

## CHAPTER IV RESULTS AND DISCUSSION



### 4.1 Catalyst Characterization

#### 4.1.1 H<sub>2</sub> Pulse Chemisorption

The catalysts with various amounts of Ni loading and the modified catalysts were characterized by using H<sub>2</sub> pulse chemisorption. The H<sub>2</sub> pulse chemisorption was used to estimate the Ni dispersion of the catalysts. Prior the pulse chemisorption, the catalysts were reduced at 600°C for 1 hour with H<sub>2</sub>. Then, the system was purged and cooled to 50°C by N<sub>2</sub> flow, which was the chemisorption temperature. The results are shown in Table 4.1.

**Table 4.1** Ni dispersion of the catalysts with various amounts of Ni loading

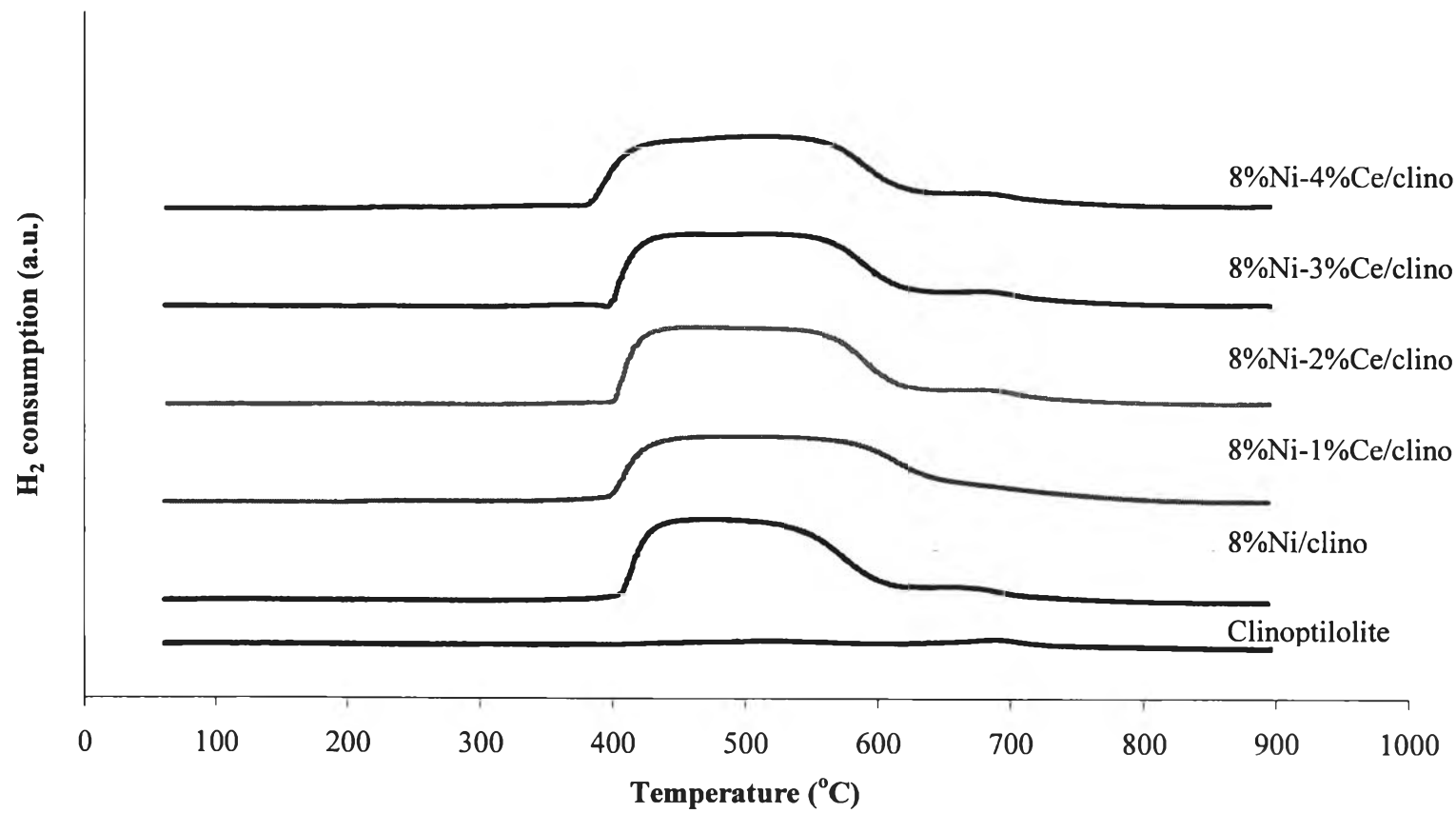
Catalysts	Dispersion (%)
5%Ni/clino	1.95
8%Ni/clino	1.02
10%Ni/clino	0.30
8%Ni-2%Ce/clino	2.15
8%Ni-2%Zr/clino	0.96
8%Ni-5%Zr/clino	0.17

It is found that the Ni dispersion tends to decrease with the amount of Ni loading after reduced at 600°C for 1 hour. This can be concluded that higher amount of Ni loading resulted in higher metal sintering. For Ce-promoted catalysts, it is found that the Ni dispersion is about two times higher than the unpromoted catalyst. It has been reported that CeO<sub>2</sub> can enhance the Ni dispersion of Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts and resulting in small Ni particle size (Wang and Lu, 1998c). The promotion

effect can be attributed to the redox and high dispersive properties of  $\text{CeO}_2$ , which can create oxygen vacancies and form M-O surface complexes. For Zr-promoted catalysts, the results show that the Ni dispersion tends to decrease with increasing amount of Zr. Therefore, it can be deduced that the Ni particle size on the catalysts with higher amount of Zr are larger than on the catalysts with lower amount of Zr.

#### 4.1.2 Temperature Programmed Reduction

The Temperature Programmed Reduction (TPR) was performed to study reduction temperature of the NiO on the catalysts. The TPR profiles of the modified catalysts are shown in Figures 4.1-4.2. In Figure 4.1, the profile of unpromoted catalyst shows a reduction peak between 408 and 600°C and small shoulder at 680°C. The small shoulder is defined as the reduction temperature of pure clinoptilolite. The area under the peak is assigned to the  $\text{H}_2$  consumption for reducing NiO to metallic Ni, which is the active site for carbon dioxide reforming of methane reaction (Wang and Lu, 1998b). The wideness of the peaks is believed to be due to the different interaction of NiO and the support. The lower reduction temperature is attributed to the small interaction of NiO and support, which is attributed to the reduction of large NiO particles. While the higher reduction temperature is attributed to the small NiO, which have stronger interaction of support and NiO (Montoya *et al.*, 2000). For the catalyst modified by 1wt%Ce, the reduction peak is slightly shifted to lower temperature, and the area under the peak is higher than the unpromoted catalyst. This can be deduced that  $\text{CeO}_2$  can enhance the reducibility of the NiO on the catalyst. However, the reduction peak is occurred between 400 and 650°C, which is broader than the unpromoted one. This can be assumed that the higher reduction temperature is the result of NiO- $\text{CeO}_2$  interaction. This might be due to the results of partial coverage of NiO by  $\text{CeO}_x$  and form strong metal-support interaction, which makes the NiO becomes hard to reduce. Moreover, partial coverage of NiO by  $\text{CeO}_x$  can prevent the metal sintering to form large metal ensembles resulting in the decreasing of the active surface area and therefore, help maintaining the Ni dispersion.



**Figure 4.1** TPR profiles of the catalysts with various amounts of Ce.

The TPR profiles of Zr-promoted catalysts are shown in Figure 4.2. The reduction temperature of 8%Ni-1%Zr/clino and 8%Ni-2%Zr/clino are broader and shift to higher temperature as compared to the unpromoted catalyst, which might be the results of broader particle size distribution of the catalysts (Montoya *et al.*, 2000). The higher reduction temperature, the stronger Ni-support interaction occurs. But when increasing amount of Zr more than 2wt%, the reduction peaks shift to lower than 400°C which is less than the unpromoted catalyst. The two peaks observed on the promoted catalysts are assigned to the different interaction between support and NiO. The peak at lower temperature is defined as large NiO particle which has a lower interaction with the support while the peak at higher temperature is the NiO with high interaction with the support. It is found that the peak at lower temperature and the H<sub>2</sub> uptake of the promoted catalysts tend to increase with the amount of Zr. Therefore, it can be concluded that ZrO<sub>2</sub> can enhance the reducibility of NiO.

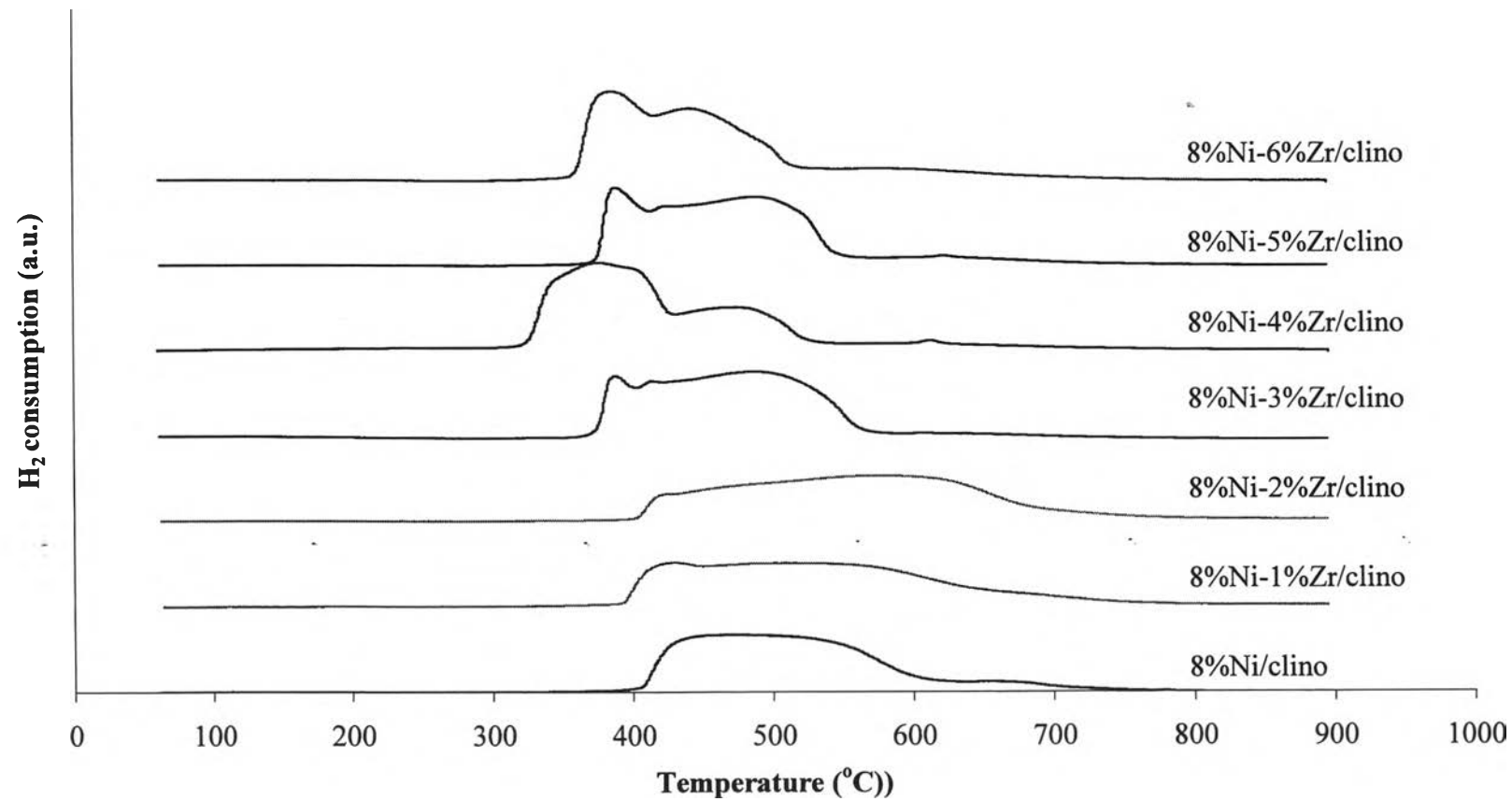
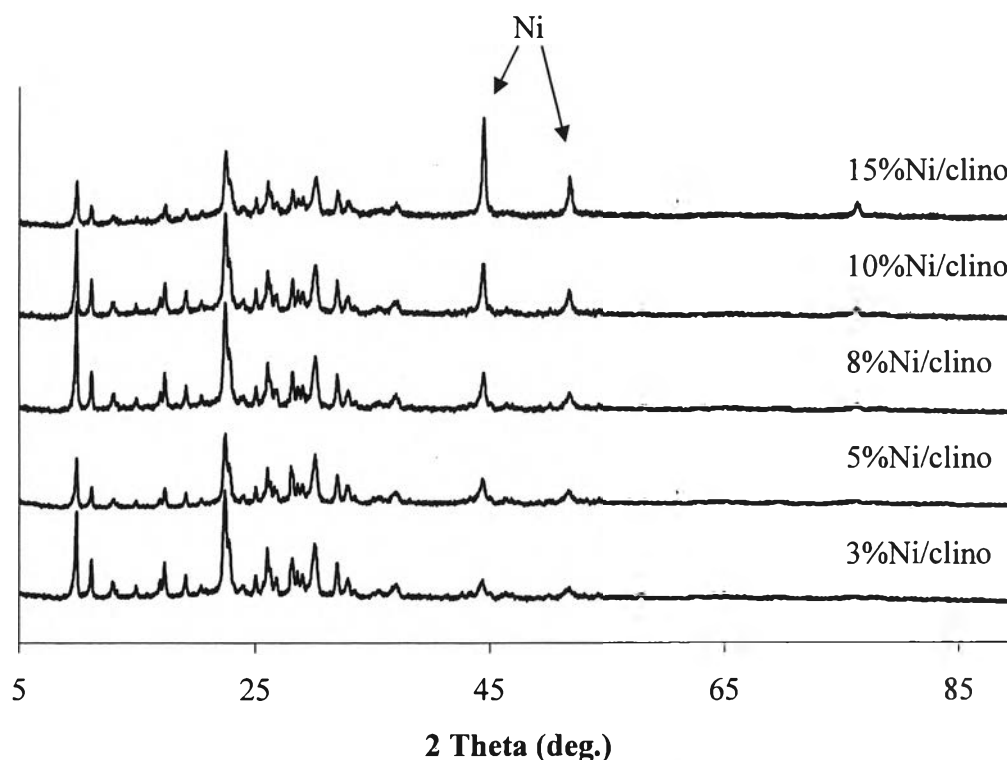


