



## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Reaction Conditions

The main purpose of this part is to select the most appropriate conditions for the catalyst deactivation study. Two parameters, CH<sub>4</sub>/CO<sub>2</sub> ratio and GHSV, were investigated.

##### 4.1.1 Effects of CH<sub>4</sub>/CO<sub>2</sub> Ratio

Figure 4.1 shows the conversion of methane as a function of time on stream at various CH<sub>4</sub>/CO<sub>2</sub> feed ratios from 1/2 to 3/1 by using Pt/5CeZ at a GHSV of 477500 h<sup>-1</sup>. Obviously, the 1/2 and 1/1 ratios had significantly high stability with only the slight drop within 8 hours of reaction time, whereas the 2/1 and 3/1 ratios gave lower conversions and significantly dropped especially for the first three hours of reaction time. The explanation for these results could be considered from methane decomposition reaction (2.1) and carbon dioxide dissociation reaction (4.1).

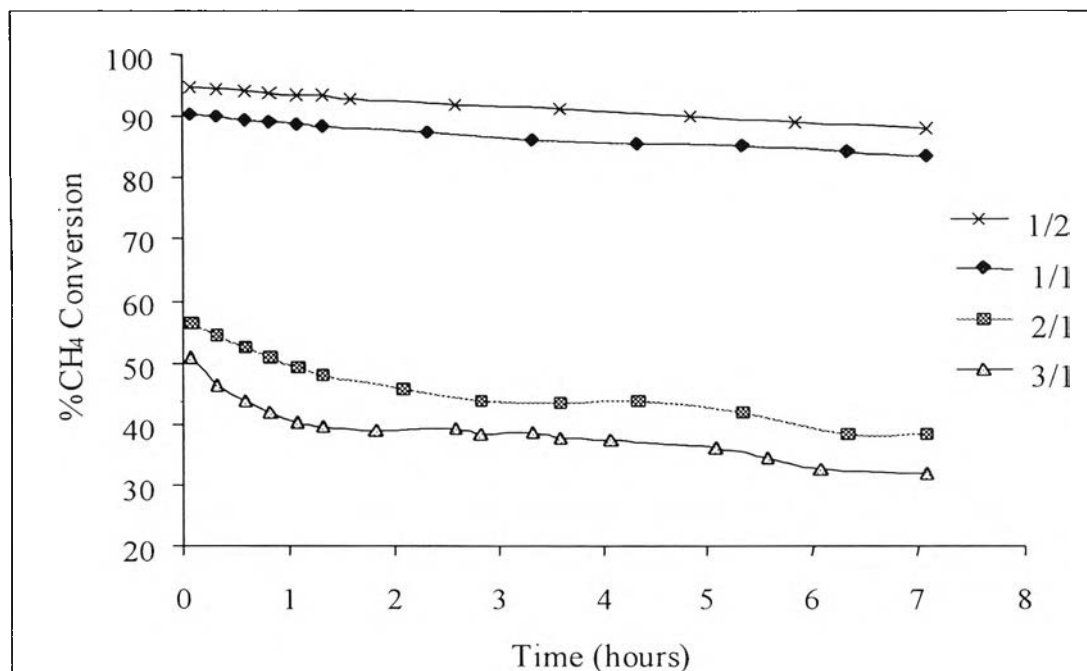
Methane decomposition:



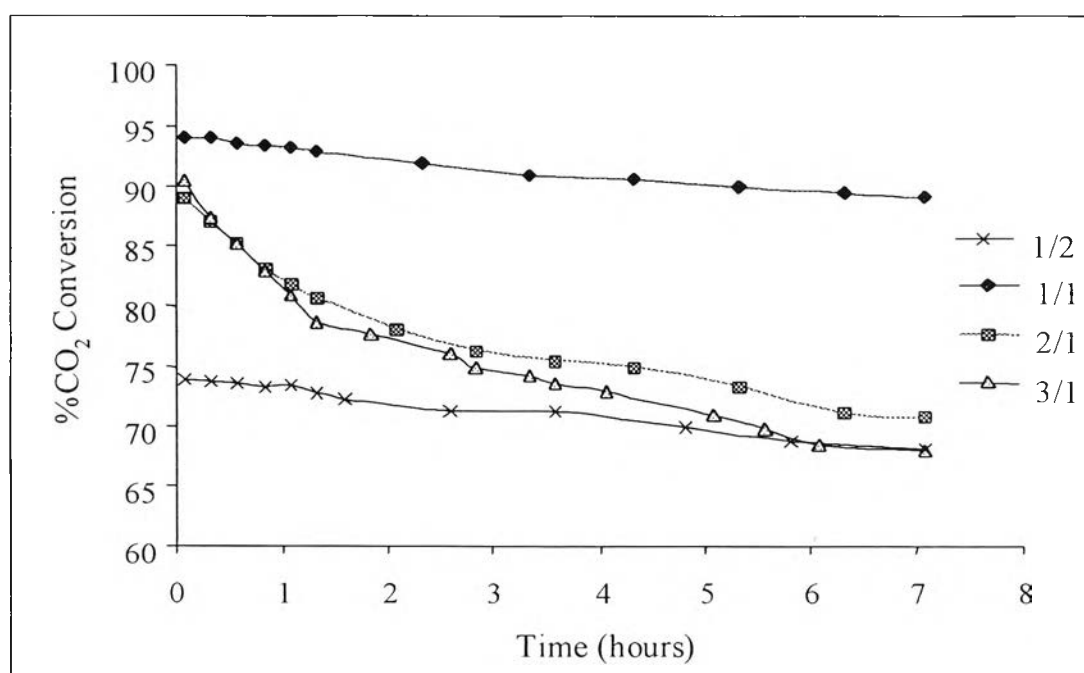
Carbon dioxide dissociation:



