

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

4.1.1 BET Surface Area

The fresh catalysts were measured for their surface areas by the multiple point BET method. Effects of Ce loading on the BET surface area were investigated. As shown in Table 4.1, it can be seen that the addition of Ce to the ZrO₂ support increased the surface area when compared with the Pt/ZrO₂ catalyst. This is because Ce can stabilize the tetragonal form of the ZrO₂, which has higher surface area than its monoclinic form (Stagg and Resasco, 1998). And this is supported by the XRD results as to be discussed next.

Table 4.1 BET surface areas of catalysts prepared.

Catalyst	BET surface area (m ² /g)
Pt/ZrO ₂	35.52
3%Ce ^a	39.49
5%Ce ^b	40.16
7%Ce ^c	43.22

^a Pt supported on 3%Ce-doped ZrO₂

^b Pt supported on 5%Ce-doped ZrO₂

^c Pt supported on 7%Ce-doped ZrO₂

4.1.2 X-ray Diffraction (XRD)

X-ray diffraction analyses were carried out on all catalysts. The relative intensities obtained from the X-ray diffraction patterns were used to

compare the tetragonal and monoclinic forms of the ZrO_2 support. As shown in Figure 4.2, the ZrO_2 in the unpromoted catalyst was mostly monoclinic while the tetragonal form of ZrO_2 was observed in the promoted catalysts. The intensity of the tetragonal form increases with an increase in Ce loading. These results also indicate that Ce can stabilize the tetragonal form of the ZrO_2 , which, in turn, results in the increase of the surface area.