Figure 4.2 TPR profiles of the catalysts with various amounts of Zr.

#### 4.1.3 X-Ray Diffraction

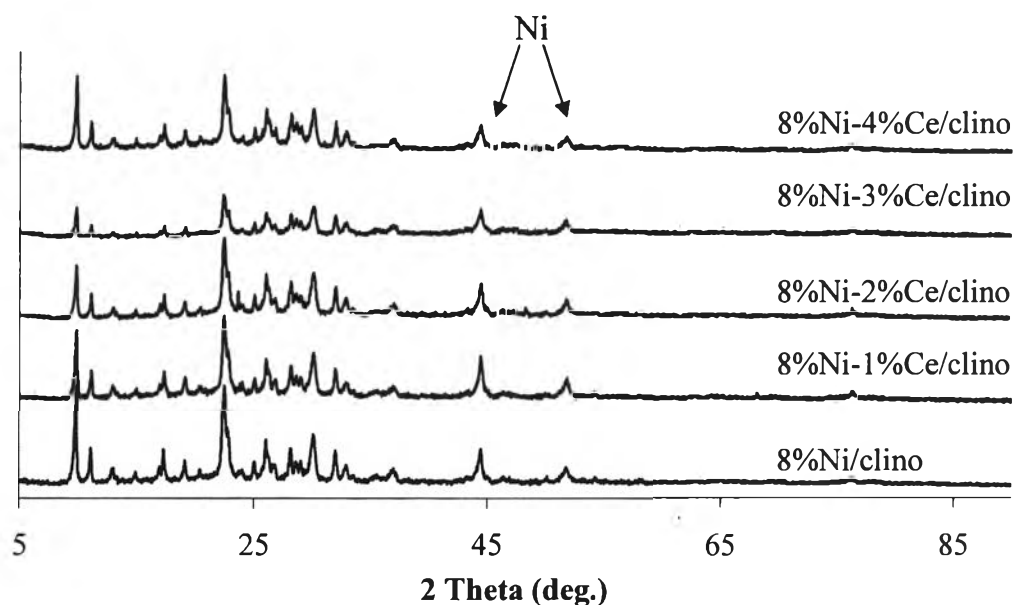
The XRD patterns of spent catalysts are illustrated in Figures 4.3 to 4.5. For the catalysts with various amounts of Ni loading, it is found that the metallic Ni peaks ( $2\theta = 44.5^\circ$  and  $52^\circ$ ) of lower metal loading catalysts are weaker and broader than the catalysts with higher metal loading. This can be suggested that the Ni crystallite size on lower Ni loading catalysts is smaller than on the catalysts with high Ni content. Larger Ni crystallite size resulting in lower Ni dispersion, which is in good agreement with the results of  $H_2$  pulse chemisorption.



**Figure 4.3** XRD patterns of the catalysts with different Ni loading after 5 hours of reaction.

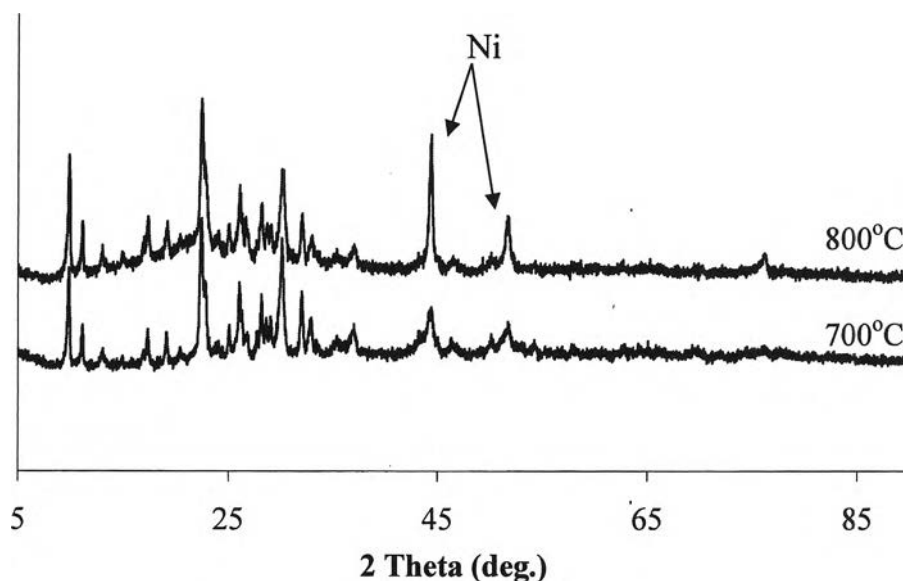
XRD patterns of Ce-promoted catalysts after 5 hours of reaction are shown in Figure 4.4. It is found that the metallic Ni peaks of spent catalysts tends to decrease and broader with increasing amount of Ce added. This can be deduced that the catalysts with higher Ce loading have higher Ni dispersion than the catalysts with lower Ce loading. Therefore, it is clearly seen that the promotion effect of Ce to the

Ni dispersion is one of the reasons that explain the improvement of the catalytic activity.



**Figure 4.4** XRD patterns of the Ce-promoted catalysts after 5 h of reaction.

In order to study the effect of reaction temperature, XRD was employed to study the crystalline phase of 8%Ni-2%Zr/clino after being used at different temperatures. The results are shown in Figure 4.5. It is found that the metallic Ni peaks of spent catalyst tend to increase when the reaction temperature is higher. This result indicates that the higher reaction temperature, the larger Ni particle size of the catalyst was observed. Therefore, it can be concluded that high temperature of reaction can promote the Ni sintering of metallic particle. Ni sintering during the reaction can cause decreasing in the metal surface exposed to the reaction and lowering metal-support interfacial area. Therefore, it makes the ability to clean carbon on metal surface decrease and results in the deactivation of the catalysts.



**Figure 4.5** XRD patterns of 8%Ni-2%Zr/clino after used at 700 and 800°C.

#### 4.1.4 Temperature Programmed Oxidation

Temperature programmed oxidation (TPO) was performed to study the oxidizing temperature of the carbon deposit on the catalysts. TPO profiles of the carbon deposition on the Ni/clino, and Ce promoted catalysts after 5 hours of reaction are shown in Figure 4.6. As can be seen, carbon is oxidized between 300 and 780°C. The 8%Ni/clino shows the peak at 645°C followed by a hump at 690°C. For Ce-promoted catalyst, the TPO profiles show that the oxidizing temperature is centered at about the same temperature. However, it is found that when increasing the amount of Ce, the area under the profiles tend to increase. This can be suggested that the higher Ce content, the higher amount of carbon is deposited. It is noted that all of the profiles are not symmetric which might be due to more than one type of carbon occurred or carbon deposits at different locations. Wang and Lu (1998) studied carbon deposition on various supports, and they found that there were two types of carbon formed on the catalysts surface; graphitic carbon and amorphous carbon. The oxidation peaks of graphitic carbon were presented between 550 and 620°C. The amorphous carbon were oxidized between 650°C and 750°C. Moreover, there were many researchers having explained the relationship between the oxidation

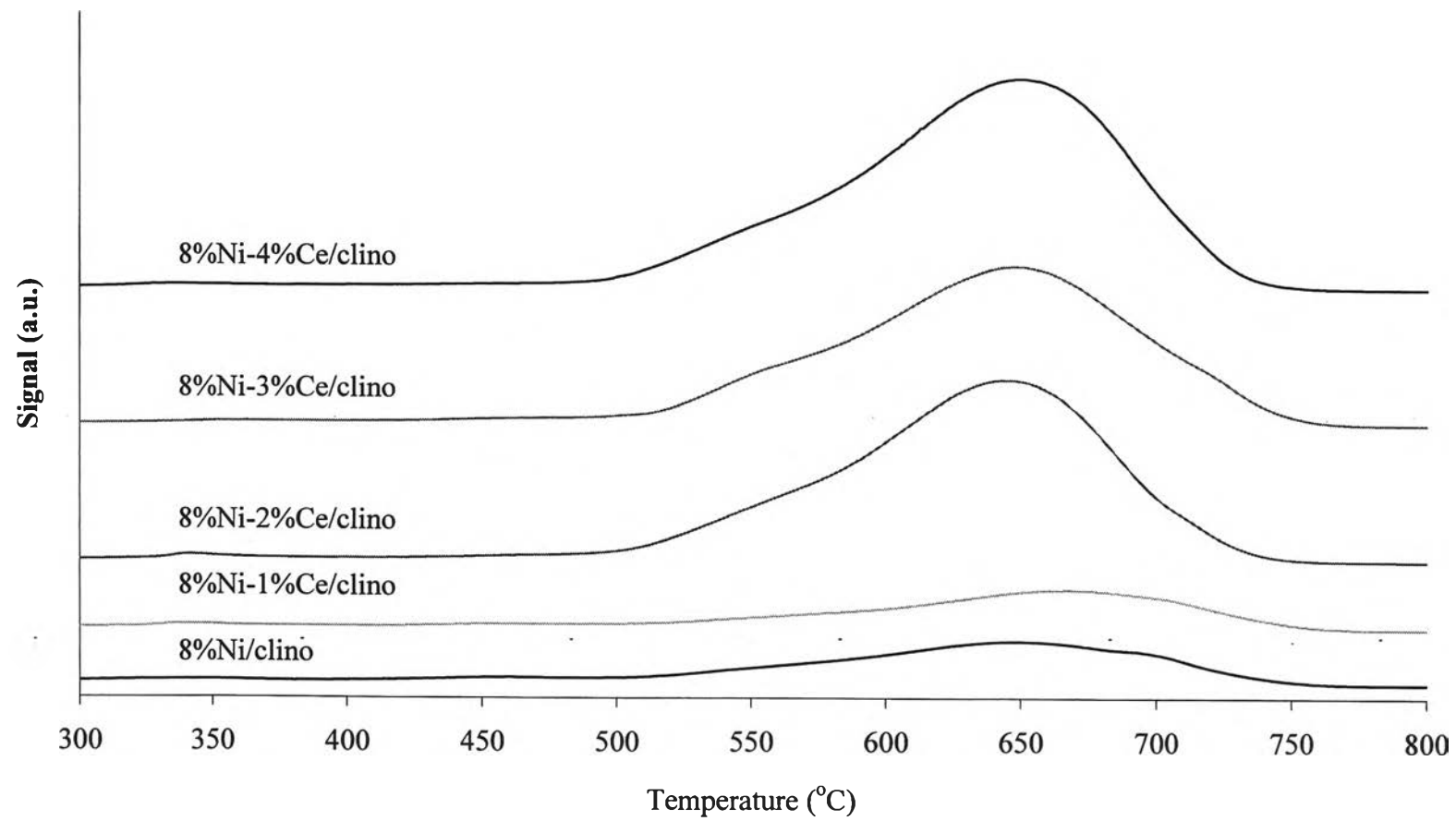


temperature and the location of the carbon on the catalyst surface. They proposed that the carbon deposited on or near the metal particles was oxidized at lower temperature than the carbon located on the support because the oxidation of carbon can be catalyzed by metal. Therefore, it can be suggested that the two peaks observed from the TPO profiles of 8%Ni/clino are attributed to the carbon at different locations and a small hump at 690°C of the unpromoted catalyst might be the oxidizing temperature of the carbon deposits on the support and hard to reduce at low temperature.