From the above reactions, when the ratio of CH<sub>4</sub> to CO<sub>2</sub> was greater than unity, the rate of reaction (2.1) exceeded the rate of reaction (4.1), so there were some net carbon deposition occurred on the metal particles, inducing catalyst deactivation.



**Figure 4.1** CH<sub>4</sub> conversion as a function of time for Pt/5CeZ at a GHSV of 477500 h<sup>-1</sup> at various CH<sub>4</sub>/CO<sub>2</sub> feed ratios

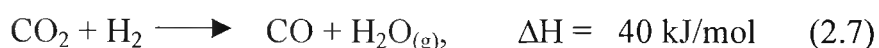


**Figure 4.2** CO<sub>2</sub> conversion as a function of time for Pt/5CeZ at a GHSV of 477500 h<sup>-1</sup> at various CH<sub>4</sub>/CO<sub>2</sub> feed ratios

The results of the CO<sub>2</sub> conversions with time on stream at various CH<sub>4</sub>/CO<sub>2</sub> ratios, as shown in Figure 4.2, show the same trend as those from the CH<sub>4</sub> conversion. However, the lowest conversion of the 1/2 ratio was in contrast to the CH<sub>4</sub> conversion. Since the reaction was based on reaction (1.1), in which the stoichiometric ratio of CH<sub>4</sub> to CO<sub>2</sub> was 1 to 1, but the reactants were fed in the ratio of 1 to 2 (CH<sub>4</sub> to CO<sub>2</sub>), so CO<sub>2</sub> excess remained in the system. This, together with some non-reacted CO<sub>2</sub>, consequently, resulted in lower conversion.

Figure 4.3 shows the H<sub>2</sub>/CO product ratios versus time. The rather stable product ratios obtained from 1/2 and 1/1 feed ratios and high deactivation rate of 2/1 and 3/1 reactant ratios could be explained in the similar manner as in the case of CH<sub>4</sub> and CO<sub>2</sub> conversions. The H<sub>2</sub>/CO ratio of 1/1 was close to unity, while it was lower than unity as CO<sub>2</sub> in the feed was higher (CH<sub>4</sub>/CO<sub>2</sub> ratio of 1/2), indicating that the H<sub>2</sub> consumption resulting from the reverse water gas shift reaction (2.7) increased due to the availability of CO<sub>2</sub>.

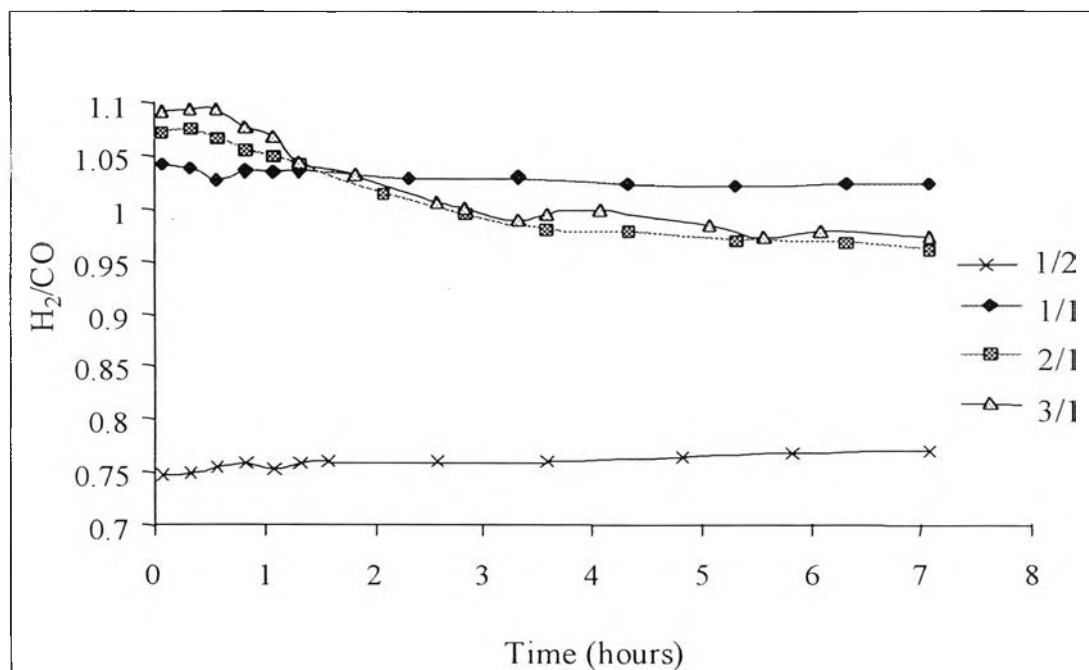
Reverse water gas shift:



For the reactant ratios of 2/1 and 3/1, the initial H<sub>2</sub>/CO product ratios were greater than unity. This might be due to the higher rate of reaction (2.1) than reaction (4.1). However, these product ratios decreased with time on stream because the net carbon depositions on the metal surface repressed the decomposition of CH<sub>4</sub> and resulted in the lower H<sub>2</sub> production.

In summary, the higher CH<sub>4</sub>/CO<sub>2</sub> ratios increased the catalyst deactivation by favoring the carbon formation. These conditions were suitable for investigating the role of the promoters on deactivation over relatively short

reaction time. Because the reactant ratios of 2/1 and 3/1 yielded about the same rate of deactivation, the ratio of 2/1 was selected in this work.



**Figure 4.3**  $H_2/CO$  product ratio as a function of time for Pt/5CeZ at a GHSV of  $477500 \text{ h}^{-1}$  at various  $CH_4/CO_2$  feed ratios

#### 4.1.2 Effects of GHSV

GHSV is the fraction of a total flow rate of inlet gas and volume of a catalyst in a reactor as shown in Equation 3.1.

$$GHSV = \frac{v}{\pi r^2 h} \quad (3.1)$$

where

$v$  = the total flow rate of inlet gas ( $\text{cm}^3/\text{h}$ );

$r$  = the inlet diameter of reactor (cm);

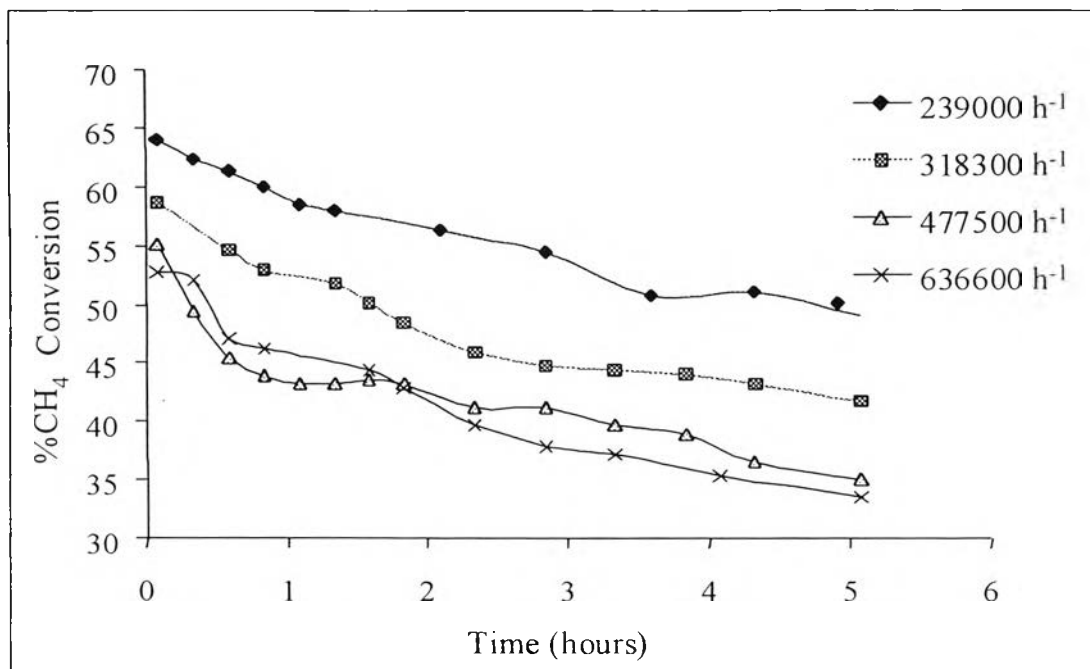
$h$  = the bed height (cm).