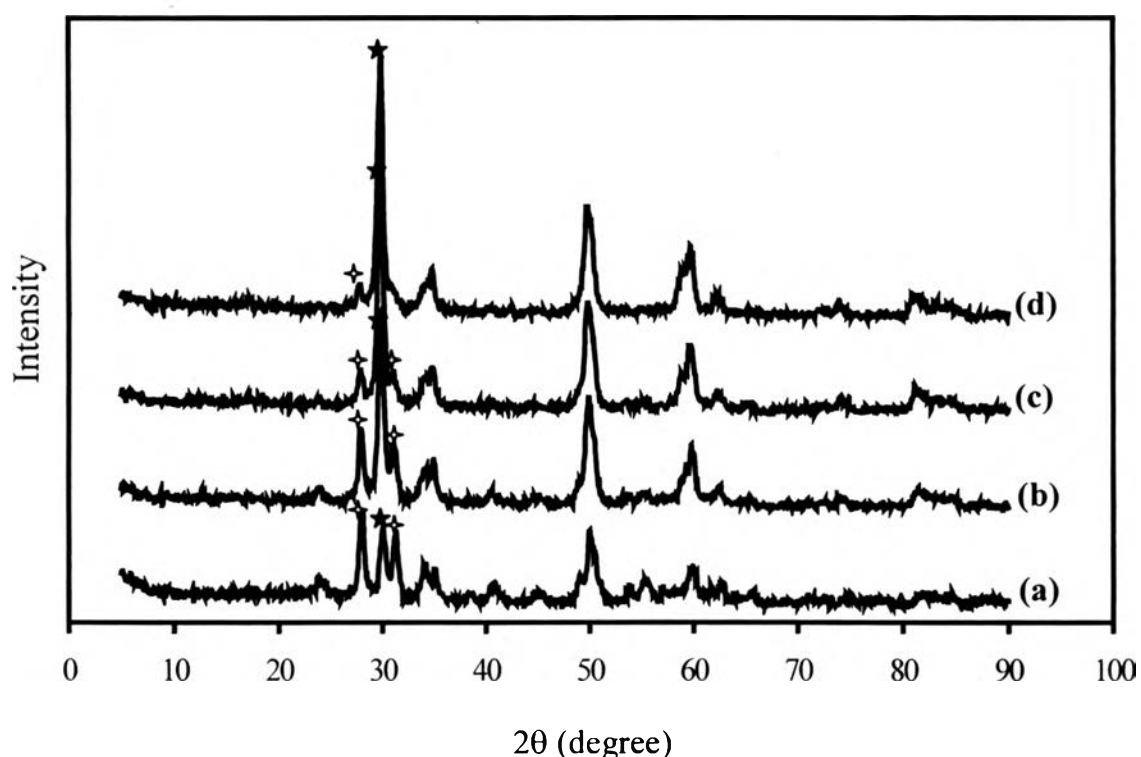


Figure 4.1 XRD patterns of fresh catalysts: (a) Pt/ ZrO_2 , (b) Pt/3%Ce- ZrO_2 , (c) Pt/5%Ce- ZrO_2 , (d) Pt/7%Ce- ZrO_2 : ★ = tetragonal form, ✦ = monoclinic form.

4.2 Methane Reforming with Carbon Dioxide

4.2.1 Effects of Oxygen Addition

Effects of oxygen addition on the CO_2 reforming over various catalysts are presented in Figures 4.2-4.5.

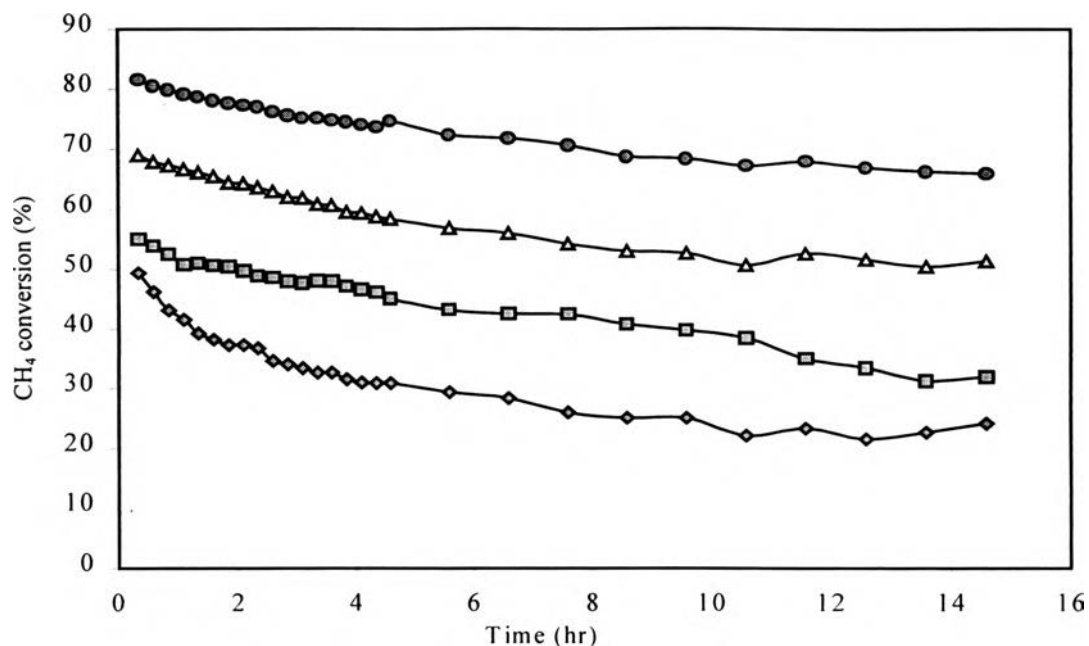


Figure 4.2 CH₄ conversion as a function of time with the 2:1 feed ratio of CH₄:CO₂ for Pt/ZrO₂; CO₂ reforming (♦), 3%O₂ added (■), 7%O₂ added (▲), 9%O₂ added (●).