The TPO profiles of Zr-promoted catalysts are shown Figure 4.7. The TPO profiles of Zr promoted catalysts show that the carbon is oxidized between 500 and 770°C. It is found that the oxidizing temperature tends to increase with increasing amount of Zr as shown in Table 4.2. The TPO profiles of Zr-promoted catalysts are asymmetric and centered at about 660°C. This can be suggested that more than one type of carbon occur on these catalysts surface or the carbon deposit at different locations. Moreover, the area under the profile shows that amount of carbon deposition increase with Zr content increase from 1 to 4% and decrease with Zr content more than 4%.

**Table 4.2** Oxidizing temperature of modified catalysts

Amount of promoters (%)	Oxidizing Temperature (°C)	
	Ce-promoted catalysts	Zr-promoted catalysts
0	650	650
1	650-670	665
2	650	660
3	650	680
4	650	680
5	-	680



**Figure 4.6** TPO profiles of the Ce-promoted catalysts after 5 hours of reaction.

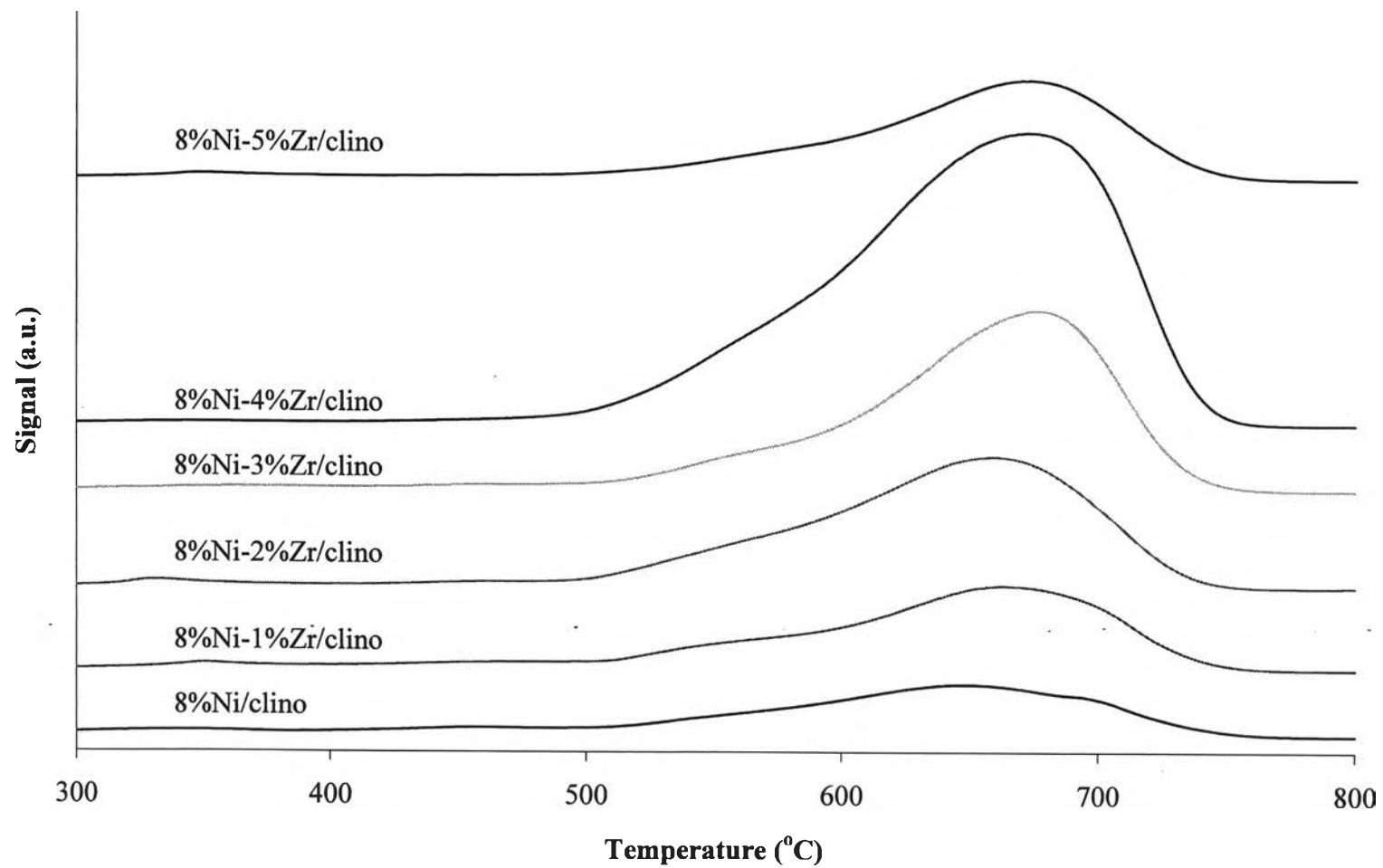
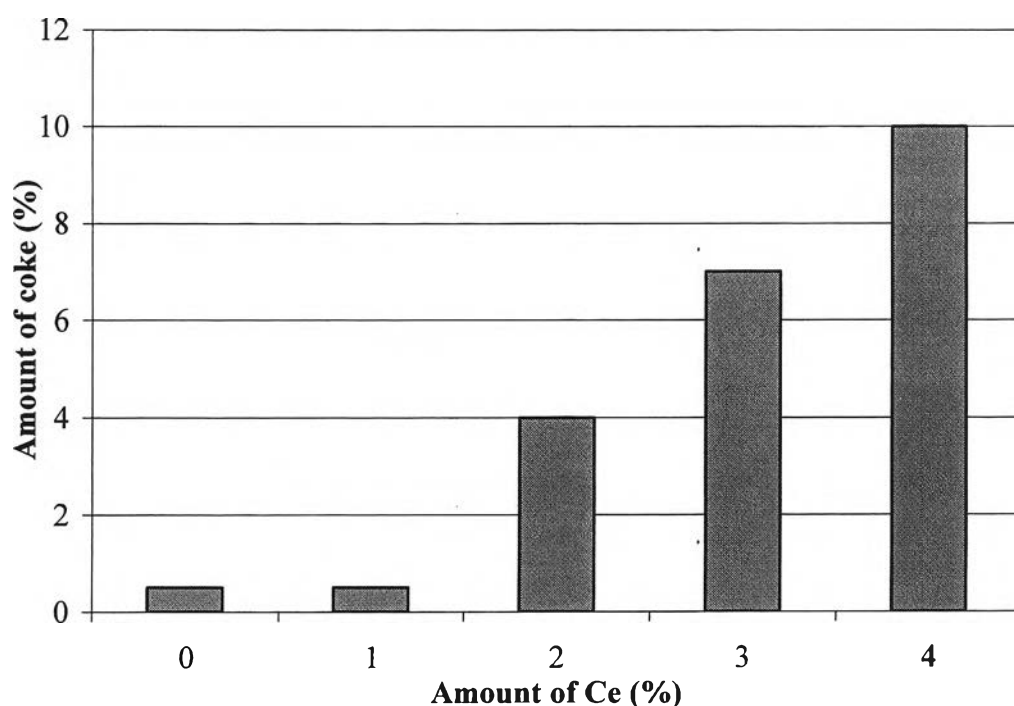


Figure 4.7 TPO profiles of the Zr-promoted catalysts after 5 hours of reaction.

#### 4.1.5 Thermogravimetric Analysis

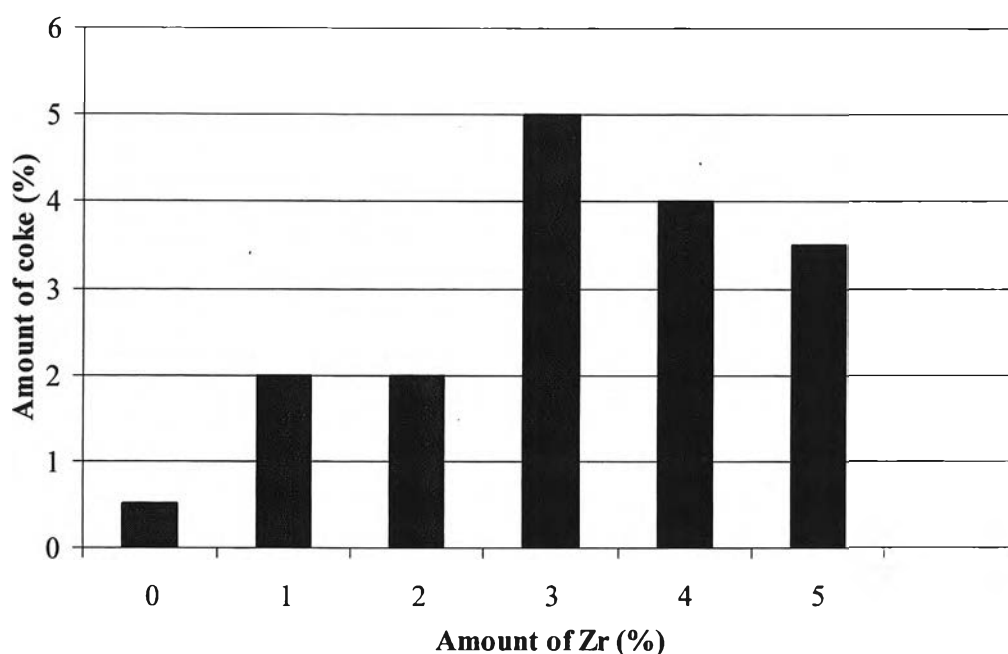
As coke deposition are a common cause for the deactivation of the catalyst, therefore Thermogravimetric Analysis (TGA) was performed to estimate the amount of carbon deposition on spent catalysts. The results are shown in Figures 4.8 to 4.10. In Figure 4.8, it is found that the amount of carbon deposited on the catalysts tends to increase with the amount of Ce. The 8%Ni-4%Ce/clino presents 10wt% of carbon deposition, which can be suggested that the rate of CH<sub>4</sub> decomposition is higher than CO<sub>2</sub> dissociation that makes carbon start to accumulate on the metal surface and blocks the active site of the catalyst, resulting in rapid deactivation.



**Figure 4.8** Amount of carbon deposited on Ce-promoted catalysts after 5 hours of reaction.

For Zr-promoted catalysts, the results are shown in Figure 4.9. It is found that the amount of carbon deposition increases with increasing Zr content from

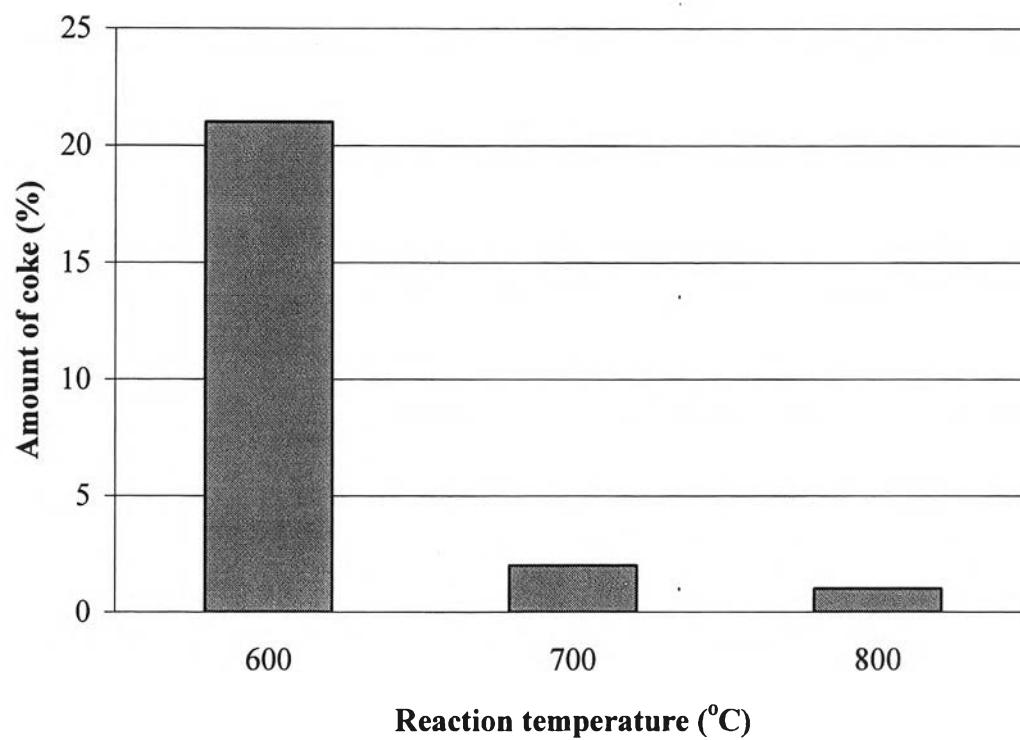
1 to 3%. But when the amount of Zr exceeds over 3%, the carbon deposition tends to decrease. 8%Ni-3%Zr/clino gives the highest amount of carbon deposition of about 5%. For higher amount of Zr loading, the decrease in amount of coke might be due to the promotion effect of  $ZrO_2$  that can facilitate carbon gasification and clean the metal surface.



