles having a lower interaction with the support. A small consumption peak at around 200°C was clearly seen in the profile of 3% ceria and the peak maximum was at 250°C. It has been reported that ceria exhibits a reduction peak at about 880°C (Dong *et al.*, 2002) and supported ceria is much easier to reduce than the bulk ceria (Loong and Ozawa, 2000).

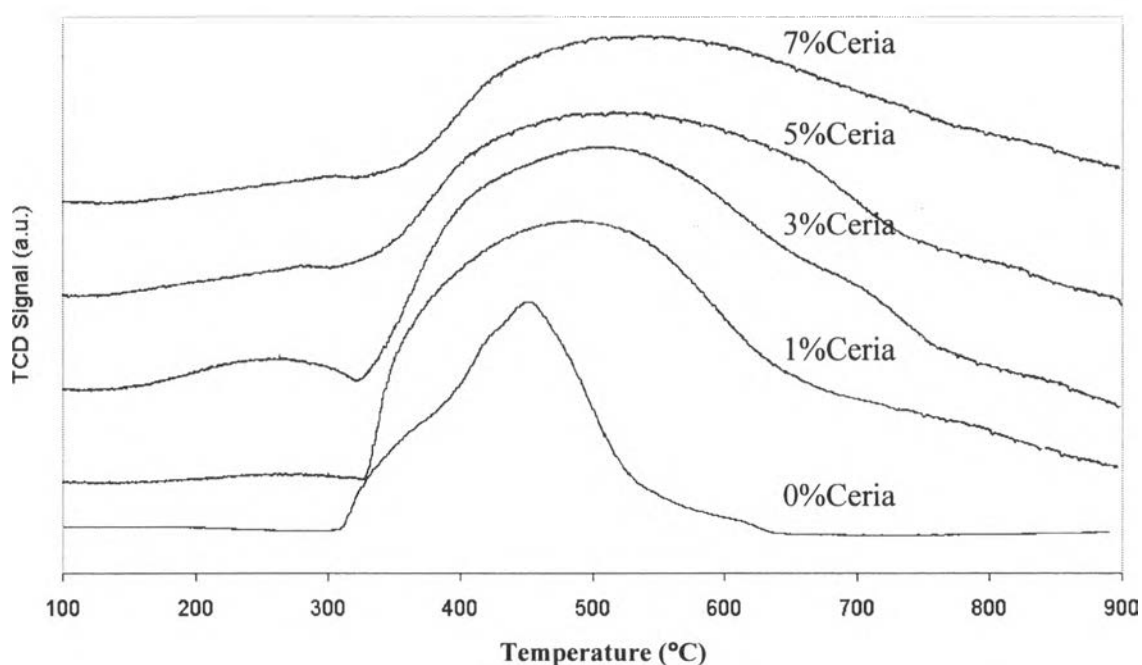


Figure 4.7 TPR patterns of ceria promoted 7%Ni/KL zeolite catalysts.

4.2 Effect of Nickel Loading

The effect of different nickel loadings (3, 7 and 15 wt%) over the KL zeolite catalyst was tested for the catalytic activity on steam reforming of methane at H_2O/CH_4 of 3. The light-off patterns of all catalysts were the same as shown in Figure 4.8. It can be clearly seen that the activity of the Ni/KL zeolite increases significantly with increasing reaction temperature from 600 to 800°C with a given Ni loading. The result shows that at 600°C, methane conversion of all catalysts is relatively low (11-31%) and sharply increases at 700°C (75-85%). At 800°C, the 7 and 15 wt% Ni/KL zeolite show about 100% methane conversion while 3 wt% Ni/KL give about 80% methane conversion.

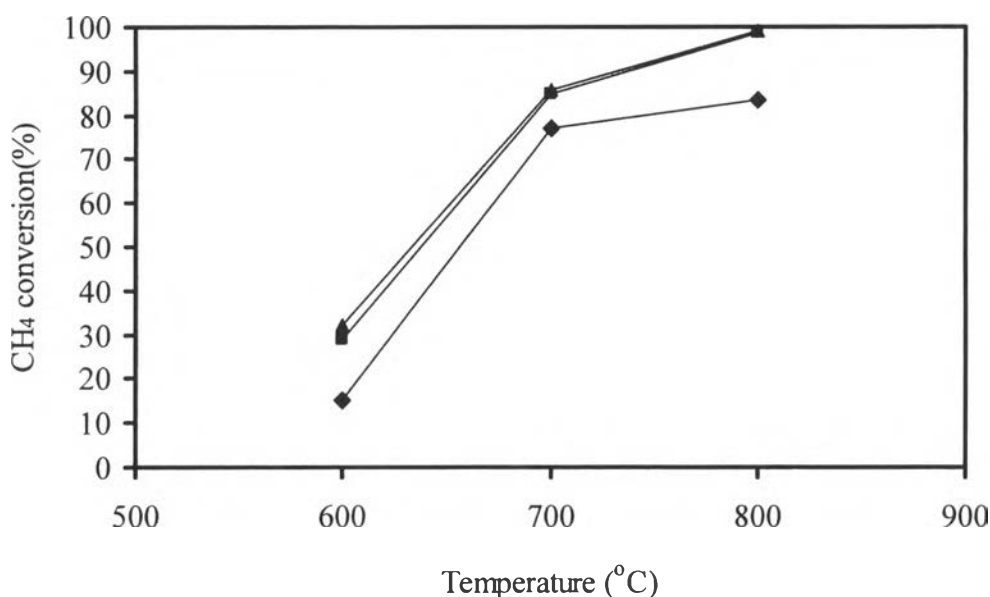


Figure 4.8 Methane conversion as a function of reaction temperatures over different nickel loadings on KL zeolite; %Ni loading: (♦) 3, (■) 7 and (▲) 15 at H_2O/CH_4 ratio of 3.

Light-off temperatures (T_{50}) of 670, 630 and 625°C were observed for 3, 7 and 15 %Ni loading over KL zeolite, respectively. 7 %Ni/KL zeolite gave almost the same light off temperature as 15%Ni/KL zeolite even increase the nickel content.

From these results, it can be suggested that loading with the Ni content of 7% is optimum content.

The KL zeolite catalysts with different Ni loadings (3, 5, 7, 10 and 15 wt%) were tested for the catalytic activity on steam reforming of methane at H_2O/CH_4 of 3 and reaction temperature of $700^\circ C$. The changes of methane conversion with time on stream over supported Ni catalysts with various Ni contents are presented in Figure 4.9.

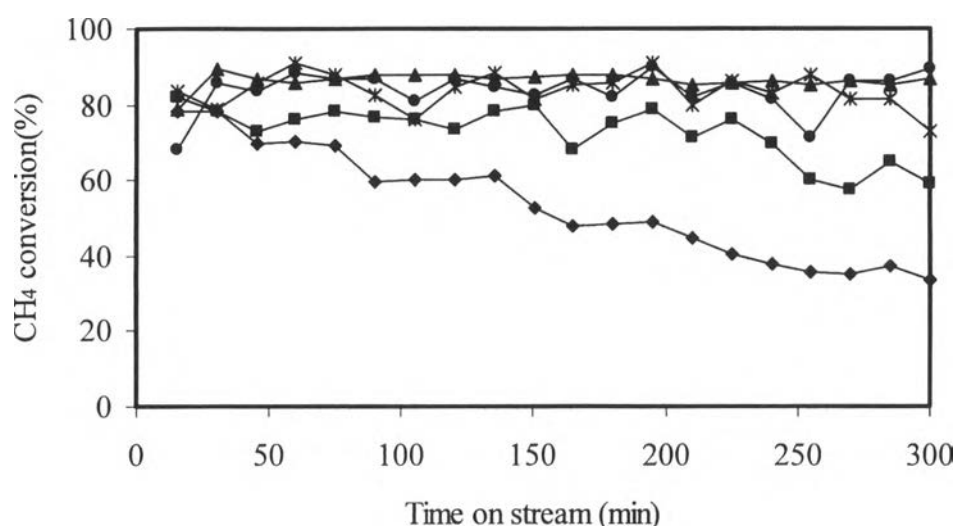


Figure 4.9 Methane conversion as a function of time on stream over different nickel loadings on KL zeolite; %Ni loadings : (♦) 3, (■) 5, (▲) 7, (●) 10 and (x) 15 at H_2O/CH_4 ratio of 3 and $700^\circ C$.