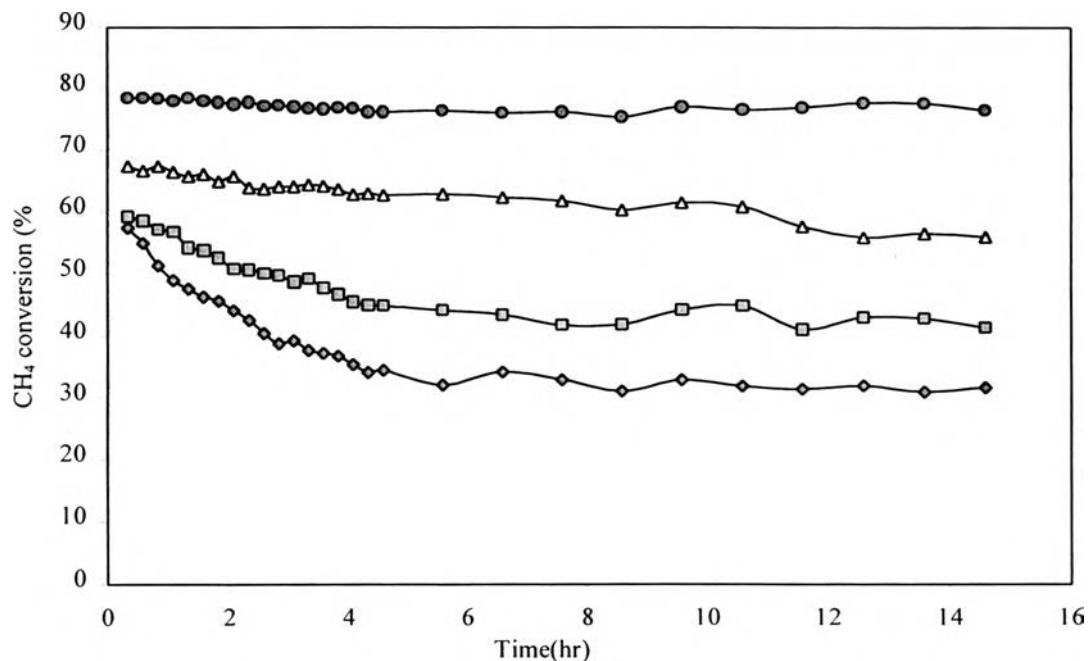


Figure 4.3 CH₄ conversion as a function of time with the 2:1 feed ratio of CH₄:CO₂ for Pt/3%Ce-ZrO₂; CO₂ reforming (♦), 3%O₂ added (■), 7%O₂ added (▲), 9%O₂ added (●).