**Figure 4.9** Amount of carbon deposited on Zr-promoted catalysts after 5 hours of reaction.

In order to study the effect of reaction temperature, TGA was conducted to determine the amount of carbon deposition on 8%Ni-2%Zr/clino after being used at different temperatures. The results are shown in Figure 4.10. It is found that the amount of carbon deposition decreases with increasing the reaction temperature. The catalyst used at 600°C presents carbon about 21%, which can cause the catalyst deactivation and make the catalytic activity of the catalyst decreases with time on stream. For the catalysts used at 700 and 800°C, the amount of carbon deposition are 2 and 1%, respectively. This can be suggested carbon removal is

facilitated at higher temperature of reaction and results in less carbon deposition on the catalyst.



**Figure 4.10** Amount of carbon deposition on 8%Ni-2%Zr/clino after being used at 600, 700, and 800°C.

## 4.2 Activity Test

### 4.2.1 Effect of Ni Loading

A series of Ni/clinoptilolite with various amounts of Ni loading were tested at 700°C for 5 hours to determine the appropriate amount of Ni loaded on clinoptilolite. The catalysts with 1, 3, 5, 8, 10, and 15wt% Ni on clinoptilolite were prepared by using incipient wetness impregnation method. Prior to the reaction, all of the catalysts were reduced by H<sub>2</sub> with 99.99% purity at 600°C for 1 hours then purged with He for 20 min. The catalytic activities of all catalysts are shown in Figures 4.11 to 4.15. Figure 4.11 shows the CH<sub>4</sub> conversion with time on stream of the catalysts with different amounts of Ni. It is clearly seen that the CH<sub>4</sub> conversion increases with increasing amounts of Ni loading from 1 to 8wt%. The 1%Ni/clino is drastically deactivated in the first hour of reaction. It shows only about 3% of CH<sub>4</sub> conversion at the initial, and then the activity is suddenly low after 2 hours of the reaction. The 5%Ni/clino gives more than 70% CH<sub>4</sub> conversion initially, which is the highest among the others. But the activity is rapidly decreased with time on stream. The 8%Ni/Clino gives almost the same CH<sub>4</sub> conversion as 5%Ni/clino in the first hour of reaction, but it shows much higher catalyst stability after 5 hours. However, the gradual decrease in activity is still observed. This result is in good agreement with catalytic performances over Ni/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> (Roh *et al.*, 2002), which gave the optimum Ni content of 9-12% and Ni/ZSI reported by Chang *et al.* (1996), which gave the optimum Ni content of 5%. When increasing Ni loading to more than 8%, the catalytic activity is decreased to 35% CH<sub>4</sub> conversion. It seems that too high amount of Ni leads to the decrease in the catalytic activity of the catalysts, which might be the results of a large amount of coke, lower Ni dispersion and larger Ni ensemble size that make the catalysts lost their active surface area for CH<sub>4</sub> decomposition (Noronha *et al.*, 2001). Figure 4.12 shows CO<sub>2</sub> conversion of the catalysts with various amounts of Ni loading. It is found that the results give the same trend as CH<sub>4</sub> conversion, which 8%Ni/clino shows the best in conversion and stability. However, the CO<sub>2</sub> conversion of all catalysts is slightly higher than CH<sub>4</sub> conversion as shown in Figure 4.13, which is the result of reverse water gas shift reaction (Bradford and Vannice, 1999).

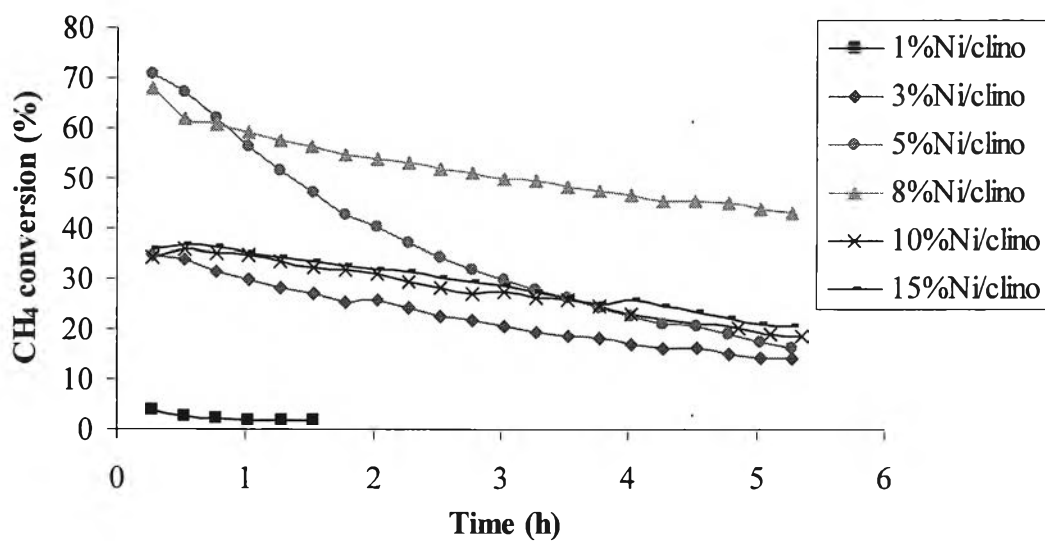


Figure 4.11 CH<sub>4</sub> conversion of the catalysts with various %Ni loadings at 700°C.

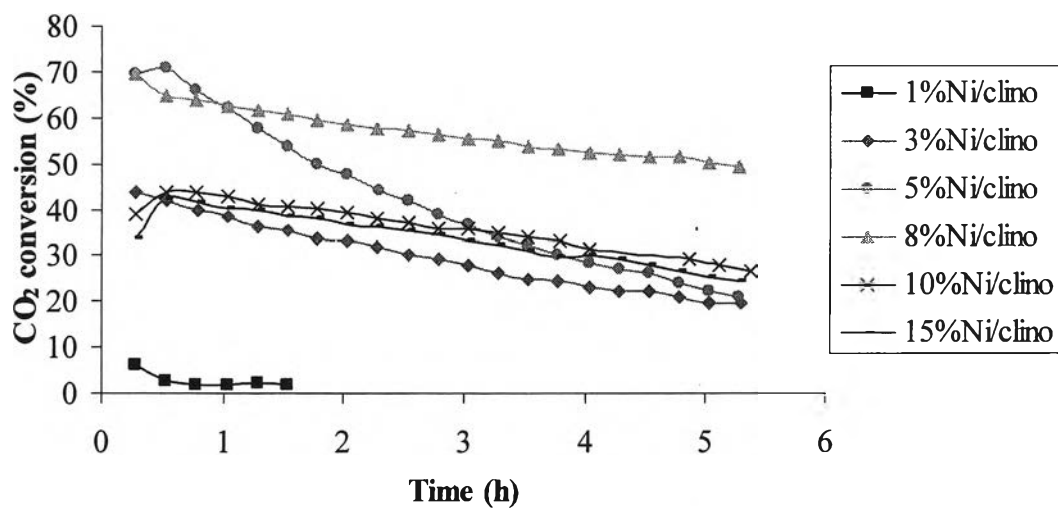
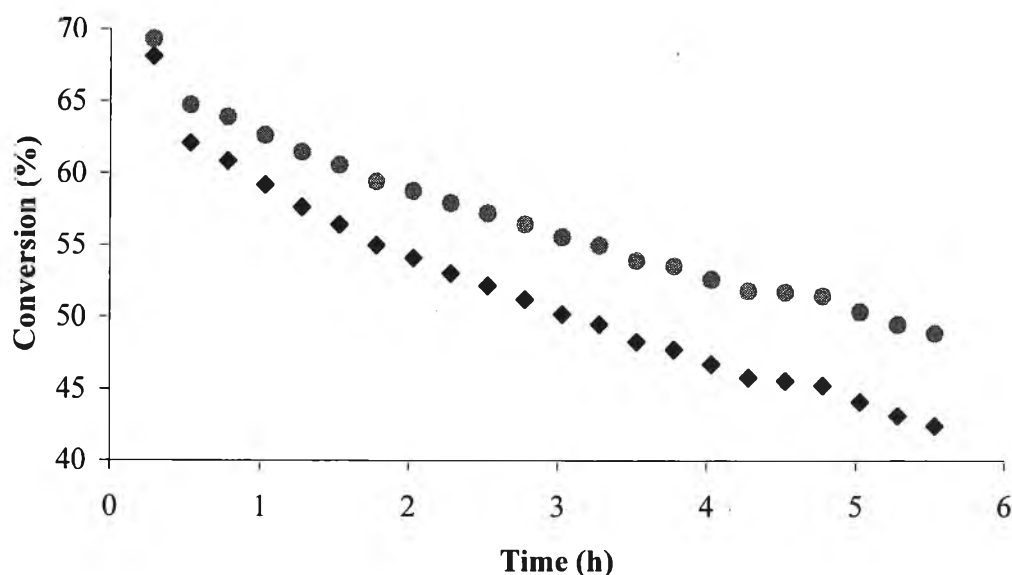


Figure 4.12 CO<sub>2</sub> conversion of the catalysts with various %Ni loadings at 700°C.





**Figure 4.13** (◆)CH<sub>4</sub> and (●) CO<sub>2</sub> conversion of 8%Ni/clino catalyst at 700°C.

The result of H<sub>2</sub> selectivity and H<sub>2</sub> yield of the catalysts are shown in Figures 4.14 and 4.15, respectively. The results show that the H<sub>2</sub> selectivity increases when increasing the amount of Ni loaded on the catalysts from 3 to 8wt% and when the Ni loading is more than 8wt%, the H<sub>2</sub> selectivity decreases, which is due to lower Ni dispersion. It is found that the H<sub>2</sub> selectivity of these catalysts occurs below 50% which can be suggested that H<sub>2</sub> was consumed in the reverse water gas shift reaction to produce H<sub>2</sub>O.

Figure 4.15 shows the H<sub>2</sub> yield of the catalysts. The H<sub>2</sub> yield is used to compare the catalytic activity and stability of the catalysts. The catalyst which gives the highest H<sub>2</sub> yield will be selected to use in the next part to study the effect of promoter on the activity and stability of this reaction, which are Ce and Zr. Among five catalysts examined, 8%Ni/clino shows the best activity along 5 hours of reaction. It gives H<sub>2</sub> yield about 34% at the initial, but decreases with time on stream to 22% in 5 hours of reaction because of the deactivation of the catalyst. Therefore, the appropriate amount of Ni loading on clinoptilolite which is selected to use in the next part is 8wt%.

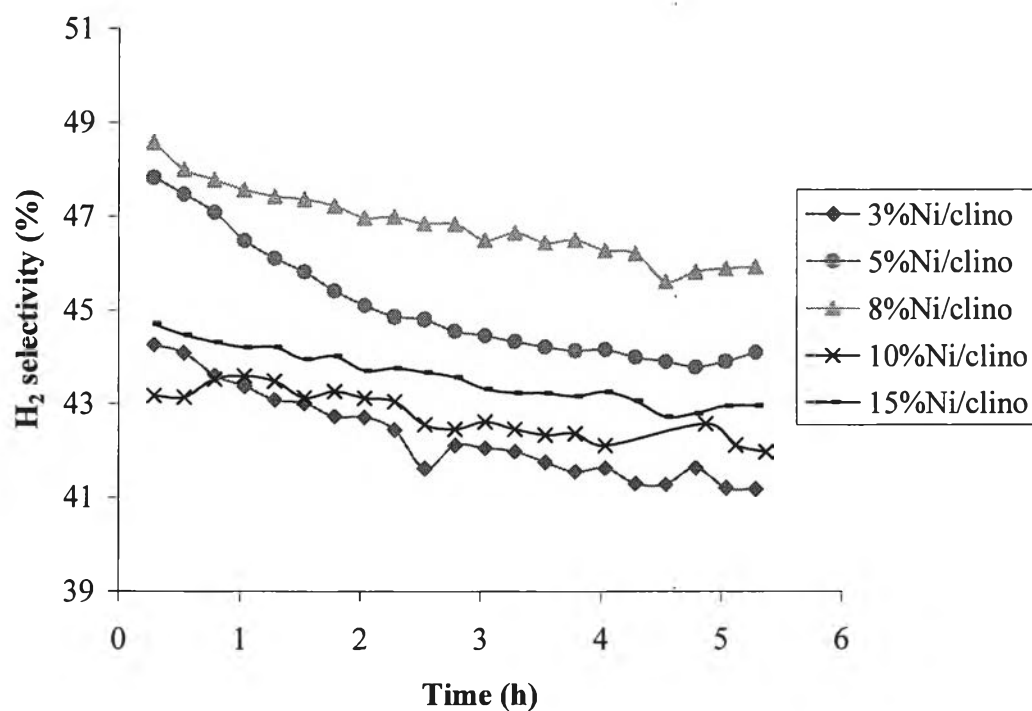


Figure 4.14 H<sub>2</sub> selectivity of the catalysts with various %Ni loadings at 700°C.