The result shows that for 3%Ni/KL zeolite catalyst shows rather high activity (78% methane conversion) at the initial stage, but the catalytic activity decreases gradually with increasing time. It shows 34% methane conversion after 300 min. And 5%Ni/KL zeolite catalyst also shows significantly deactivation because at the beginning, it exhibits 82% methane conversion but the activity decreases to 59% methane conversion after 300 min. At the beginning, the conversion of methane increases with increasing of Ni content from 3 to 7 wt% at the same reaction temperature but remains almost constant for nickel contents of higher than 7 wt%. The catalyst with Ni contents of 7, 10 and 15 wt% did not show

significant difference of methane conversion throughout time on steam although the Ni content was increased and did not also show significant deactivation within 300 min of reaction time.

Figure 4.10 shows the changes of hydrogen yield with time on stream. The trend is as same as the methane conversion due to hydrogen yield defined as a function of methane conversion and hydrogen selectivity. The changes of hydrogen selectivity with time on stream are shown in Figure 4.11. For 3%Ni/KL zeolite, hydrogen yield and hydrogen selectivity decreases with increasing time corresponding to methane conversion. 5%Ni/KL zeolite shows the decrease of hydrogen yield while hydrogen selectivity remains almost constant with time on stream, and the higher contents of Ni shows almost both constant hydrogen yield and hydrogen selectivity. The changes of carbon monoxide selectivity are presented in Figure 4.12. Within 5-15 wt% range of Ni content, selectivity of carbon monoxide is also constant within 300 min of reaction time except 3%Ni/KL zeolite catalyst in which it shows rather high carbon monoxide selectivity with increasing time. However, at 270-300 min time on stream, it shows slightly decrease in carbon monoxide selectivity due to an increase in hydrogen selectivity. In conclusion, 7% Ni catalyst, which is found to be an optimum Ni content gave 85% methane conversion, 65% hydrogen yield, 71% hydrogen selectivity and 19% carbon monoxide selectivity. This result is in good agreement with catalytic performance over Ni/ γ -Al₂O₃ (Zhang *et al.*, 2003) which had the optimum Ni content of more than 12wt%.

Therefore, the catalyst with 7wt% of nickel content was chosen for studying the effect of ceria as a catalyst promoter.

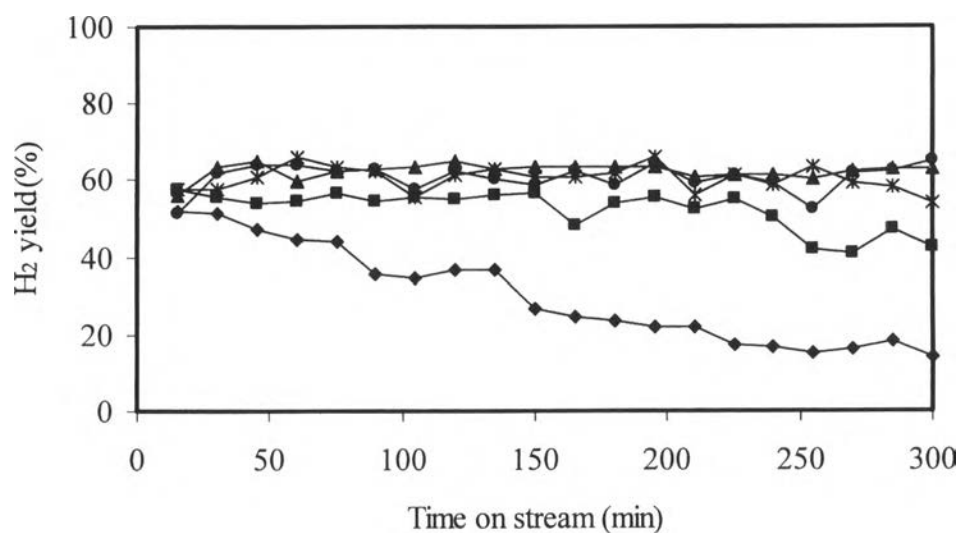


Figure 4.10 Hydrogen yield as a function of time on stream over different nickel loadings on KL zeolite; %Ni loadings : (♦) 3, (■) 5, (▲) 7, (●) 10 and (×) 15 at H₂O/CH₄ ratio of 3 and 700°C.

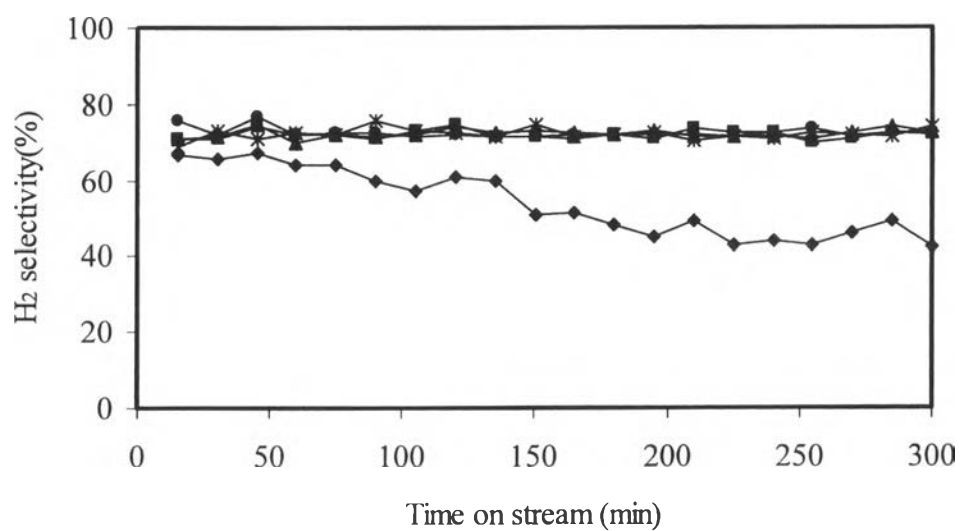


Figure 4.11 Hydrogen selectivity as a function of time on stream over different nickel loadings on KL zeolite; %Ni loadings : (♦) 3, (■) 5, (▲) 7, (●) 10 and (×) 15 at H₂O/CH₄ ratio of 3 and 700°C.

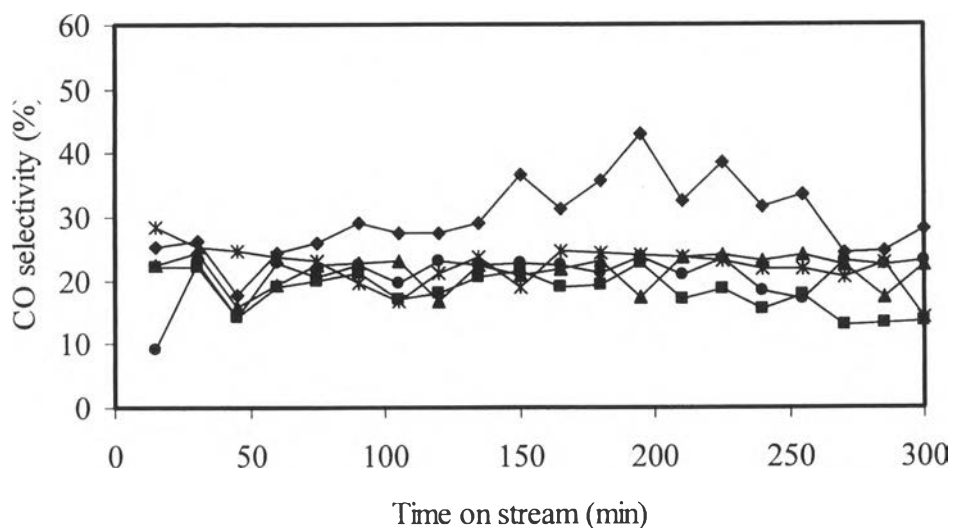


Figure 4.12 Carbon monoxide selectivity as a function of time on stream over different nickel loadings on KL zeolite; %Ni loadings : (♦) 3, (■) 5, (▲) 7, (●) 10 and (×) 15 at H₂O/CH₄ ratio of 3 and 700°C.

4.3 Effect of Ceria Content

The 7%Ni/KL zeolite catalysts promoted with different ceria contents (1, 3, 5 and 7 wt%) were tested for the catalytic activity on steam reforming of methane at H₂O/CH₄ of 3 and the reaction temperature of 700°C. The changes of methane conversion with time on stream over ceria promoted Ni/KL zeolite catalysts are presented in Figure 4.13.