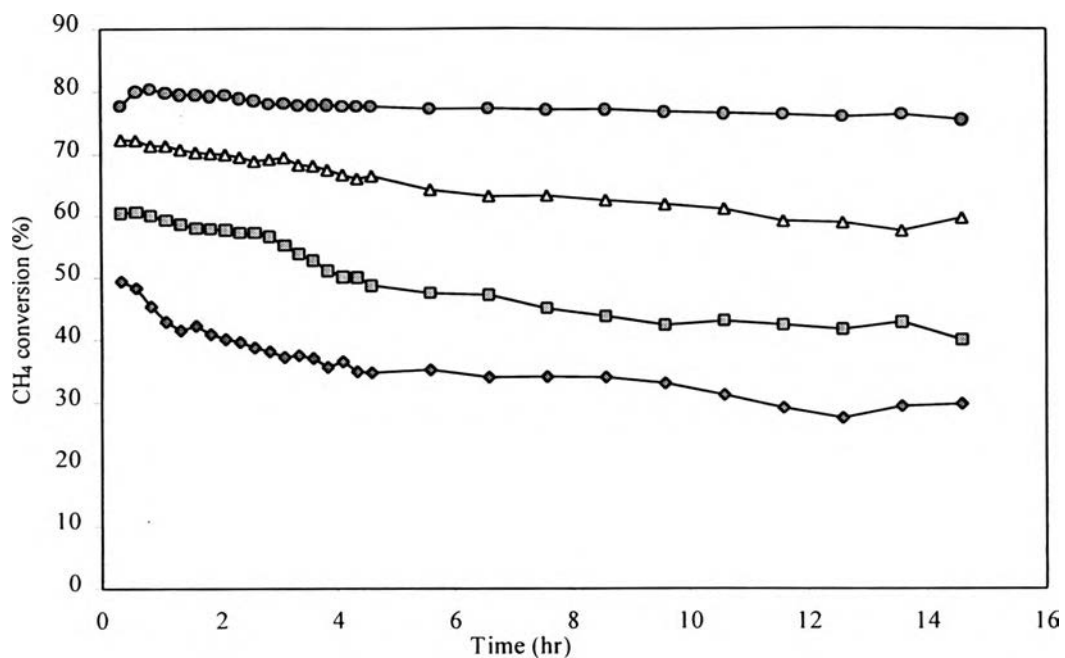


Figure 4.4 CH₄ conversion as a function of time with the 2:1 feed ratio of CH₄:CO₂ for Pt/5%Ce-ZrO₂; CO₂ reforming (♦), 3%O₂ added (■), 7%O₂ added (▲), 9%O₂ added (●).

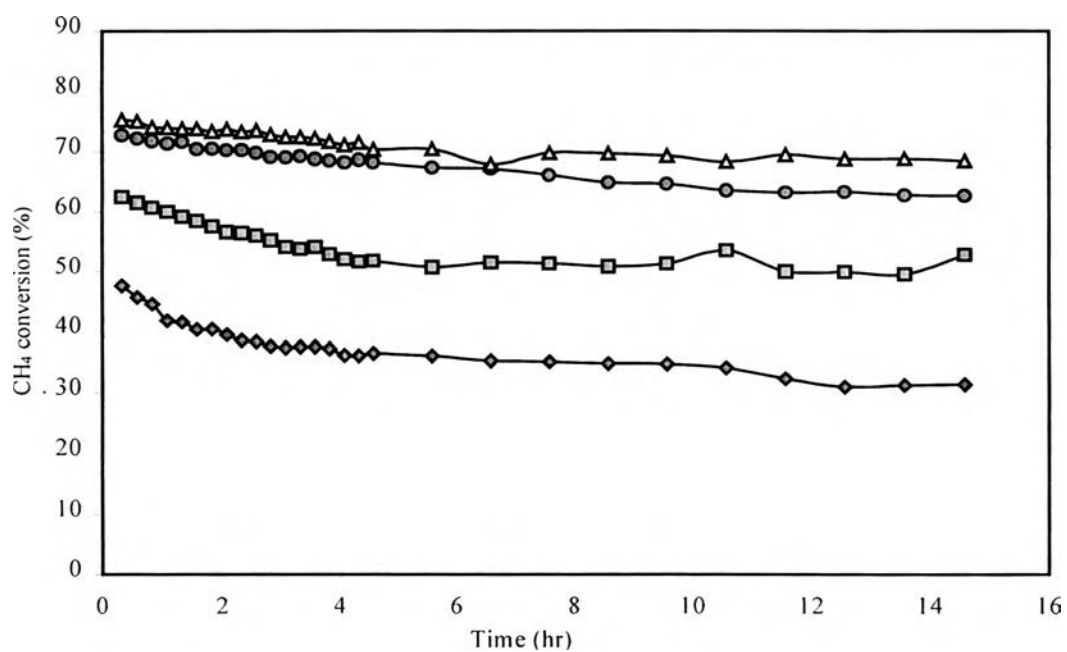


Figure 4.5 CH₄ conversion as a function of time with the 2:1 feed ratio of CH₄:CO₂ for Pt/7%Ce-ZrO₂; CO₂ reforming (♦), 3%O₂ added (■), 7%O₂ added (▲), 9%O₂ added (●).