From the above equation, a higher GHSV can be obtained with a low volume of catalyst in a reactor or a high total flow rate of inlet gas. The results from Figures 4.4 and 4.5 showed that the increase in GHSV decreased both CH<sub>4</sub> and CO<sub>2</sub> conversions. The GHSV of 477500 h<sup>-1</sup> was considered to be the most suitable value in this work because the conversions were neither too low nor too high to compare the behaviors of the catalysts in the next part. Moreover, the catalyst deactivation could be clearly observed in a short period of time.

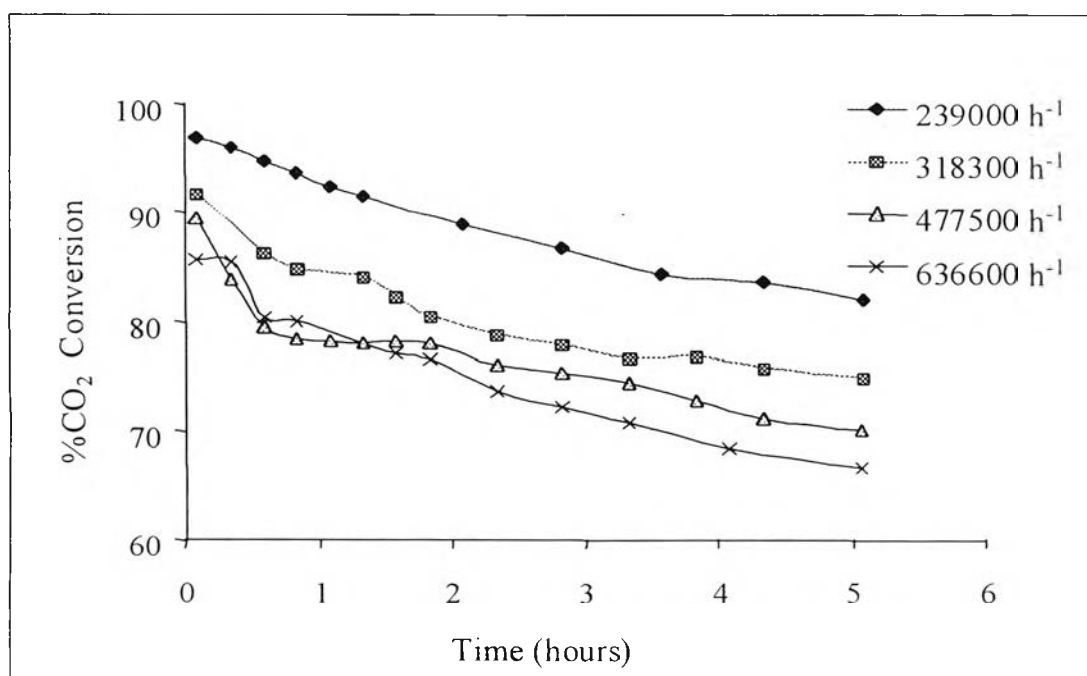
## 4.2 Catalyst Activity and Stability

### 4.2.1 Effects of Ce

Table 4.1 shows BET surface area, pore volume, and metal dispersion of the unpromoted catalyst and Ce-promoted catalysts. It could be clearly seen from the results that all Ce-promoted catalysts had higher surface area, pore volume, and %metal dispersion than the unpromoted catalyst. The BET surface area could be confirmed by the X-ray diffraction result, Figure 4.6. The tetragonal form of zirconia is represented by the star (★) while the dot (●) represents the monoclinic form. The result showed that, in the unpromoted catalyst, zirconia was monoclinic. The tetragonal form was obtained by ceria promotion. For Pt/3CeZ, partial stabilization of the tetragonal form with a small fraction of monoclinic form was presented, while for Pt/5CeZ, Pt/7CeZ, and Pt/9CeZ, complete tetragonal stabilization was observed.