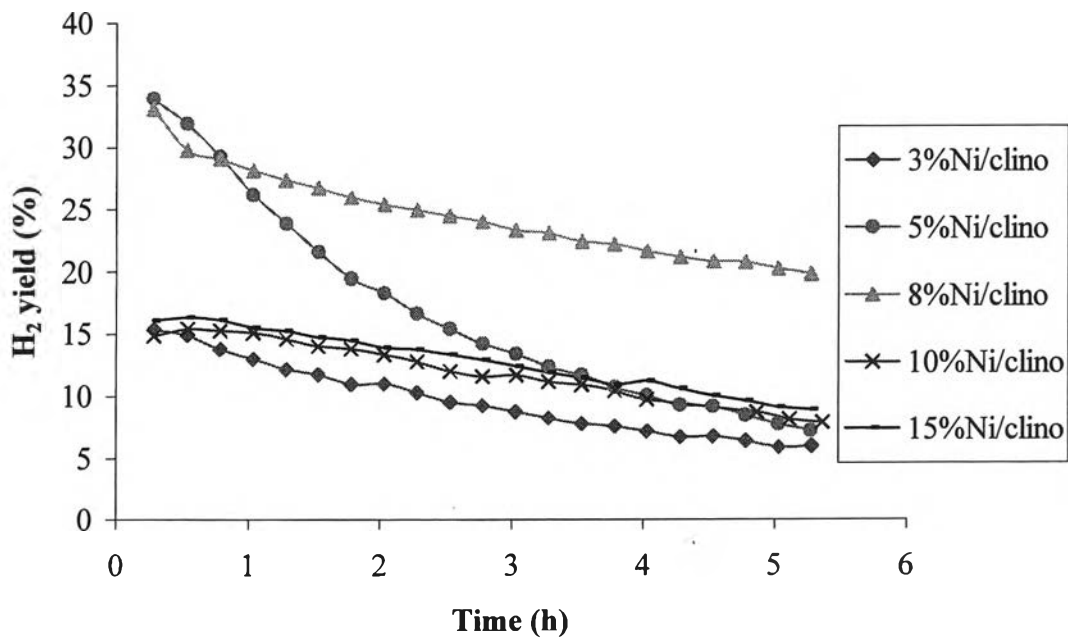


Figure 4.15 H<sub>2</sub> yield of the catalysts with various %Ni loadings at 700°C.

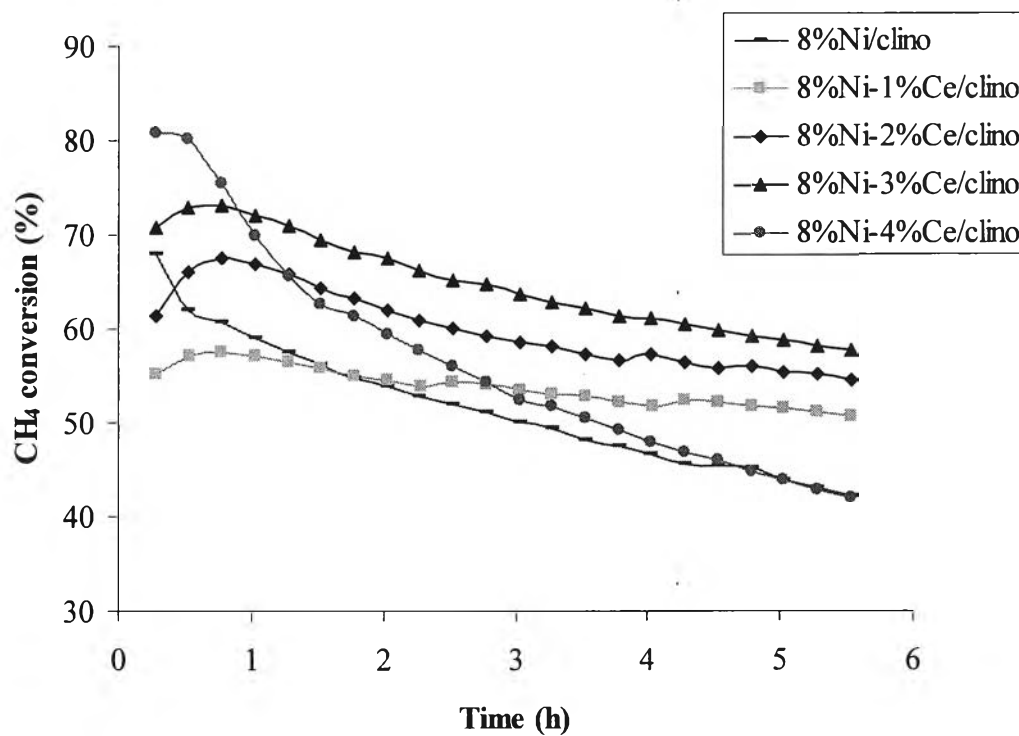
## 4.2.2 Effect of Promoters

### 4.2.2.1 *Effect of Ce Loading*

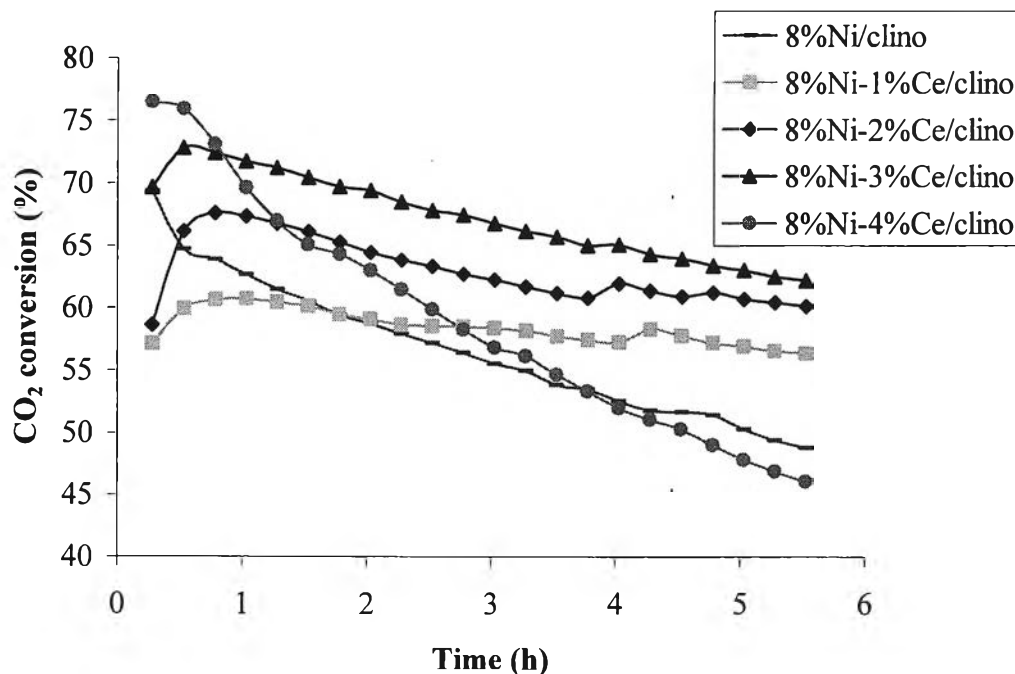
All of the catalysts were tested at 700°C for more than 5 hours. The results are shown in Figures 4.16 to 4.19. Figure 4.16 shows CH<sub>4</sub> conversion of Ce-promoted catalysts. It is found that Ce can enhance the catalytic activity of the catalysts. The CH<sub>4</sub> conversion increases with the amount of Ce adding to the catalysts from 1 to 3wt%. But when the amount of Ce increases to 4wt%, the catalyst deactivates rapidly even though it initially gives around 80% CH<sub>4</sub> conversion but within 5 hours of reaction, the conversion drops to 42%, which is equal to the unpromoted catalyst. Addition of Ce promoter to Ni/clinoptilolite results not only in an increase of the catalytic activity but also in the improvement of catalyst stability except 8%Ni-4%Ce/clino. 8%Ni-1%Ce/clino shows the best stability among the others. However, it gives CH<sub>4</sub> conversion of about 55%, which is less than 8%Ni-2%Ce/clino and 8%Ni-3%Ce/clino, which give more than 60% of CH<sub>4</sub> conversion. Even though a slight deactivation of 8%Ni-3%Ce/clino has been found, but it shows the best catalytic activity compared to the others. The CO<sub>2</sub> conversion of Ce-promoted catalysts is shown in Figure 4.17. The results show that the 8%Ni-3%Ce/clino gives the highest CO<sub>2</sub> conversion along 5 hours of reaction, but the CO<sub>2</sub> conversion still decreases with time on stream. With 5 h of reaction, the conversion decreases from 73 to 65%. For 8%Ni-4%Ce/clino, CO<sub>2</sub> conversion drastically decreases with time on stream. It is found that CO<sub>2</sub> conversion of 8%Ni-4%Ce/clino is less than the unpromoted catalyst after 4 hours of reaction.

From the results, it can be concluded that the appropriate amount of Ce can enhance both stability and catalytic activity of the catalysts. Based on two paths 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 the carbon deposition, inhibiting the methane decomposition. CeO<sub>2</sub> is known as the high oxygen storage capacity material, which can help increasing the oxygen transfer of the support to oxidize the carbon produced from methane decomposition on the metal surface. Moreover, higher oxygen transfer of the support results in higher oxygen vacancies

and an increase in the  $\text{CO}_2$  dissociation. Therefore, adding  $\text{CeO}_2$  as the promoter can help increasing the rate of carbon removal from the metal surface and clean the active site for  $\text{CH}_4$  decomposition (Noronha *et al.*, 2001).