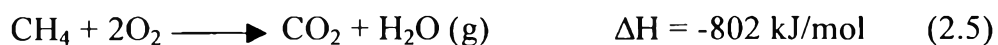
The results from Pt/ZrO₂, Pt/3%Ce-ZrO₂ and Pt/5%Ce-ZrO₂ catalysts suggested that the CH₄ conversion increased as the amount of oxygen increases. However, as shown in Figure 4.5 the CH₄ conversion decreased when oxygen concentration reached 9% for the Pt/7%Ce-ZrO₂ catalyst. This was probably due to the oxidation of Pt metal. It could be postulated that when Ce loading was high, the amount of oxygen released from the substrate, together with 9%O₂ added to the system was high enough to oxidize the Pt metal to become PtO, which is not an active form for CO₂ reforming reaction. The metal oxide is not active for reforming reaction because it does not easily dissociate methane to surface carbon species (Diskin *et al.*, 1998).

Oxygen did not only increase CH₄ conversion but also increased the catalyst stability, which could be observed from the slope of the deactivation curve in Figures 4.2-4.5. The lower the slope, the more stable the catalyst. The effect of oxygen on the catalyst stability could be explained by the “cleaning mechanism” (Stagg *et al.*, 1998). Referring to the cleaning mechanism, oxygen could react with the carbon deposited on the metal particles or dissociate to give an oxygen adsorbed species. This adsorbed oxygen could also react with the carbon on the metal particles. As mentioned earlier, the deactivation of the catalyst by coking is a major problem in designing a suitable catalyst. Therefore, the presence of oxygen, which, in turn, reacted with carbon deposited on the metal particles, results in high stability of the catalysts. Furthermore, the increase in CH₄ conversion or catalyst activity with increasing the amount of oxygen could be viewed by reaction (1.5).



Because the carbon deposition on the metal particles was obtained from CH₄ decomposition, the reaction could be accelerated as the carbon was removed from the metal particles, resulting in higher CH₄ conversion or

catalyst activity. Moreover, CH₄ could be converted by oxygen towards CO₂ and H₂O via CH₄ combustion, reaction (2.5).



CO₂ and H₂O could also react with CH₄ by CO₂ reforming and steam reforming of CH₄, resulting in an overall increase of CH₄ conversion. In addition, steam could play an important role in preventing the catalyst deactivation, by reacting with carbon deposited on metal particles via steam/carbon gasification, reaction (2.2).



Therefore, the addition of oxygen helped to increase catalyst stability and activity. Similar result was also reported earlier by O'Conner and Ross (1998).

TPO data, Figure 4.6, could be used to support the above argument. As shown in the figure, carbon deposition on the metal particles decreased with increasing the oxygen concentration.