Within 300 min of time on stream, all catalysts show almost constant methane conversion and do not show deactivation. In order to ease the evaluation of ceria effect, a typical dependence of average of methane conversion on ceria content is illustrated in Table 4.2.

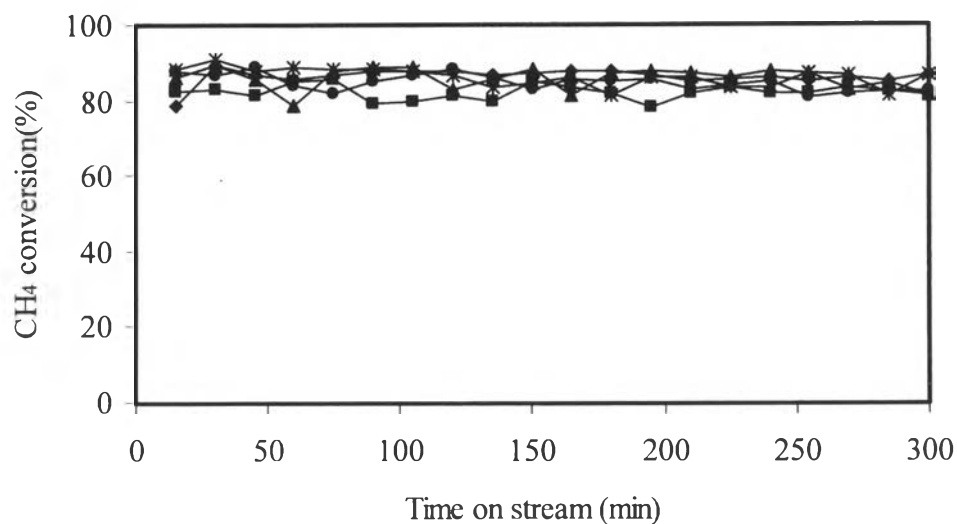


Figure 4.13 Methane conversion as a function of time on stream over ceria promoted Ni/KL zeolite catalysts; %ceria contents: (♦) 0, (■) 1, (▲) 3, (●) 5 and (×) 7 at H₂O/CH₄ ratio of 3 and 700°C.

Table 4.2 Effect of ceria content on catalytic activity

Number	Ceria (%)	CH ₄ conversion (%)	H ₂ yield (%)	H ₂ selectivity (%)	CO selectivity (%)
1	0	85.5	61.8	72.2	21.4
2	1	82.4	60.0	72.7	19.4
3	3	85.7	62.1	72.4	21.3
4	5	84.5	60.8	72.0	23.1
5	7	86.1	62.6	72.7	22.8

Reaction conditions: 700°C, 1 atm, H₂O:CH₄ = 3

From Table 4.2, methane conversion was hardly affected by an increase in ceria content. The results show that the ceria promoted Ni/KL zeolites did not exhibit significant difference on catalytic performance as compared to unpromoted Ni/KL zeolite catalyst within 300 min.

The changes of hydrogen yield with time on stream and average values are presented in Figure 4.14 and Table 4.2, respectively. The promoted catalysts do not display the effect on hydrogen yield, and the hydrogen yield of all catalysts remains constant within 300 min. The hydrogen yield is in the same trend as methane conversion.

Hydrogen and carbon monoxide selectivity with time on stream of all catalysts and their average values are shown in Figures 4.15 and 4.16, and Table 4.2, respectively. The promoted catalysts do not affect on hydrogen and carbon monoxide selectivity. From average values, it can be suggested that hydrogen selectivity and carbon monoxide depend on methane conversion.

Although the addition of ceria to 7%Ni/KL zeolite catalyst did not show significant difference in terms of catalytic activity, but it reduced carbon deposition on catalyst. The main purpose of addition of ceria to catalyst is, therefore, to reduce carbon deposition. In this part, it can be concluded that the addition of ceria to Ni/KL zeolite catalyst can greatly decrease the coke deposition of the Ni supported on KL zeolite catalyst. TPO results of ceria promoted catalysts are shown in Table 4.3.

Table 4.3 TPO results of ceria promoted 7Ni/KL zeolite catalyst after 5 hours of reaction

Number	Ceria content (%)	Coke deposition (%)
1	0	0.35
2	1	0.31
3	3	0.29
4	5	0.25
5	7	0.24

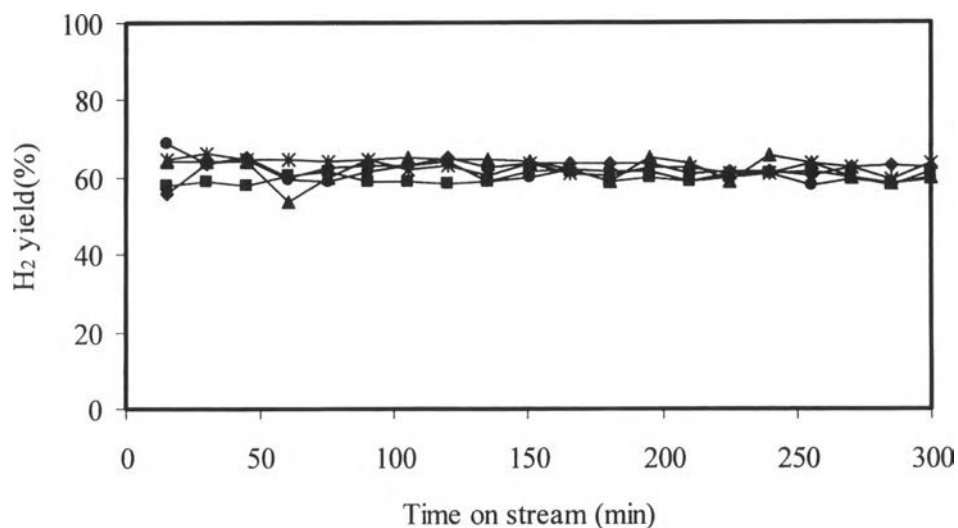


Figure 4.14 Hydrogen yield as a function of time on stream over ceria promoted Ni/KL zeolite catalysts; %ceria contents: (◆) 0, (■) 1, (▲) 3, (●) 5 and (×) 7 at H₂O/CH₄ ratio of 3 and 700°C.

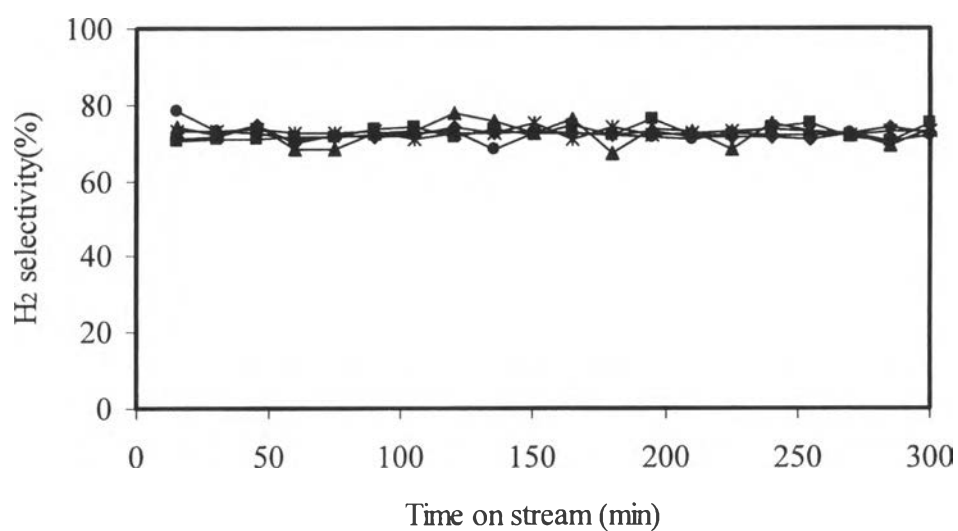


Figure 4.15 Hydrogen selectivity as a function of time on stream over ceria promoted Ni/KL zeolite catalysts; %ceria contents: (◆) 0, (■) 1, (▲) 3, (●) 5 and (×) 7 at H₂O/CH₄ ratio of 3 and 700°C.