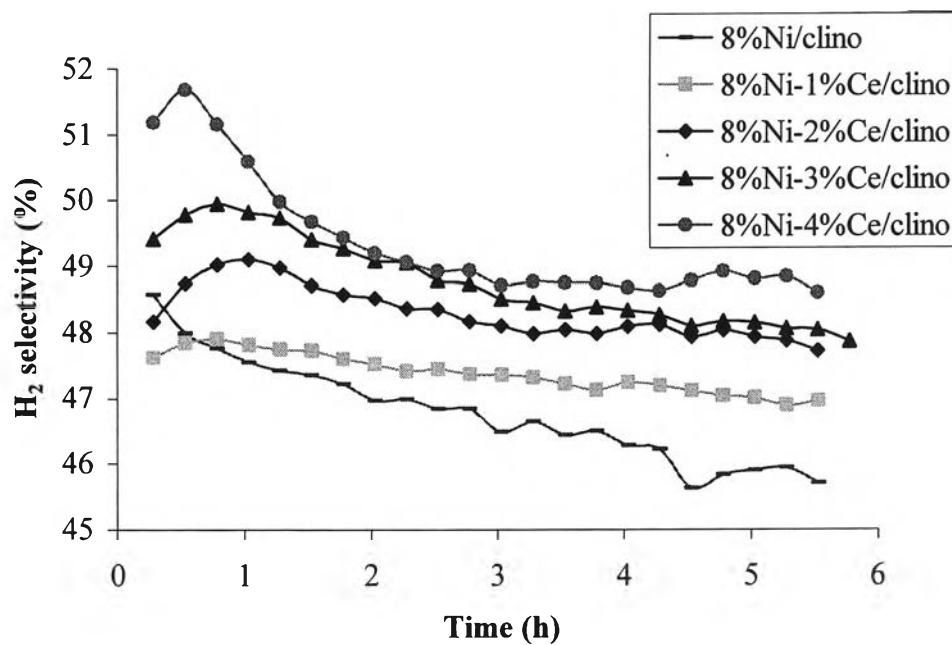


**Figure 4.16**  $\text{CH}_4$  conversion of the catalysts with various amounts of Ce at  $700^\circ\text{C}$ .

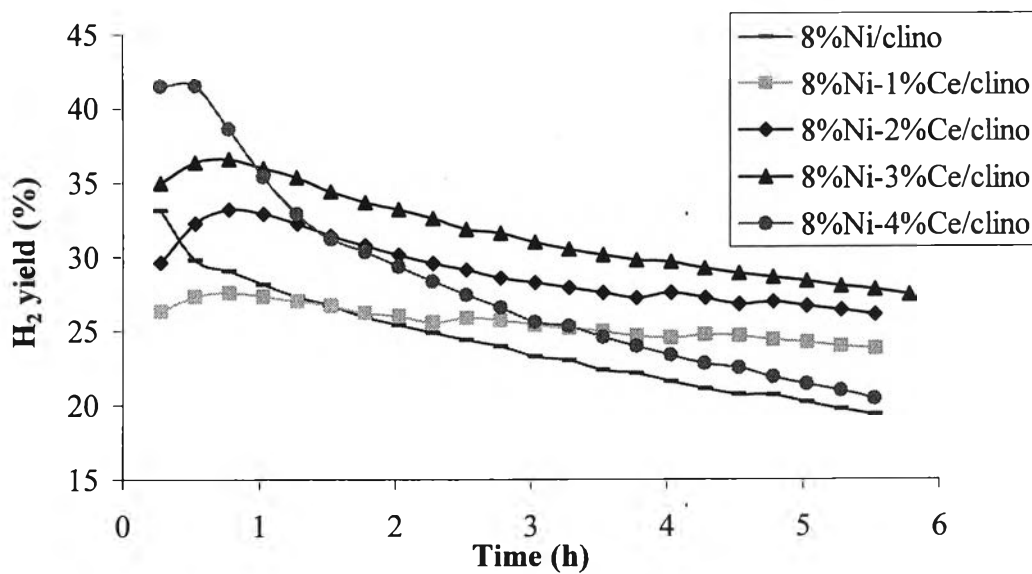


**Figure 4.17** CO<sub>2</sub> conversion of the catalysts with various amounts of Ce at 700°C.

Figure 4.18 shows the H<sub>2</sub> selectivity of Ce-promoted catalysts. The results show that the H<sub>2</sub> selectivity is increased with the amount of Ce added to the catalyst, which could be attributed to the higher dispersion of metal active sites for methane decomposition to produce H<sub>2</sub>. However, 8%Ni-4%Ce/clino gives the H<sub>2</sub> selectivity more than 50% in the first hour of reaction. But the selectivity is drastically decreased along the reaction. This might be due to the rate of carbon deposition is higher than the rate of carbon removal that makes the catalyst lost its active sites and decreases in catalytic activity, which gives good agreement with the TGA results. Figure 4.19 shows the H<sub>2</sub> yield of the Ce-promoted catalysts. The H<sub>2</sub> yield is used to select the catalyst with the best performance in terms of catalytic activity and stability. It was found that 8%Ni-3%Ce/clino gave the highest H<sub>2</sub> yield as compared to the other amounts of Ce. It gave 36% H<sub>2</sub> yield at the beginning and within 5 hours of reaction the selectivity was decreased to 27%. The catalytic activity of this catalyst was to compare with the Zr-promoted catalyst in order to select the best catalyst for studying in the next part further.



**Figure 4.18** H<sub>2</sub> selectivity of the catalysts with various amounts of Ce at 700°C.



**Figure 4.19** H<sub>2</sub> yield of the catalysts with various amounts of Ce at 700°C.

#### 4.2.2.2 Effect of Zr Loading

All of the prepared catalysts were tested for the activity at 700°C. It is found that Zr can enhance both catalytic activity and stability of the catalysts than unpromoted catalyst. It shows that Zr, which is a promoter, can play a significant role by promoting the dissociation of CO<sub>2</sub> for this reaction. Figure 4.20 shows the CH<sub>4</sub> conversion of 8%Ni/clino with 1 to 6wt% of Zr. The results show that the catalysts with 1wt% and 2wt% of Zr give lower initial conversion than the unpromoted catalyst. But within 2 hours, the CH<sub>4</sub> conversion was higher than the unpromoted catalyst due to the promotion effect of Zr that makes the catalysts have higher stability. 8%Ni-2%Zr/clino presents the highest stability along the reaction. It shows the conversion that almost constant at 58% during 5 hours of reaction. The results show that for the catalysts with 1 to 5wt% of Zr, it is found that CH<sub>4</sub> conversion increases with increasing the amount of Zr. 8%Ni-5%Zr/clino shows highest CH<sub>4</sub> conversion at 75%. However, the deactivation of the catalyst is still observed along 5 hours of reaction. When the amount of Zr more than 5wt%, the CH<sub>4</sub> conversion is dropped to 45% and decreased to almost 20% after 5 hours, which is lower than the unpromoted catalyst. This can be explained that excess amount of Zr may act to decrease the density of CO<sub>2</sub> adsorption sites near the metal particle, reducing the effectiveness of the support for CO<sub>2</sub> reforming of CH<sub>4</sub>.

The results of CO<sub>2</sub> conversion are shown in Figure 4.21. The CO<sub>2</sub> conversion of the Zr-promoted catalysts is increased with the amount of Zr between 1 and 5wt%. 8%Ni-5%Zr/clino gives CO<sub>2</sub> conversion about 75% at the beginning but the slightly decreased with time on stream is still observed. The 8%Ni-2%Zr/clino showed the best stability at 60% conversion along 5 hours of reaction. The 8%Ni-6%Zr shows the lowest conversion compared to the others that might be the results of adding too high amount of Zr, which is the reducible metal oxide and leads to the coverage of the Ni active sites of the catalyst. The enhancement of Zr to the catalytic activity and stability of the catalysts can be ascribed to the results of the promotion effect of Zr to enhance the reduction rate and the reducibility at lower temperature of the catalysts more than the unpromoted catalyst. This makes the catalysts have higher active sites than the unpromoted catalyst and resulting in higher catalytic activity.

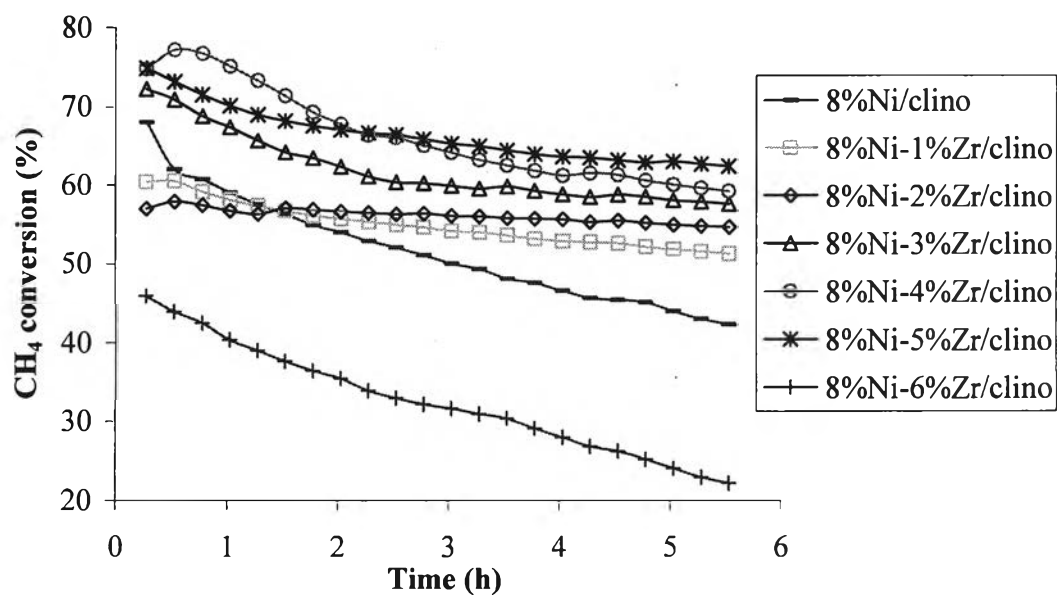


Figure 4.20 CH<sub>4</sub> conversion of the catalysts with various amounts of Zr at 700°C.

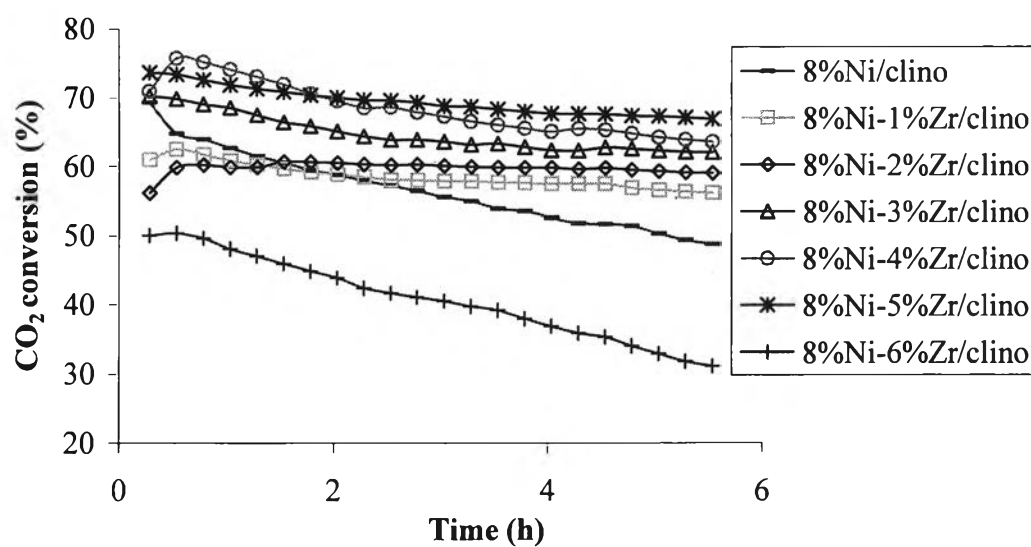


Figure 4.21 CO<sub>2</sub> conversion of the catalysts with various amounts of Zr at 700°C.



The H<sub>2</sub> selectivity and H<sub>2</sub> yield of the modified catalysts are shown in Figures 4.22 and 4.23. The H<sub>2</sub> selectivity of the catalysts with amount of Zr from 1 to 5wt% is found to be higher than for the unpromoted catalyst. 4%Zr gives higher H<sub>2</sub> selectivity than 5% Zr at the first 2 hours of reaction. But within 2 hours, the H<sub>2</sub> selectivity is about the same at 49%. For 1, 2, and 3%Zr show almost the same value along 5 hours of reaction. They present around 48% selectivity, which can be suggested that increasing amount of Zr can enhance the H<sub>2</sub> selectivity of the catalyst. However, when 6wt% of Zr is added to the catalyst, the H<sub>2</sub> selectivity is decreased to 47% at the initial and 43% at the end of reaction, which is lower than the unpromoted catalyst. The H<sub>2</sub> yield of the catalysts shows that 8%Ni-5%Zr/clino shows the best activity. It gives H<sub>2</sub> yield of more than 30% even though a slightly decrease with time on stream is occurred. However, the catalyst that shows the best in terms of stability is 8%Ni-2%Zr/clino. It present about 28% yield along 5 hours of reaction. The higher stability of 8%Ni-2%Zr/clino over 8%Ni-5%Zr/clino might be the results of less amount of carbon deposition and lower oxidizing temperature, which can enhance the ability to clean carbon deposition at lower temperature while producing H<sub>2</sub>. From the results, it can be concluded that 8%Ni-5%Zr/clino shows the best activity among Zr-promoted catalysts. Moreover, when comparing the activity results with the 8%Ni-3%Ce/clino, 8%Ni-5%Zr/clino presents better activity and stability than 8%Ni-3%Ce/clino. Therefore, 8%Ni-5%Zr/clino is selected to study in the next part. However, 8%Ni-2%Zr/clino that presents the highest stability as compared to all promoted catalysts is one of the most interesting catalysts to study in the next part.