**Figure 4.4** CH<sub>4</sub> conversion as a function of time for Pt/5CeZ at a CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 at various GHSV



**Figure 4.5** CO<sub>2</sub> conversion as a function of time for Pt/5CeZ at a CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 at various GHSV

**Table 4.1** BET surface area, pore volume, and %metal dispersion of the Ce-promoted catalysts compared with unpromoted catalyst at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>

Catalyst	Surface area (m <sup>2</sup> /g)	Pore Volume x 10 <sup>-2</sup> (cc/g)	Metal dispersion (%)
Pt/Z	35.52	1.212	8.77
Pt/3CeZ	39.49	1.354	9.74
Pt/5CeZ	40.16	1.464	11.56
Pt/7CeZ	43.22	1.601	10.06
Pt/9CeZ	41.33	1.547	8.88

Actually, zirconia has three crystallographic forms; cubic, tetragonal, and monoclinic. The cubic form is stable at very high temperatures, so it is not important in this system. The tetragonal form is stable at temperatures higher than 1000°C, which are also higher than the reaction temperature in this work. At room temperature to about 1000°C, the stable form is monoclinic. This is the most stable phase at any temperatures in this work. When this stable phase is formed, the zirconia loses surface area. However, during the catalyst preparation, a metastable tetragonal is formed. This metastable phase has a high surface area, but it is not totally stable. Therefore, if starting with the metastable tetragonal form, which has a high surface area and then heat up to 800°C, the crystallographic form of the zirconia will go to the monoclinic phase and lose its surface area. However, adding some additives can anchor the surface area and retard the transition from the tetragonal to monoclinic form, so the surface area can be preserved. This leads to the conclusion that the addition of Ce to ZrO<sub>2</sub> increases the catalyst surface area by stabilizing the tetragonal form of zirconia.

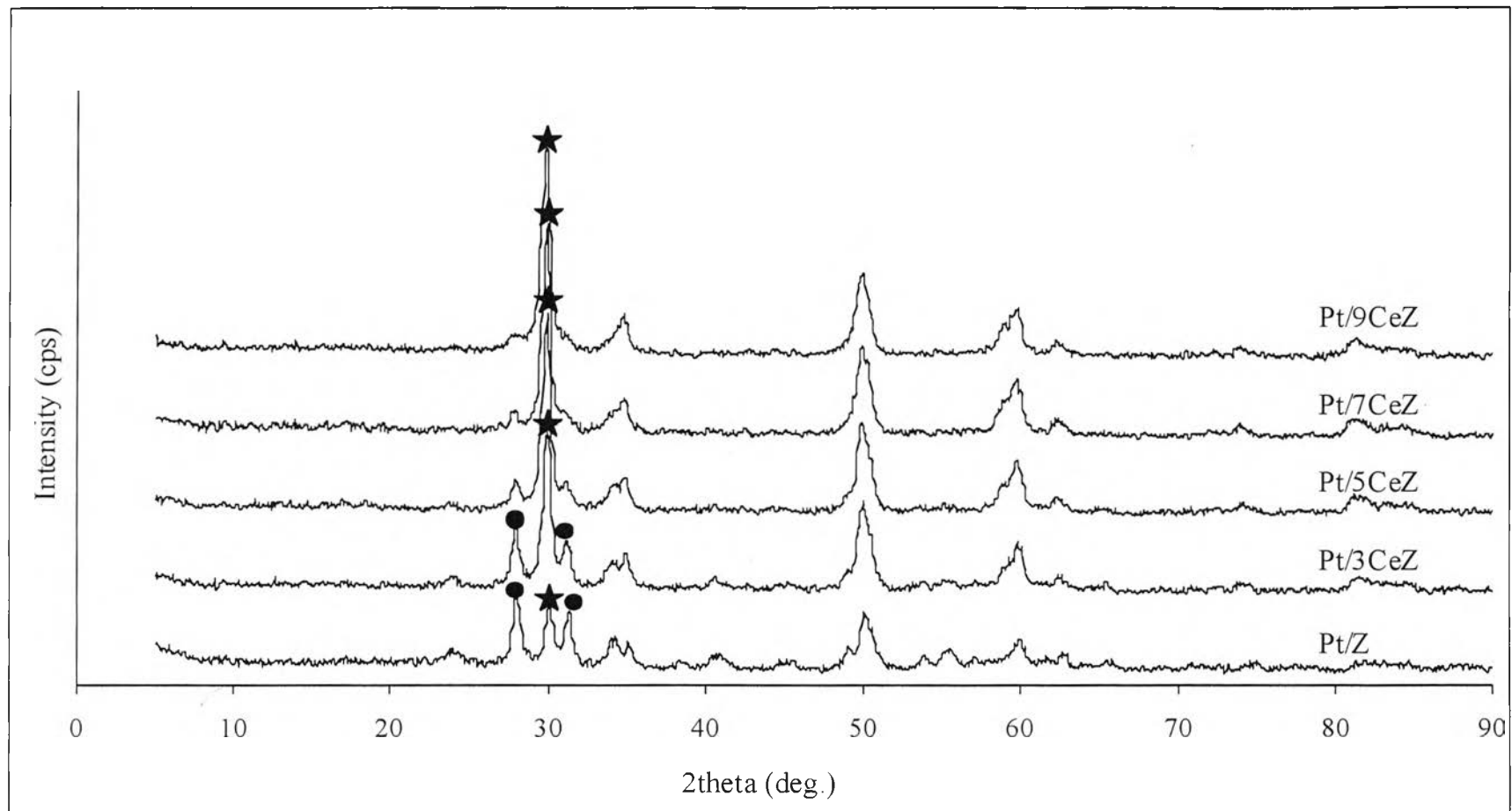
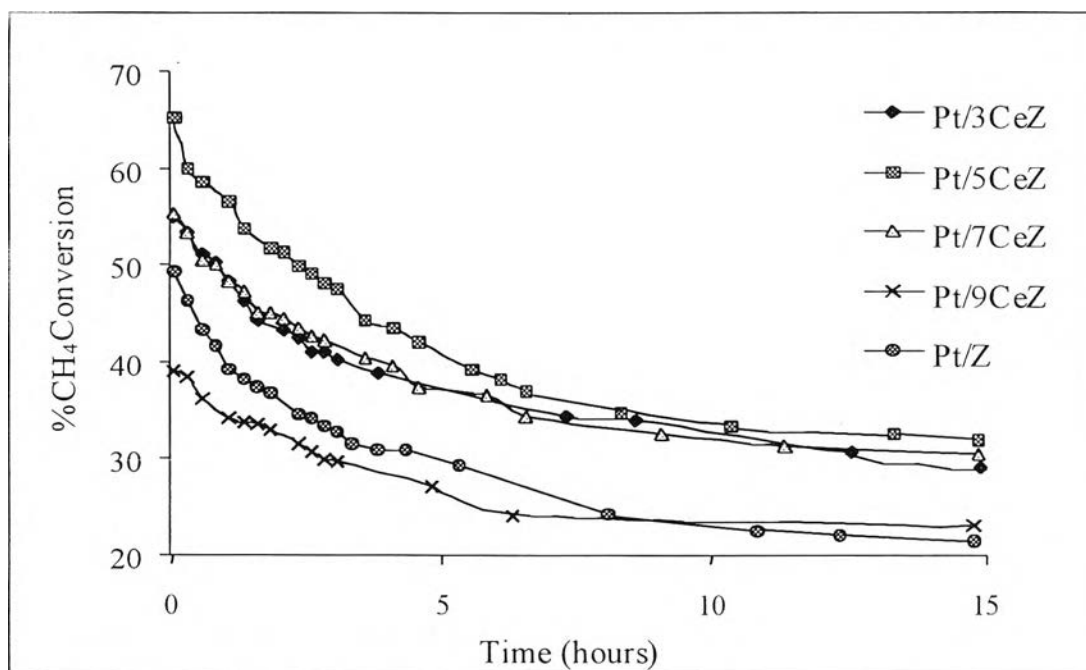