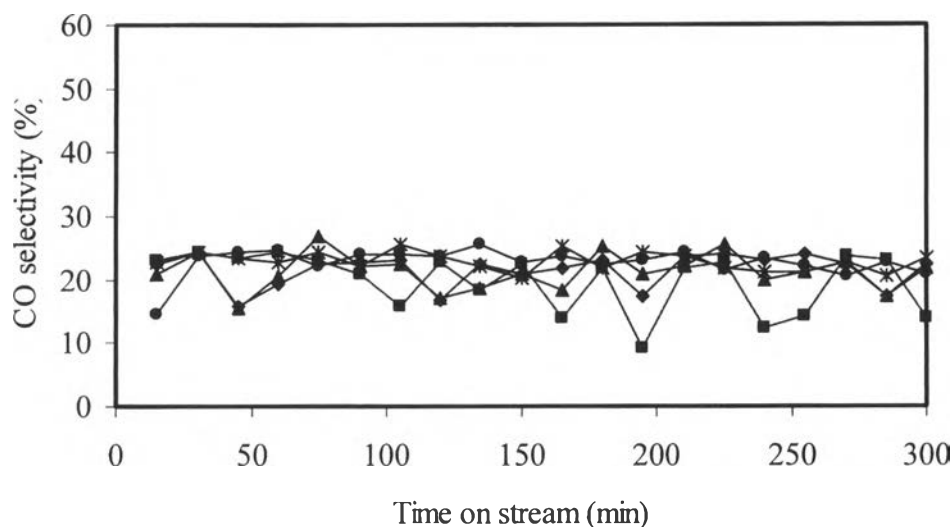


Figure 4.16 Carbon monoxide selectivity as a function of time on stream over ceria promoted Ni/KL zeolite catalysts; %ceria contents: (\blacklozenge) 0, (\blacksquare) 1, (\blacktriangle) 3, (\bullet) 5 and (\times) 7 at $\text{H}_2\text{O}/\text{CH}_4$ ratio of 3 and 700°C .

4.4 Effect of Steam to Methane Ratio

The effect of steam to methane ratios on methane conversion, hydrogen yield, hydrogen selectivity and carbon monoxide selectivity are discussed in this section. The 7%Ni/KL zeolite catalyst was tested for the catalytic activity on steam reforming of methane at 700°C and the $\text{H}_2\text{O}/\text{CH}_4$ ratios of 1, 2 and 3. The changes of methane conversion with time on stream are presented in Figure 4.17.

The results show at the beginning, methane conversion of 7%Ni/KL zeolite at different $\text{H}_2\text{O}/\text{CH}_4$ ratios are almost the same (89% conversion). After the time on stream of 300 min, methane conversion of 7%Ni/KL zeolite at $\text{H}_2\text{O}/\text{CH}_4$ ratio of 1 slightly decreases. It shows 84% methane conversion. On the other hand, methane conversion of 7%Ni/KL zeolite at $\text{H}_2\text{O}/\text{CH}_4$ ratios of 2 and 3 does not show significant decrease due to excess steam condition within 300 min.

Hydrogen yields with time on stream are shown in Figure 4.18. Hydrogen yield of 7%Ni/KL zeolite catalyst at different $\text{H}_2\text{O}/\text{CH}_4$ ratios are in the same trend as methane conversion.

Hydrogen and carbon monoxide selectivity with time on stream are shown in Figures 4.19 and 4.20, respectively. The results show that hydrogen and carbon monoxide selectivity at different H_2O/CH_4 ratios remain almost constant throughout time on stream. The average values of hydrogen selectivity at H_2O/CH_4 ratio (1, 2 and 3) are 72.14, 72.46 and 72.48%, respectively, and average values of carbon monoxide selectivity at H_2O/CH_4 ratio (1, 2 and 3) are 21.67, 21.45 and 21.41%, respectively. It can be seen that with the increase of H_2O/CH_4 ratio, hydrogen selectivity tends to increase while carbon monoxide selectivity tend to decrease due to the water gas shift reaction (WGSR) occurring at excess steam condition. In this part, it can be concluded that KL zeolite still gave good catalytic activity even operated at different steam to methane ratios.

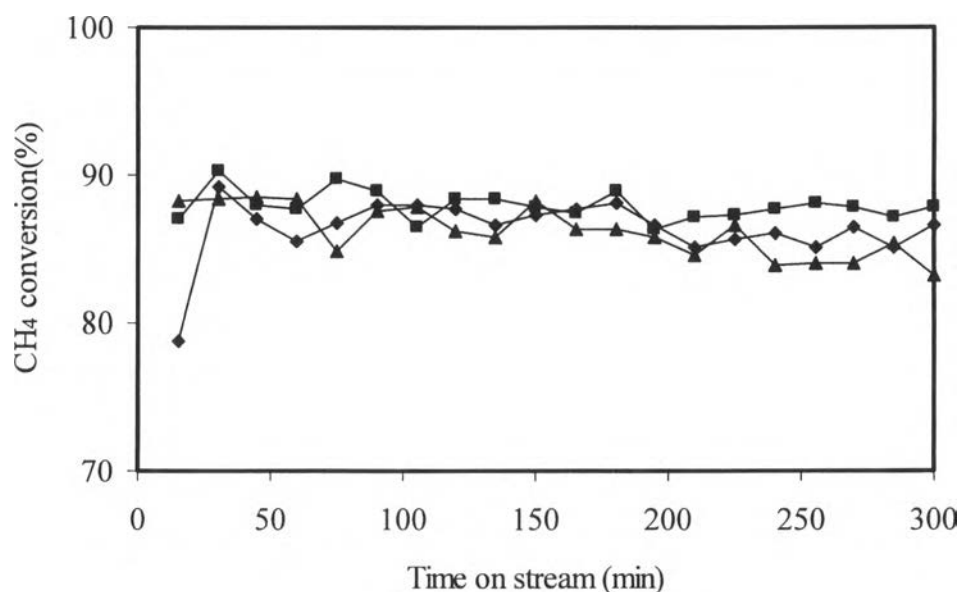


Figure 4.17 Methane conversion as a function of time on stream over 7%Ni/KL zeolite catalysts at 700°C and H_2O/CH_4 ratio of (▲) 1, (■) 2 and (◆) 3.

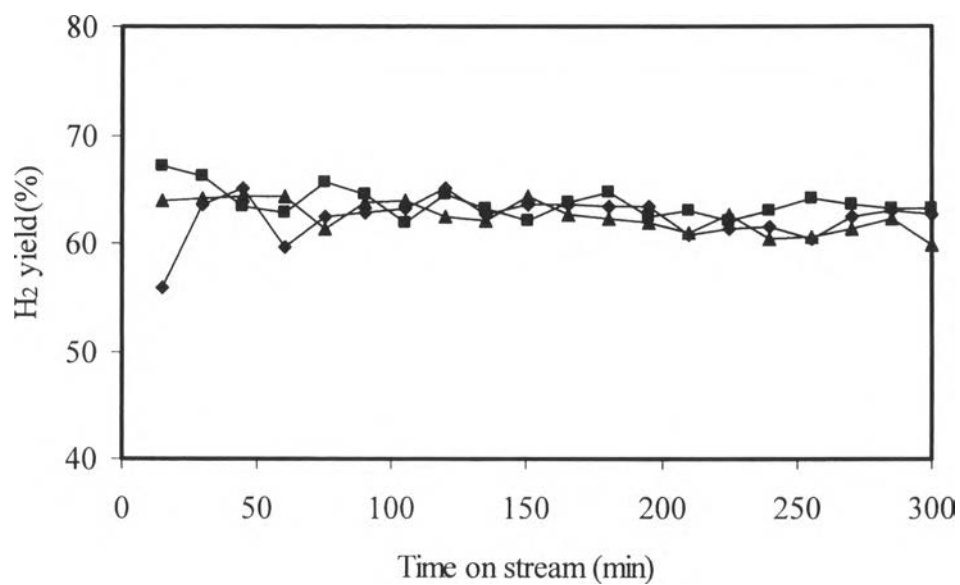


Figure 4.18 Hydrogen yield as a function of time on stream over 7%Ni/KL zeolite catalysts at 700°C and H₂O/CH₄ ratio of (▲) 1, (■) 2 and (◆) 3.