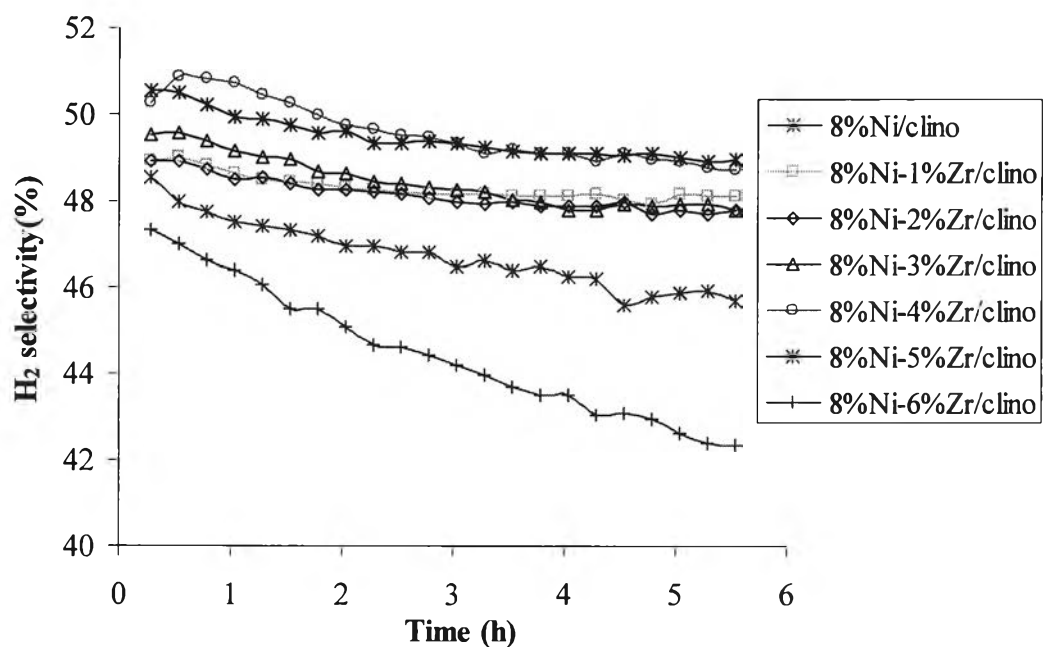


Figure 4.22 H<sub>2</sub> selectivity of the catalysts with various amounts of Zr at 700°C.

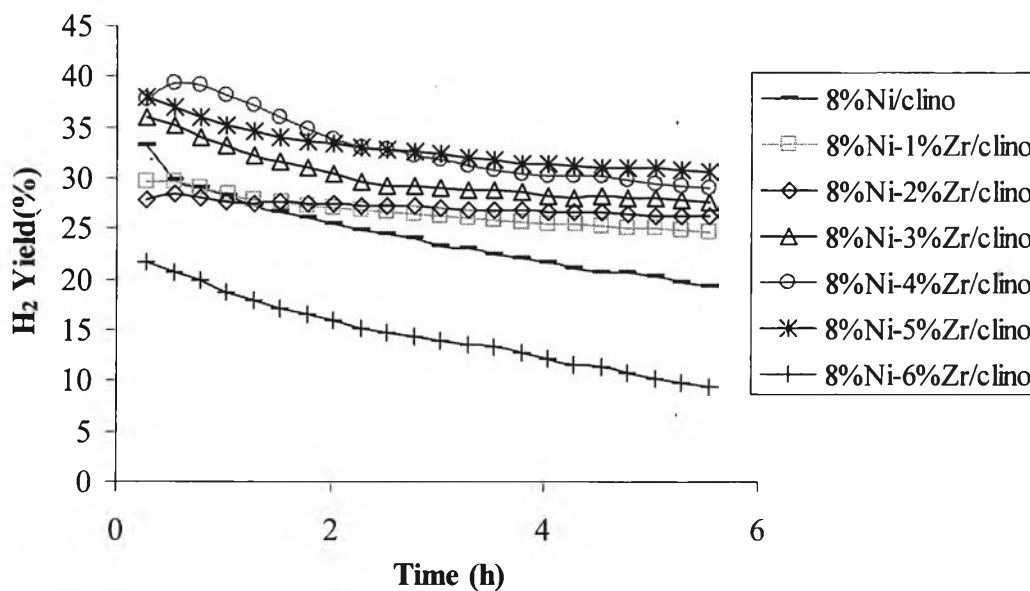
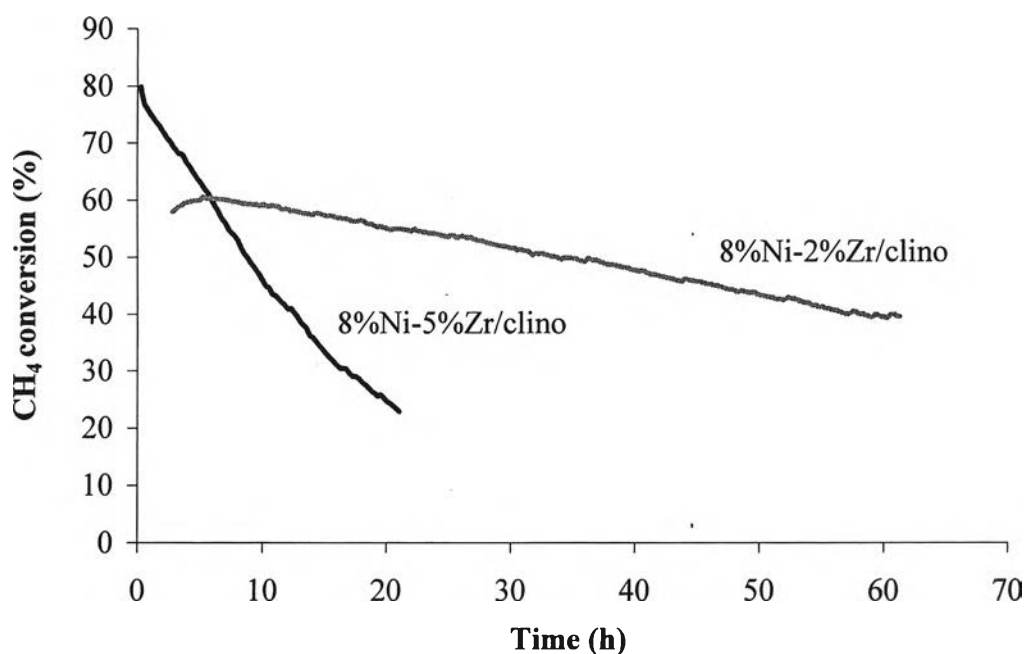


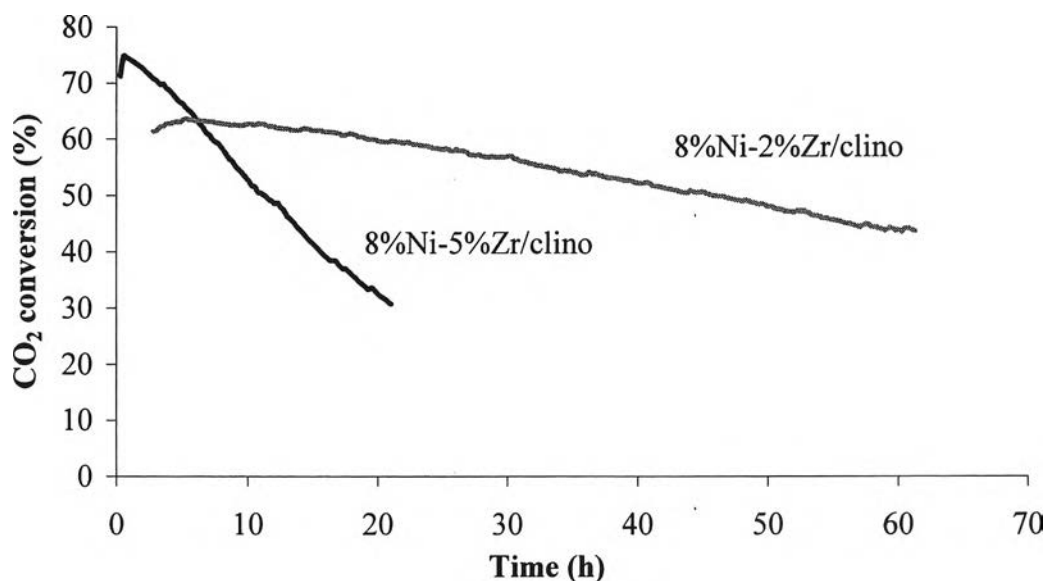
Figure 4.23 H<sub>2</sub> yield of the catalysts with various amounts of Zr at 700°C.

#### 4.2.2.3 Stability Test

8%Ni-2%Zr/clino and 8%Ni-5%Zr/clino were selected to study the stability testing at 700°C. The results are shown in Figures 4.24 to 4.27. It is found that 8%Ni-5%Zr/clino presents rapid deactivation of the catalyst during twenty hours of reaction. It gives more than 70% conversion at the beginning, but within 20 hours the CH<sub>4</sub> conversion drops to 20%. 8%Ni-2%Zr/clino shows much higher stability than 8%Ni-5%Zr/clino. Even though it gives less conversion than 8%Ni-5%Zr/clino at the beginning but within 7 hours the conversion becomes higher. However, the conversion decreases almost to 20% within 60 hours of reaction. CO<sub>2</sub> conversion is slightly higher than CH<sub>4</sub> conversion, which is the result of reverse water gas shift reaction.

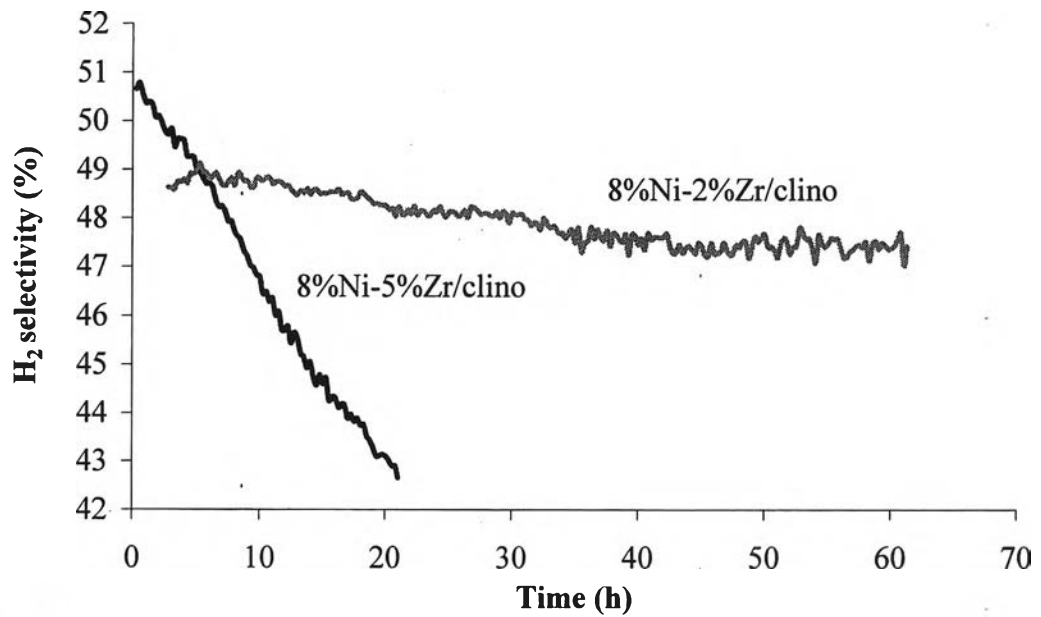


**Figure 4.24** CH<sub>4</sub> conversion of 8%Ni-2%Zr/clino and 8%Ni-5%Zr/clino at 700°C.

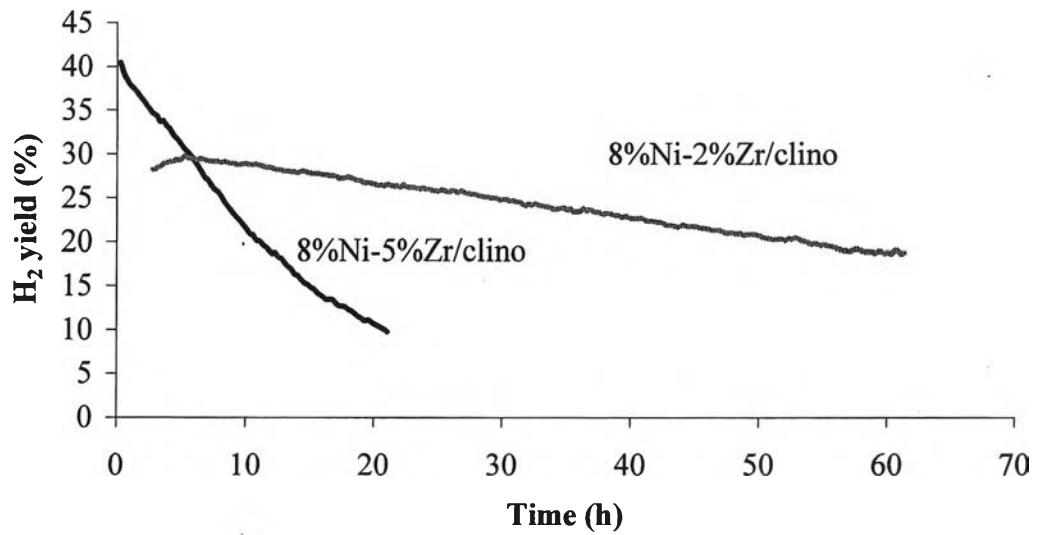


**Figure 4.25** CO<sub>2</sub> conversion of 8%Ni-2%Zr/clino and 8%Ni-5%Zr/clino at 700°C.

The H<sub>2</sub> selectivity and H<sub>2</sub> yield results are shown in Figures 4.26 and 4.27, respectively. It is found that the H<sub>2</sub> selectivity of 8%Ni-2%Zr/clino slightly decreases but the H<sub>2</sub> selectivity of 8%Ni-5%Zr/clino decreases rapidly with time on stream. This might be due to the result of higher amount of carbon deposition on 8%Ni-5%Zr/clino catalyst, making the catalyst lost its active site for CH<sub>4</sub> decomposition. The selectivity of these two catalysts is less than 50%, which can confirm that the reverse water gas shift reaction occurs. The H<sub>2</sub> yield of 8%Ni-2%Zr/clino decreases from 28 to 18% within 60 hours of reaction. The decrease in the activity of this catalyst is known to be due to the carbon deposition. Therefore, it is desired to develop this catalyst further in order to improve the stability toward carbon deposition.