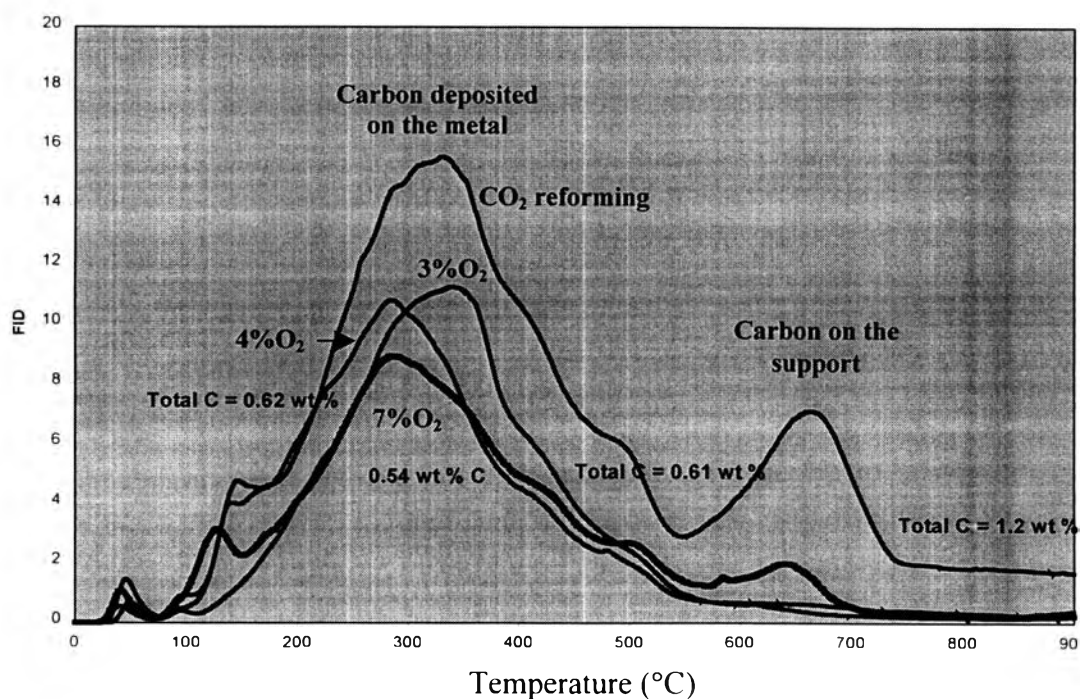


Figure 4.6 TPO data for Pt/5%Ce-ZrO₂ catalysts.

4.2.2 Effects of Ce Concentrations

Effects of Ce loading on the Pt/ZrO₂ catalyst at constant oxygen concentration are shown in Figures 4.7-4.9. From Figures 4.7 and 4.8, when 3% and 7%O₂ were added to the CO₂ reforming reaction, the CH₄ conversion increased as the Ce loading increased. On the other hand, when 9%O₂ was added to the system, Pt/7%Ce-ZrO₂ catalyst gave the lowest CH₄ conversion while Pt/3%Ce-ZrO₂ and Pt/5%Ce-ZrO₂ catalysts gave the highest CH₄ conversion. This could also be explained by the oxidation of Pt metal to PtO as mentioned before. Considering the effects of Ce loading alone, it is indicated that addition of Ce on the Pt/ZrO₂ catalyst increases CH₄ conversion or catalyst activity. This was because the presence of Ce helped to stabilize the tetragonal form of the ZrO₂, which has higher surface areas than the monoclinic form, as shown in Table 4.1.