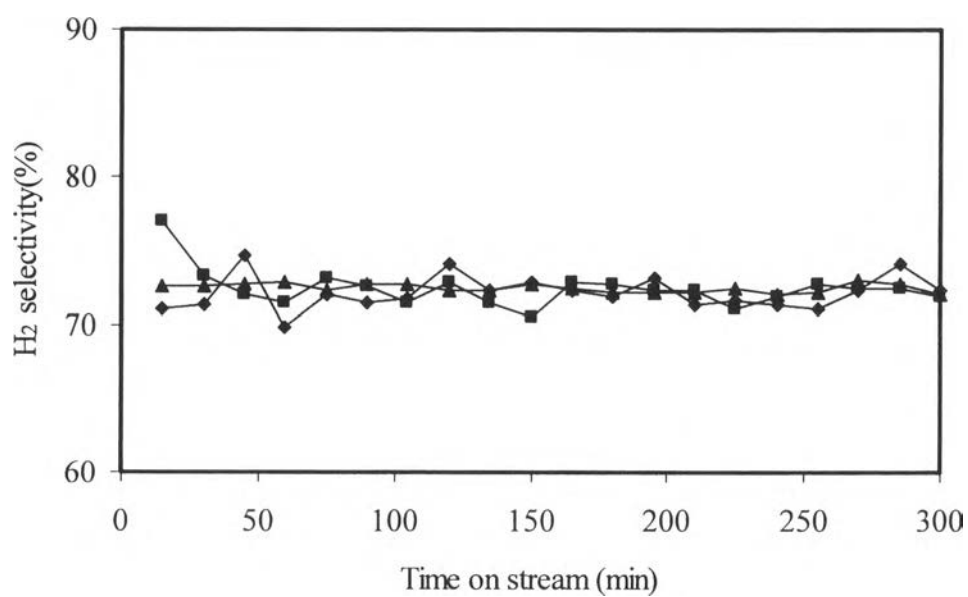


Figure 4.19 Hydrogen selectivity as a function of time on stream over 7%Ni/KL zeolite catalysts at 700°C and H₂O/CH₄ ratio of (▲) 1, (■) 2 and (◆) 3.

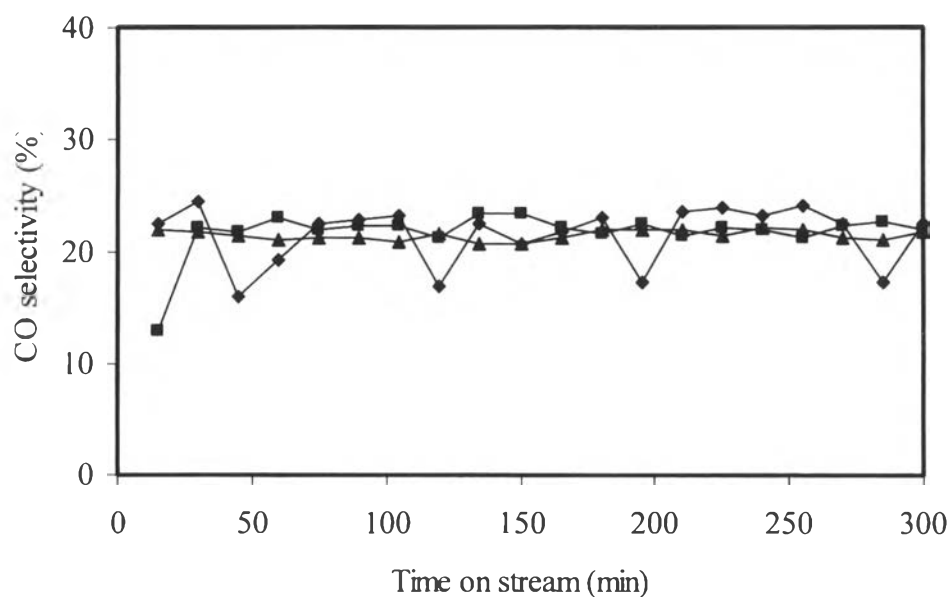


Figure 4.20 Carbon monoxide selectivity as a function of time on stream over 7%Ni/KL zeolite catalysts at 700°C and H₂O/CH₄ ratio of (▲) 1, (■) 2 and (◆) 3.

4.5 Comparison between KL Zeolite and Commercial Catalyst

In this section, α -alumina is defined as commercial catalyst support (Lee, 1997), the 7%Ni/KL zeolite and 7%Ni/ α -alumina catalysts were tested for comparison of catalytic activity on steam reforming of methane at 700°C with H₂O/CH₄ ratio of 1 and 3

4.5.1 At H₂O:CH₄ = 3:1

The changes of methane conversion with time on stream of 7%Ni/KL zeolite and 7%Ni/ α -alumina are shown in Figure 4.21. The results show that methane conversion of 7%Ni/ α -alumina is higher than 7%Ni/KL zeolite. Both catalysts showed no deactivation throughout 300 min of time on stream.

Hydrogen yield with time on stream is in the same trend as methane conversion and shown in Figure 4.22.

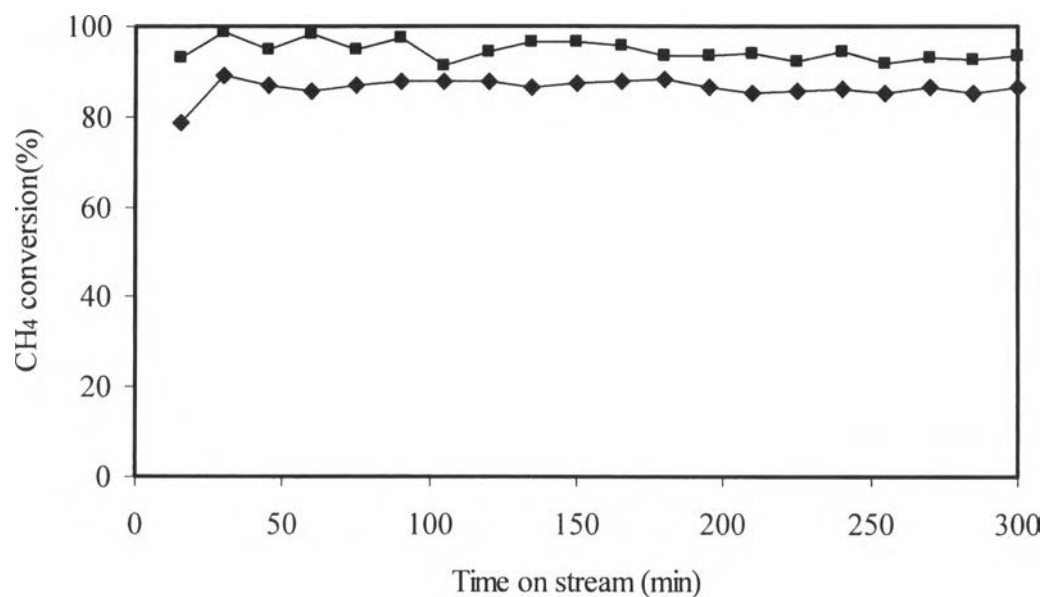


Figure 4.21 Methane conversion as a function of time on stream over 7%Ni/KL zeolite catalyst (\blacklozenge) and 7%Ni/ α -alumina catalyst (\blacksquare) at 700°C and H₂O/CH₄ ratio of 3.

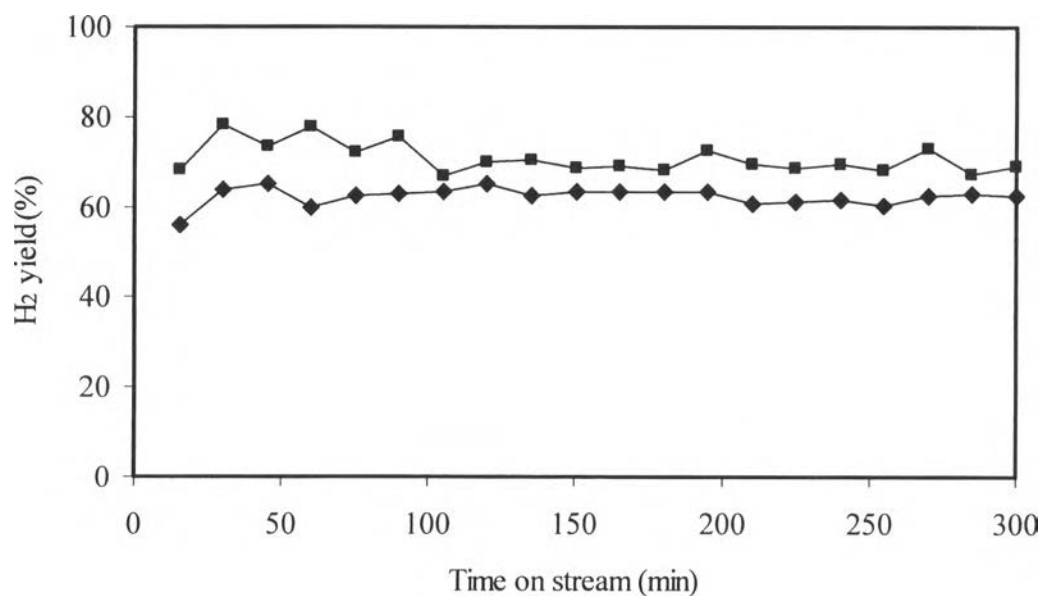


Figure 4.22 Hydrogen yield as a function of time on stream over 7%Ni/KL zeolite catalyst (\blacklozenge) and 7%Ni/ α -alumina catalyst (\blacksquare) at 700°C and H₂O/CH₄ ratio of 3.