**Figure 4.26** H<sub>2</sub> selectivity of 8%Ni-2%Zr/clino and 8%Ni-5%Zr/clino at 700°C.



**Figure 4.27** H<sub>2</sub> yield of 8%Ni-2%Zr/clino and 8%Ni-5%Zr/clino at 700°C.

### 4.2.3 Effect of Reaction Temperature

8%Ni-2%Zr/clino is used for studying the effect of reaction temperature at 600, 700, and 800°C. The results are illustrated in Figures 4.28 to 4.31. It is obvious that the CH<sub>4</sub> and CO<sub>2</sub> conversions increase with the reaction temperature. As expected, the CH<sub>4</sub> conversion increases with reaction temperature. It shows the interference of the reverse water-gas shift reaction, at low temperatures the reverse water-gas shift reaction is more favored. At 800°C, the catalyst gives the initial conversion about 90%, but the conversion is drastically decreased compared to the conversion at 600 and 700°C. The activity of the catalyst at 700°C shows the highest stability, the CH<sub>4</sub> and CO<sub>2</sub> conversions are almost constant at 60%.

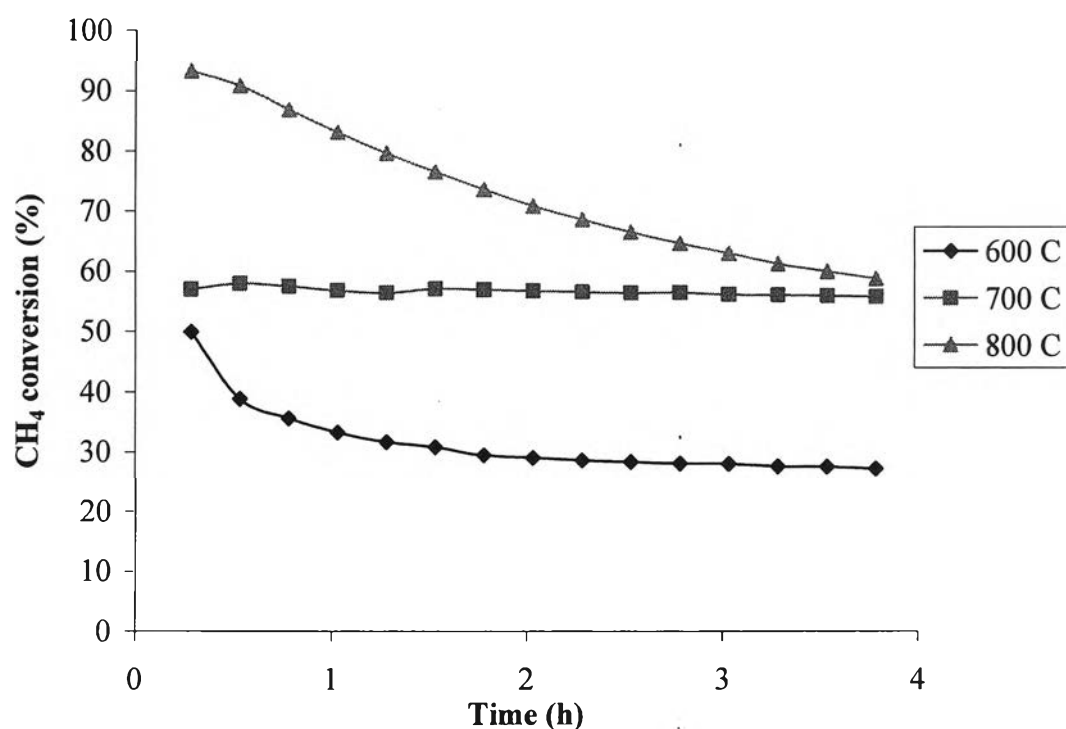
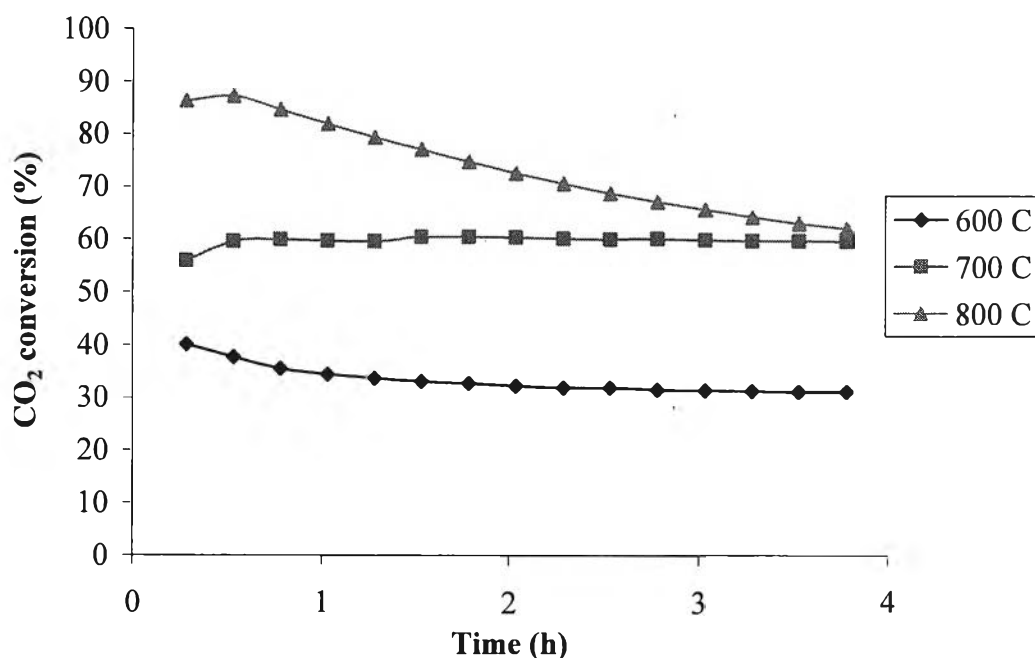


Figure 4.28 CH<sub>4</sub> conversion of 8%Ni-2%Zr/clino at 600, 700, and 800°C.



**Figure 4.29** CO<sub>2</sub> conversion of 8%Ni-2%Zr/clino at 600, 700, and 800°C.

The H<sub>2</sub> selectivity results show that at 800°C the selectivity is over 50%, which can be assumed that high reaction temperature can prevent reverse water gas shift reaction. However, the H<sub>2</sub> yield of the reaction at 800°C still presents rapid deactivation with time on stream, and it is expected to be lower than for 700°C after 4 hours of reaction. From TGA results, the amount of carbon deposits on the catalyst after being used at 800°C is less than 1%, while the XRD patterns show that Ni sintering of the catalysts occurred after used at 800°C. Therefore, the Ni sintering is the major cause of catalyst deactivation, not the carbon deposition, and makes the catalyst lose its active surface area. Therefore, it can be deduced that the appropriate temperature for operating the CO<sub>2</sub> reforming of methane reaction is 700°C.

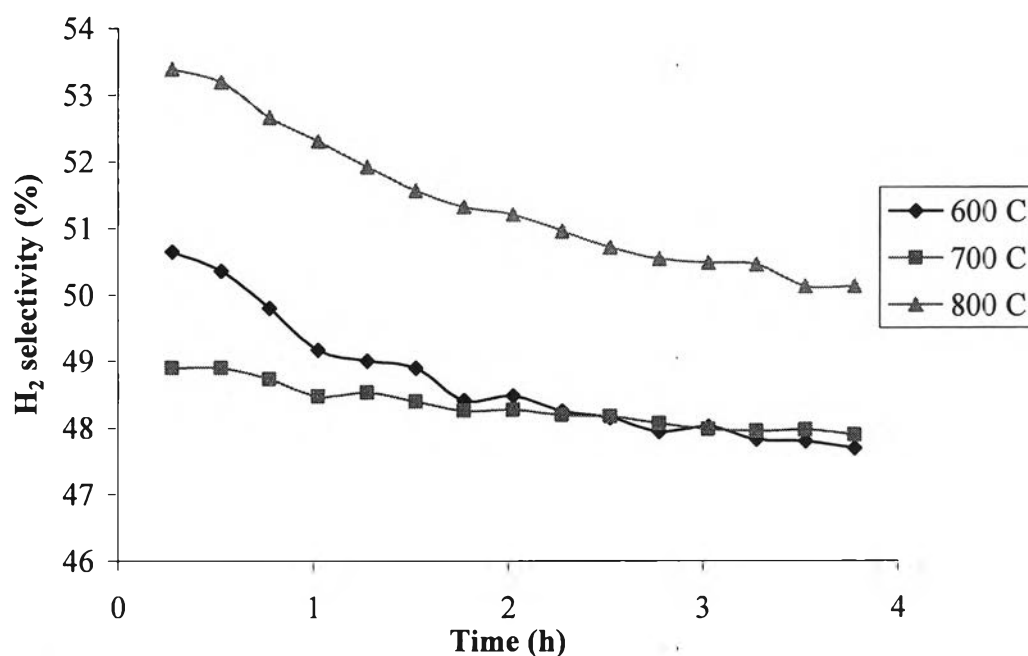


Figure 4.30 H<sub>2</sub> selectivity of 8%Ni-2%Zr/clino at 600, 700, and 800°C.

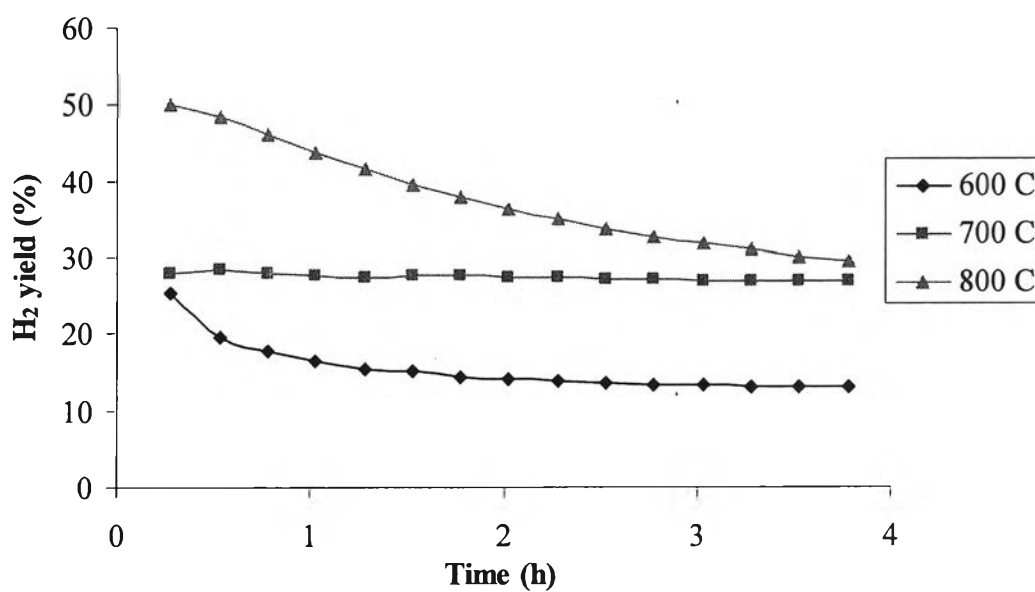


Figure 4.31 H<sub>2</sub> yield of 8%Ni-2%Zr/clino at 600, 700, and 800°C.