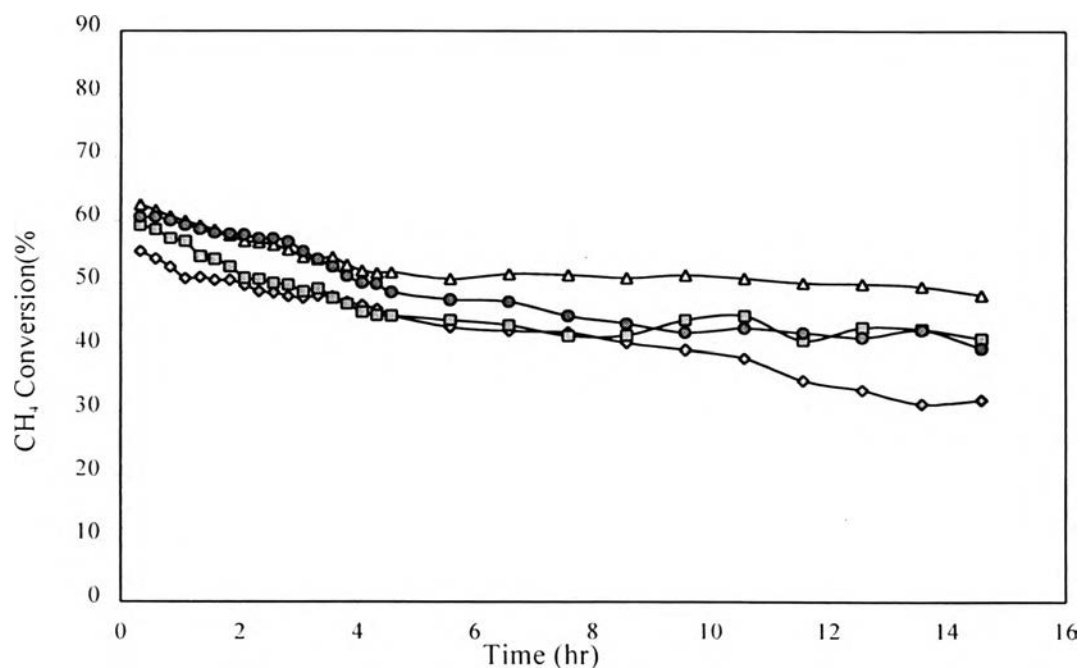


Figure 4.7 CH₄ conversion as a function of time with a 2:1 feed ratio of CH₄:CO₂ with 3%O₂; Pt/ZrO₂ (♦), Pt/3%Ce-ZrO₂ (■), Pt/5%Ce-ZrO₂ (●), Pt/7%Ce-ZrO₂ (▲).

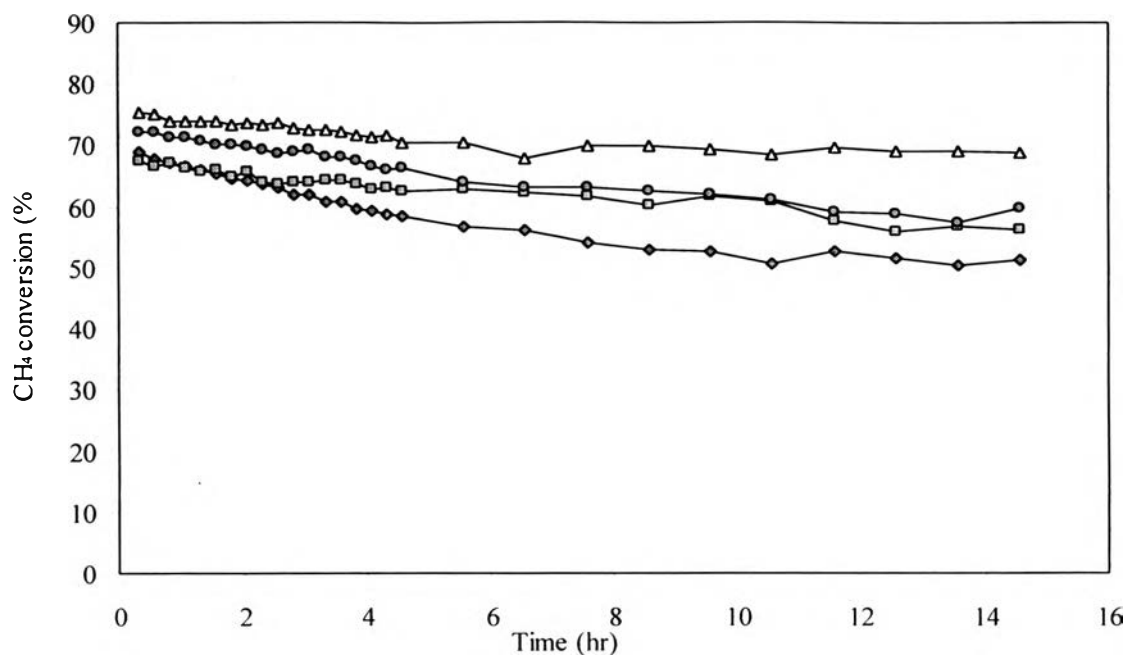


Figure 4.8 CH₄ conversion as a function of time with a 2:1 feed ratio of CH₄:CO₂ with 7%O₂; Pt/ZrO₂ (♦), Pt/3%Ce-ZrO₂ (■), Pt/5%Ce-ZrO₂ (●), Pt/7%Ce-ZrO₂ (▲).