The changes of hydrogen and carbon monoxide selectivity with time on stream are shown in Figures 4.23 and 4.24, respectively. The average value of hydrogen selectivity for 7%Ni/ α -alumina and 7%Ni/KL zeolite are 72.48 and 74.87%, respectively, and the average value of carbon monoxide selectivity for 7%Ni/ α -alumina and 7%Ni/KL zeolite are 18.02 and 21.41%, respectively. The results show that hydrogen selectivity of 7%Ni/ α -alumina was slightly higher than 7%Ni/KL zeolite while carbon monoxide selectivity of 7%Ni/ α -alumina was slightly lower than 7%Ni/KL zeolite. It can be suggested that 7%Ni/ α -alumina catalyst promoted more water gas shift reaction (WGSR) than 7%Ni/KL zeolite catalyst.

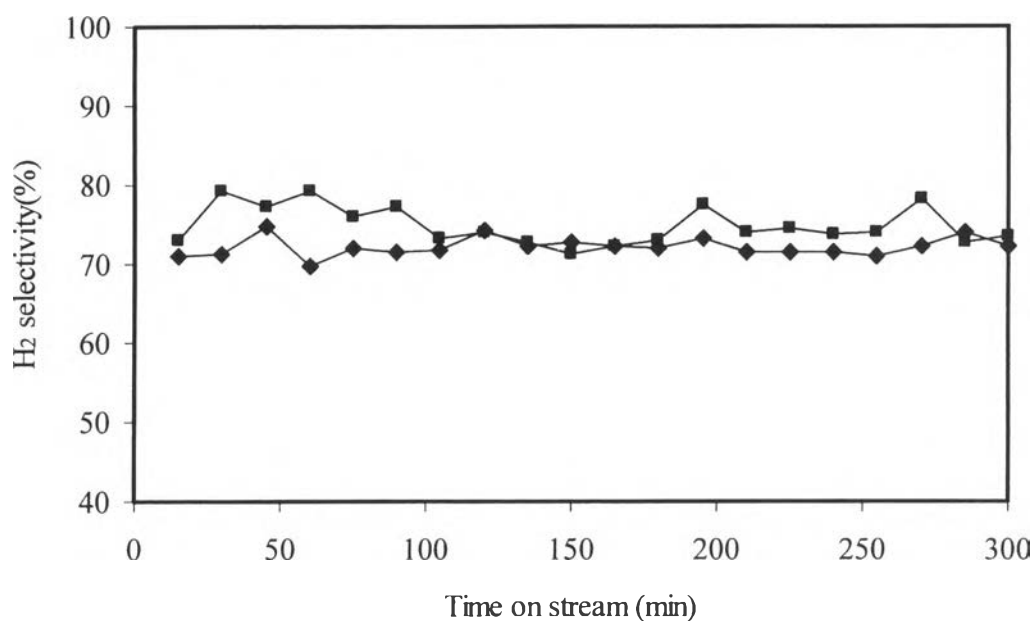


Figure 4.23 Hydrogen selectivity as a function of time on stream over 7%Ni/KL zeolite catalyst (\blacklozenge) and 7%Ni/ α -alumina catalyst (\blacksquare) at 700°C and H₂O/CH₄ ratio of 3.

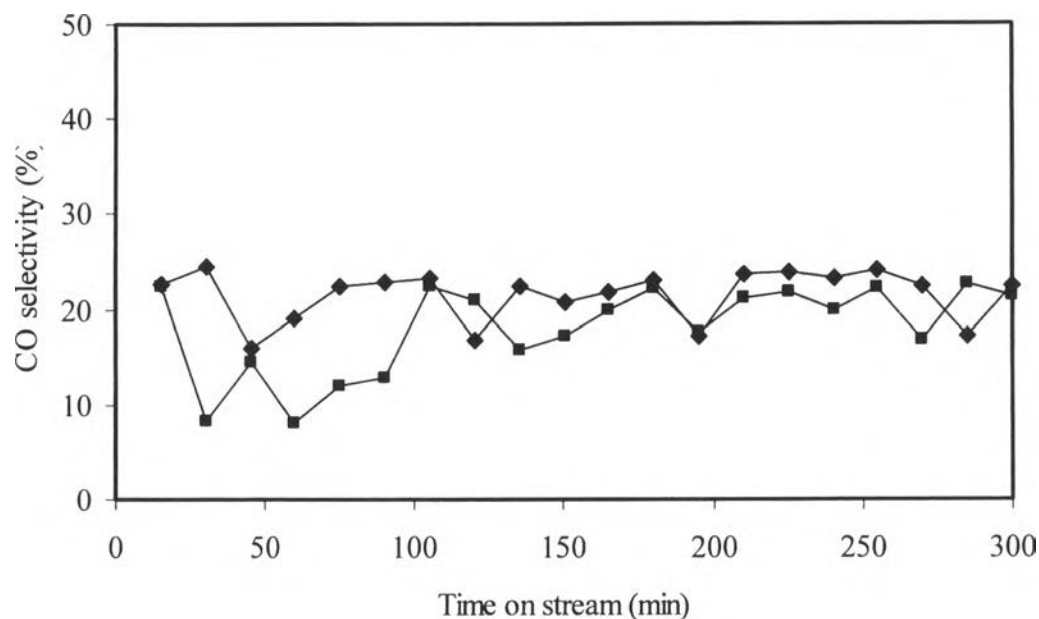


Figure 4.24 Carbon monoxide selectivity as a function of time on stream over 7%Ni/KL zeolite catalyst (♦) and 7%Ni/α-alumina catalyst (■) at 700°C and H₂O/CH₄ ratio of 3.

4.5.2 At H₂O:CH₄ = 1:1

The changes of methane conversion with time on stream of 7%Ni/KL zeolite and 7%Ni/α-alumina are shown in Figure 4.25. The results show that methane conversion of 7%Ni/KL zeolite is slightly higher than 7%Ni/α-alumina. Both catalysts show methane conversion decreasing gradually with increasing of time due to carbon formation during steam reforming of methane.

Hydrogen yield with time on stream is in the same trend as methane conversion and shown in Figure 4.26.

Hydrogen and carbon monoxide selectivity with time on stream are shown in Figures 4.27 and 4.28. The results show that hydrogen and carbon monoxide selectivity of both 7%Ni/KL zeolite and 7%Ni/α-alumina remain almost constant at this condition. The average value of hydrogen selectivity for 7%Ni/α-alumina and 7%Ni/KL zeolite are 72.18 and 72.48%, respectively, and the average value of carbon monoxide selectivity for

7%Ni/ α -alumina and 7%Ni/KL zeolite are 20.88 and 21.41%, respectively. 7%Ni/KL zeolite gives hydrogen and carbon monoxide selectivity slightly higher than 7%Ni/ α -alumina with methane conversion of 7%Ni/KL zeolite slightly higher than 7%Ni/ α -alumina.