Figure 4.6 XRD patterns for Ce-promoted catalysts compared with unpromoted catalyst; tetragonal form (★), monoclinic form (●)



As seen in Table 4.1, with increasing Ce concentration, the surface area increased. However, the slight drop in the surface area of Pt/9CeZ compared to Pt/7CeZ might be due to some pore blocking. This implied that the catalyst prepared by impregnation method had the limitation in loading capacity.



**Figure 4.7** CH<sub>4</sub> conversion as a function of time for Ce-promoted catalysts compared with unpromoted catalyst at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>

The catalytic activity and stability of the Ce-promoted catalysts compared with the unpromoted catalyst are displayed in Figure 4.7. All of Ce-promoted catalysts had higher conversion and lower deactivation than unpromoted catalysts. Although Pt/9CeZ had the lower initial conversion than Pt/Z, but within 10 hours of reaction time, the conversion was higher. This clearly indicated that Pt/CeZ had the higher activity and stability than Pt/Z. Considering the effect of Ce concentration, Pt/5CeZ had the highest conversion. Since Pt/3CeZ had the lower surface area and %metal dispersions

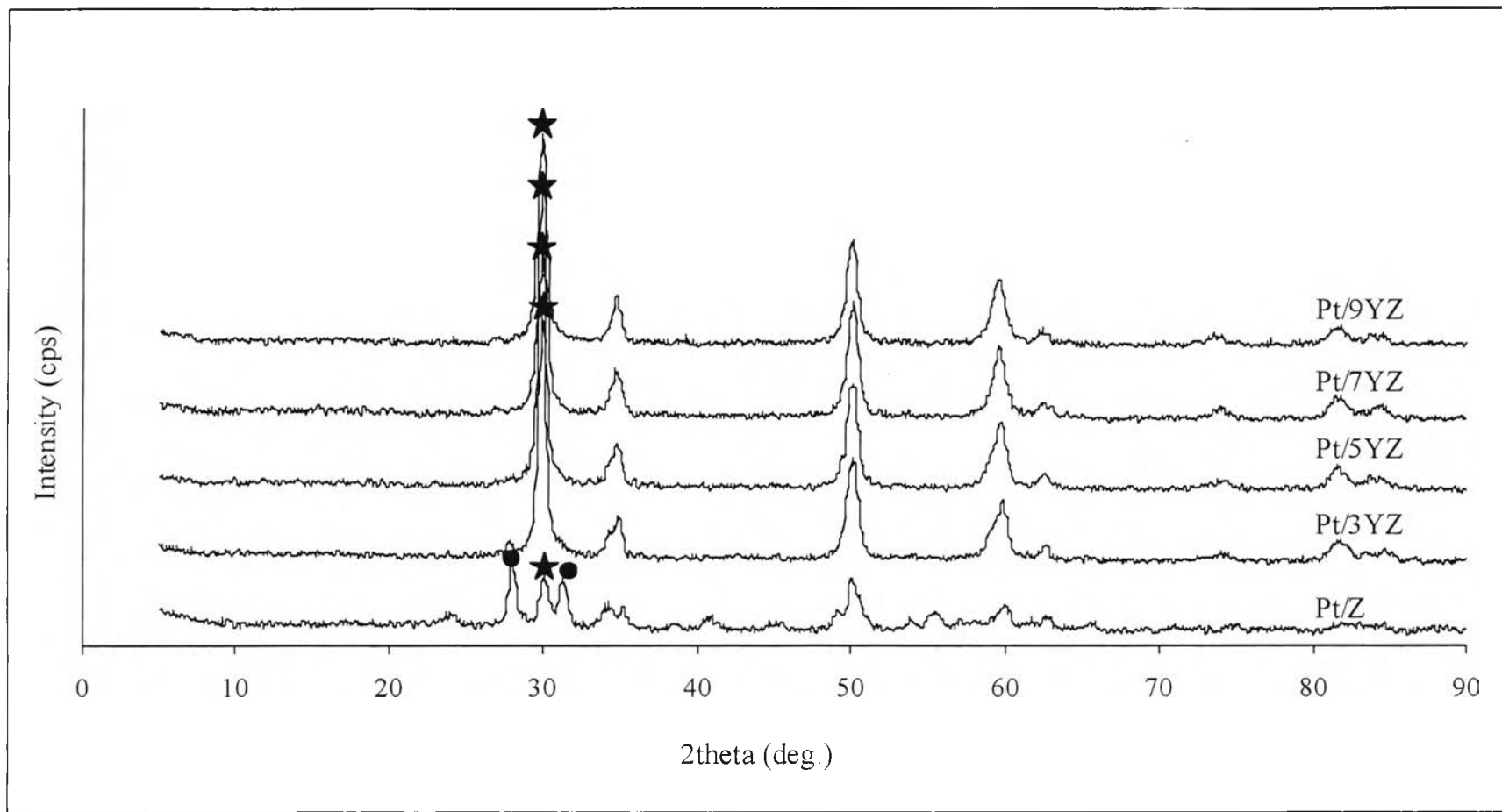
than Pt/5CeZ, the conversion were lower. Although Pt/7CeZ and Pt/9CeZ had higher surface area than Pt/5CeZ, but the %metal dispersion were lower, so the conversions were lower. The decrease in %metal dispersion with an increase in Ce concentration might be a result of the adding too large amount of Ce, which covered the most surface area of ZrO<sub>2</sub> support. This led to suppress Pt loading ability and decreased %metal dispersion.

#### 4.2.2 Effects of Y

The BET surface area and pore volume of Y-promoted catalyst at various Y concentrations compared with the unpromoted catalyst are shown in Table 4.2. The results demonstrated that all Y-promoted catalysts had higher surface area and pore volume than unpromoted catalyst. Results from the XRD study in Figure 4.8 showed that yttrium addition effectively stabilized the tetragonal form of zirconia, as only the tetragonal form for all Y-promoted catalysts was observed. Table 4.2 also displays the increase in surface area and pore volume when Y concentration increased. However, the effect of pore blocking also occurred for this type of promoter. It could be seen that Pt/9YZ had a slightly drop in surface area and pore volume.