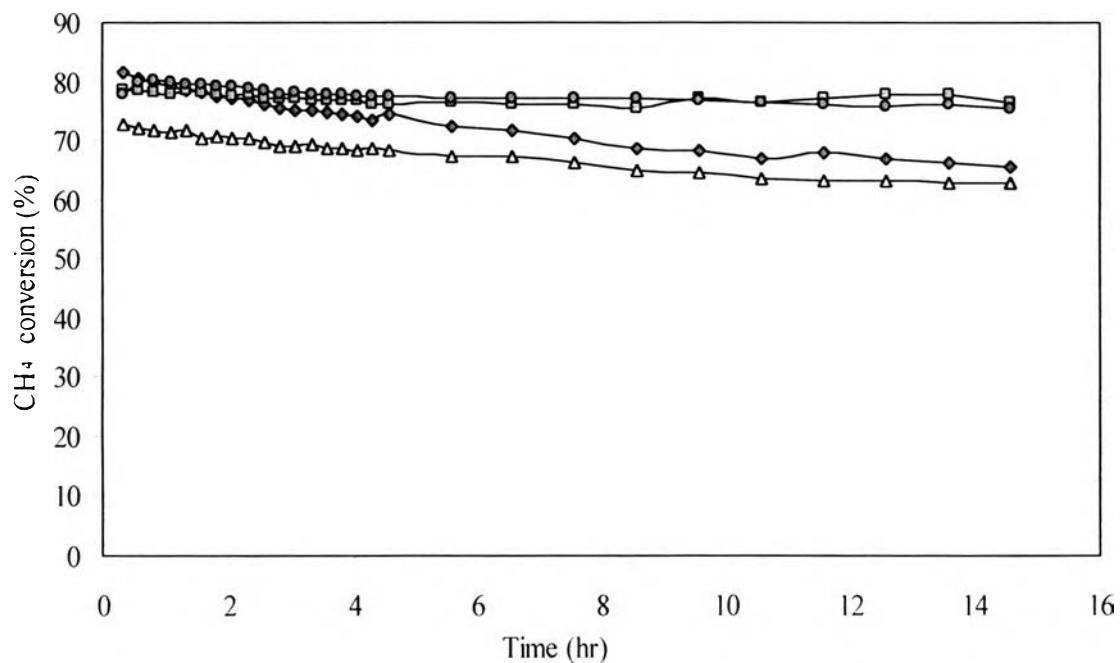


Figure 4.9 CH₄ conversion as a function of time with a 2:1 feed ratio of CH₄:CO₂ with 9%O₂; Pt/ZrO₂ (♦), Pt/3%Ce-ZrO₂ (■), Pt/5%Ce-ZrO₂ (●), Pt/7%Ce-ZrO₂ (▲).

4.3 Product Ratios

As mentioned before, one of the advantages of the CO₂ reforming of methane over the other methods used to produce syngas is that it produces lower H₂:CO ratio, approximately one. Therefore, it is of interest to look at the effects of oxygen and Ce loading on the product ratio. Table 4.2 showed that oxygen concentration had more effect on the product ratio than Ce loading. Because when oxygen was added to the CO₂ reforming, it could accelerate CH₄ decomposition reaction, resulting in a more H₂ production. Furthermore, in the case that CH₄ combustion occurs, steam had an effect on H₂ production by water gas shift reaction (WGS)



From this reaction, the presence of steam resulted in more H₂ production. Hence, the more oxygen addition the more H₂ production or higher H₂-to-CO ratio.

However, the product ratio when oxygen and cerium were present was approximately one.

Table 4.2 H₂:CO ratio produced from various oxygen concentrations and Ce loadings.

O ₂ concentration (%)	Catalyst			
	Pt/ZrO ₂	3%Ce ^a	5%Ce ^b	7%Ce ^c
CO ₂ reforming	1.05-0.80	1.10-0.86	1.03-0.87	1.05-0.87
3%	1.05-0.92	1.18-1.08	1.11-1.01	1.18-1.10
7%	1.30-1.25	1.22-1.18	1.25-1.23	1.10-1.05
9%	1.30-1.21	1.23-1.21	1.25-1.24	1.21-1.15

^a Pt/3%Ce-ZrO₂ catalyst, ^b Pt/5%Ce-ZrO₂ catalyst, ^c Pt/7%Ce-ZrO₂ catalyst