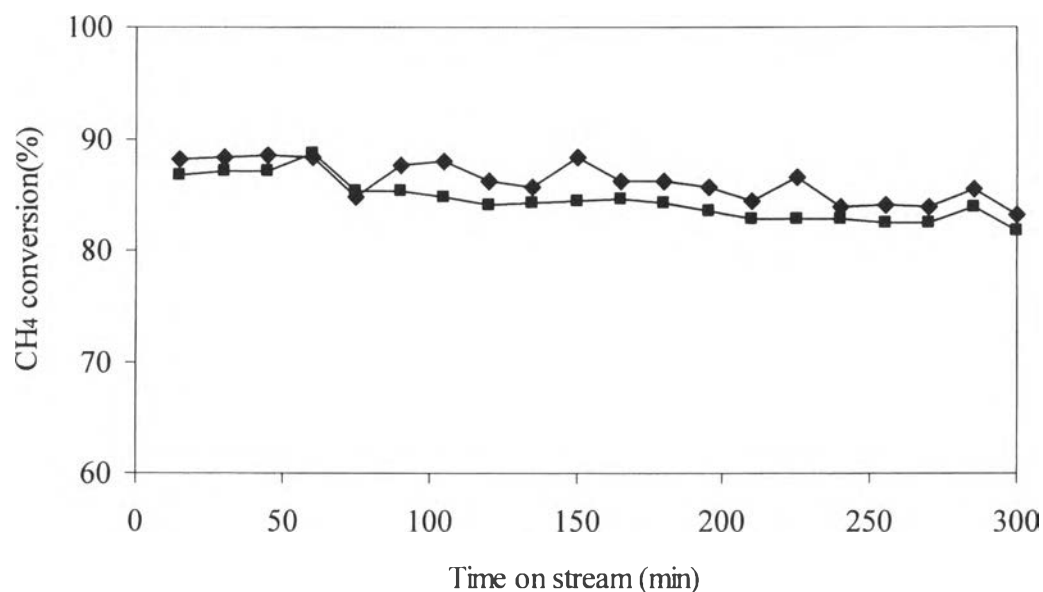


Figure 4.25 Methane conversion as a function of time on stream over 7%Ni/KL zeolite catalyst (\blacklozenge) and 7%Ni/ α -alumina catalyst (\blacksquare) at 700°C and H₂O/CH₄ ratio of 1.

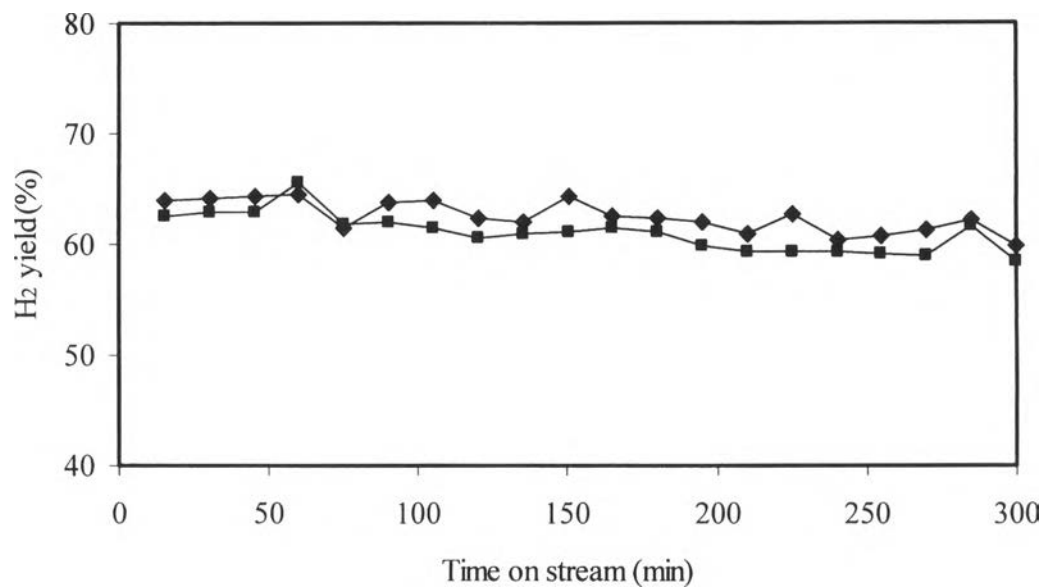


Figure 4.26 Hydrogen yield as a function of time on stream over 7%Ni/KL zeolite catalyst (♦) and 7%Ni/α-alumina catalyst (■) at 700°C and H₂O/CH₄ ratio of 1.

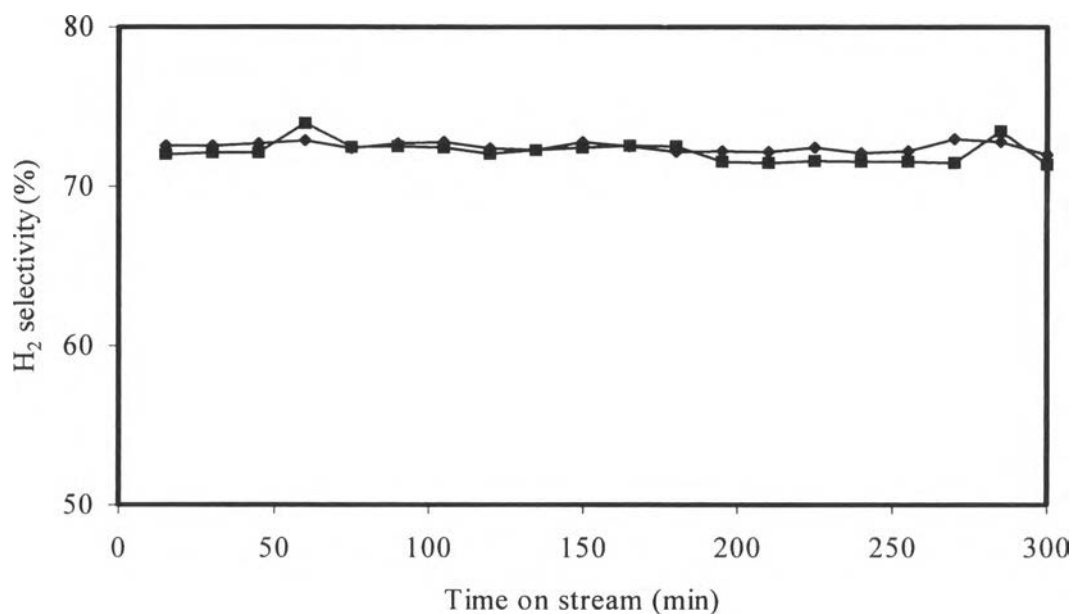


Figure 4.27 Hydrogen selectivity as a function of time on stream over 7%Ni/KL zeolite catalyst (♦) and 7%Ni/α-alumina catalyst (■) at 700°C and H₂O/CH₄ ratio of 1.

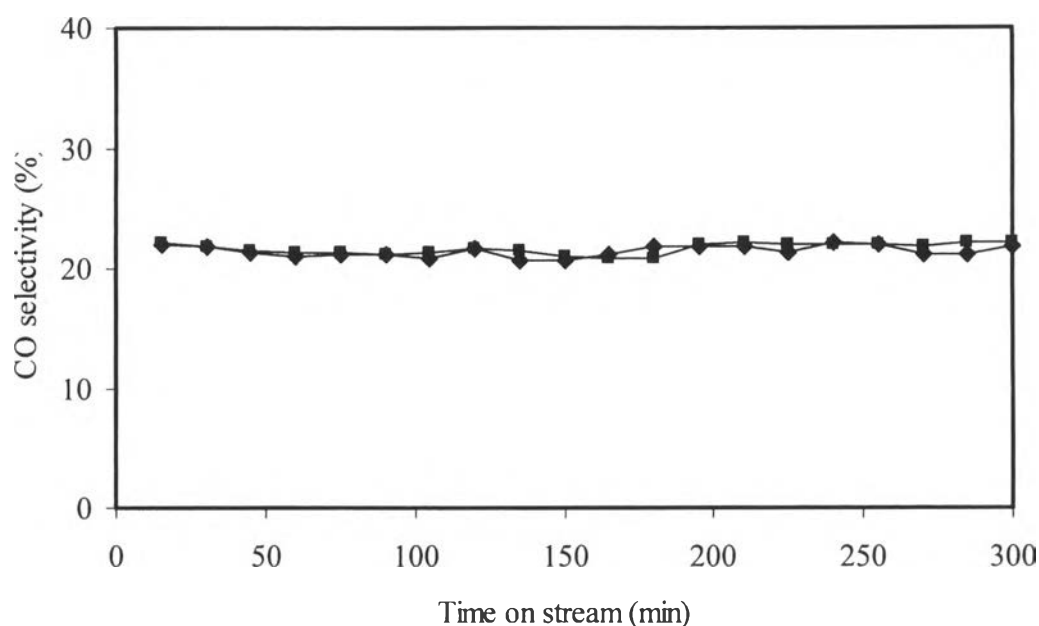


Figure 4.28 Carbon monoxide selectivity as a function of time on stream over 7%Ni/KL zeolite catalyst (♦) and 7%Ni/α-alumina catalyst (■) at 700°C and H₂O/CH₄ ratio of 1.

4.6 Stability Test

7%Ni/KL zeolite, 7%Ni/α-alumina and 7%Ni-3%Ce/KL zeolite were selected to study for the stability at the H₂O/CH₄ of 3 and 700°C with time on stream of 48 hours. The changes of methane conversion with time on stream of all catalysts are shown in Figure 4.29. The results show that 7%Ni/KL zeolite gives constant methane conversion at the beginning and until 800 min the methane conversion dramatically decreases and reaches around 30% at 48 hours of time on stream suggesting a certain instability of 7%Ni/KL zeolite catalyst in this reaction. This result is in agreement with our XRD result. From XRD patterns of 7%Ni/KL catalyst (Figure 4.4), the characteristic peaks of metallic Ni were observed in the spent catalyst. This incident is probably caused by sintering of the catalyst during the reaction. 7%Ni/α-alumina also gives constant methane conversion at the beginning and until 960 min the

methane conversion dramatically decreases and reaches around 67% at 48 hours of time on stream. The conversion of 7%Ni-3%Ce/KL zeolite remains almost unchanged throughout 48 hours of time on stream. In conclusion, KL zeolite and α -alumina catalysts show the significant deactivation with increasing time while the ceria promoted KL zeolite catalyst gives high stability because ceria probably enhanced the carbon formation resistant of catalyst. The results show the same trend as methane conversion. The SEM results reported by Xu *et al.* (1999) indicated that the addition of rare earth oxides (CeO_2 or La_2O_3) cause the particles of catalyst to become smaller than the unpromoted $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst. It has been reported the addition of rare earth oxide on the $\text{Ni}/\text{Al}_2\text{O}_3$ might lead to a mono-layer dispersion of rare earth oxide which can significantly improve Ni dispersion and increase the activity and thermal stability of the catalyst. The changes of hydrogen yield with time on stream of all catalysts are shown in Figure 4.31.

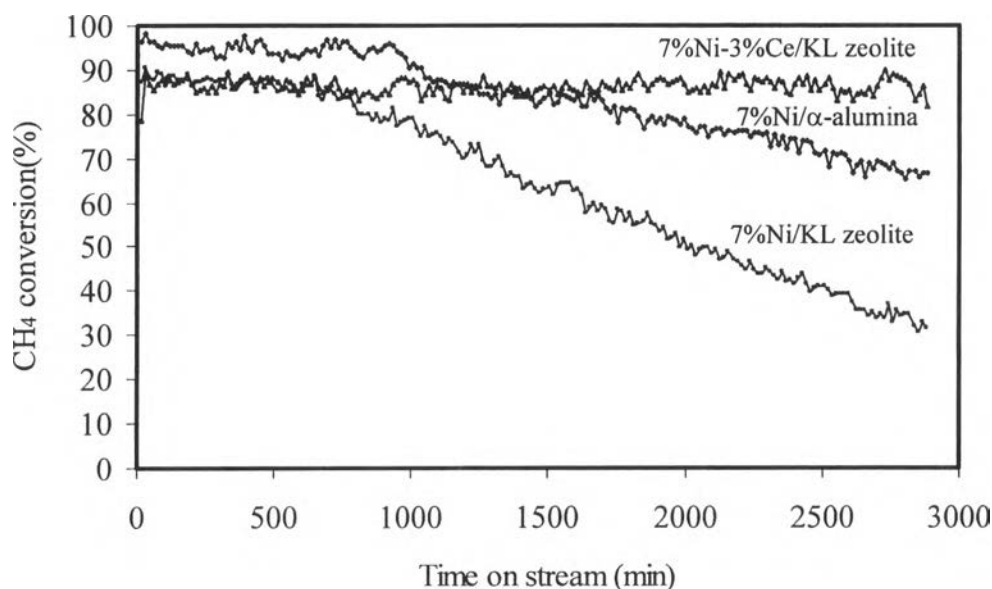


Figure 4.29 Methane conversion as a function of time on stream at $\text{H}_2\text{O}/\text{CH}_4$ ratio of 3 and 700°C .

The changes of hydrogen selectivity with time on stream of all catalysts are shown in Figure 4.30. The results show that 7%Ni/KL zeolite gives constant hydrogen selectivity at the beginning and until 900 min the hydrogen selectivity dramatically decreases. 7%Ni/ α -alumina also gives constant hydrogen selectivity (around 75%) at the beginning and slightly decreases (around 71%) at 48 hours of time on stream. The hydrogen selectivity of 7%Ni-3%Ce/KL zeolite remains almost unchanged throughout 48 hours of time on stream.

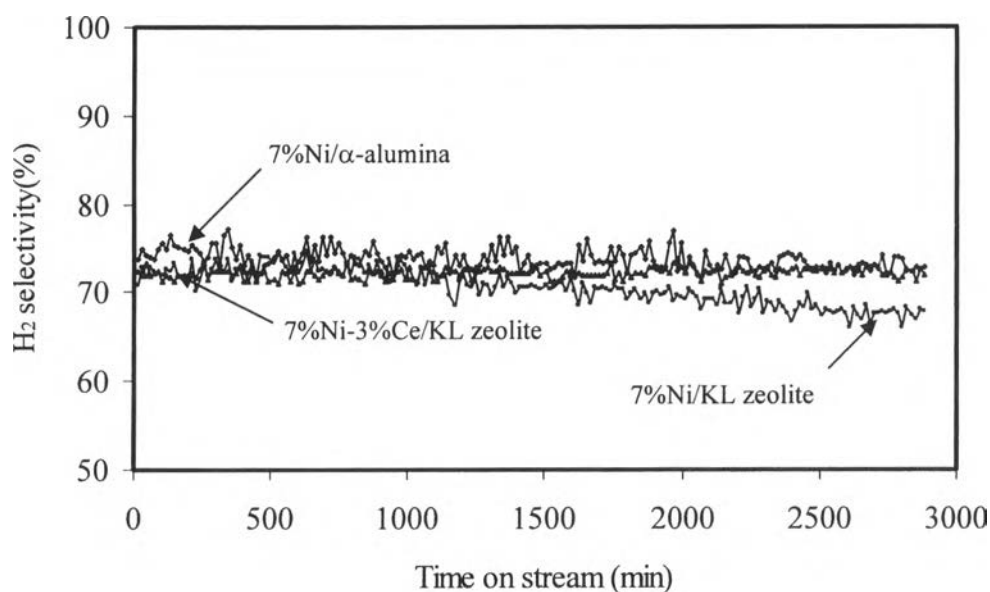


Figure 4.30 Hydrogen selectivity as a function of time on stream at H₂O/CH₄ ratio of 3 and 700°C.

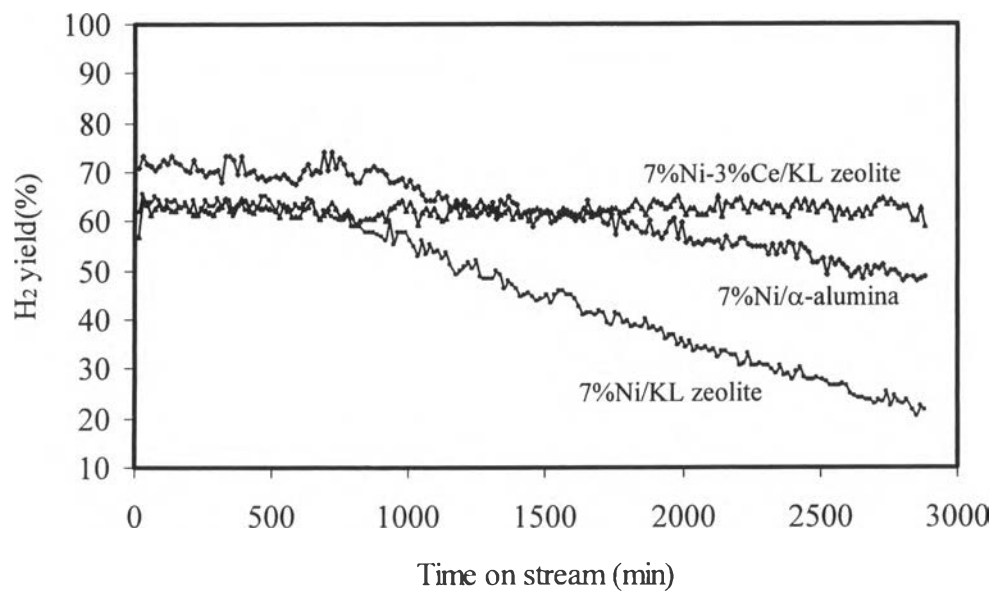


Figure 4.31 Hydrogen yield as a function of time on stream at H₂O/CH₄ ratio of 3 and 700°C.