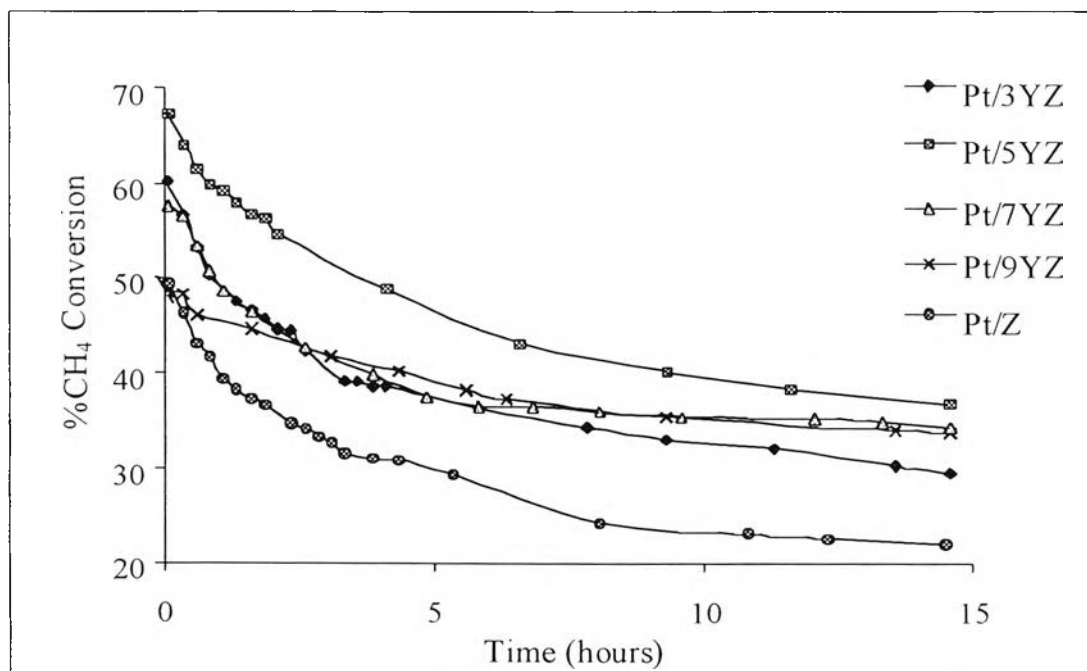
**Table 4.2** BET surface area and pore volume of Y-promoted catalysts compared with unpromoted catalyst at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>

Catalyst	Surface area (m <sup>2</sup> /g)	Pore volume x 10 <sup>-2</sup> (cc/g)
Pt/Z	35.52	1.212
Pt/3YZ	39.61	1.475
Pt/5YZ	41.06	1.503
Pt/7YZ	47.60	1.714
Pt/9YZ	46.18	1.647



**Figure 4.8** XRD patterns for Y-promoted catalysts compared with unpromoted catalyst; tetragonal form (★), monoclinic form (●)

The  $\text{CH}_4$  conversion as a function of time on stream is plotted in Figure 4.9. It could be clearly seen that Pt/YZ catalysts yielded higher conversion than Pt/Z catalyst. At various Y concentrations, the initial  $\text{CH}_4$  conversions were in the following order: Pt/5YZ > Pt/3YZ > Pt/7YZ > Pt/9YZ. These results could be explained in the same way as in the case of Pt/CeZ that too high amount of promoter loading would suppress the ability of Pt loading.



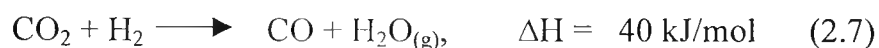
**Figure 4.9**  $\text{CH}_4$  conversion as a function of time for Y-promoted catalysts compared with unpromoted catalyst at  $\text{CH}_4/\text{CO}_2$  ratio of 2/1 and GHSV of  $477500 \text{ h}^{-1}$

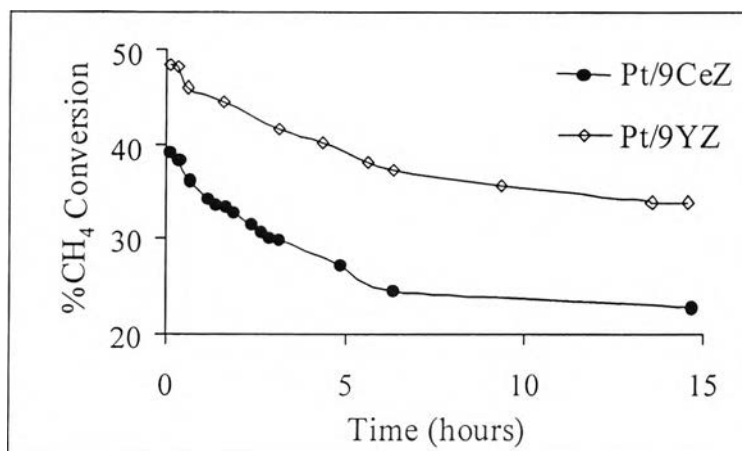
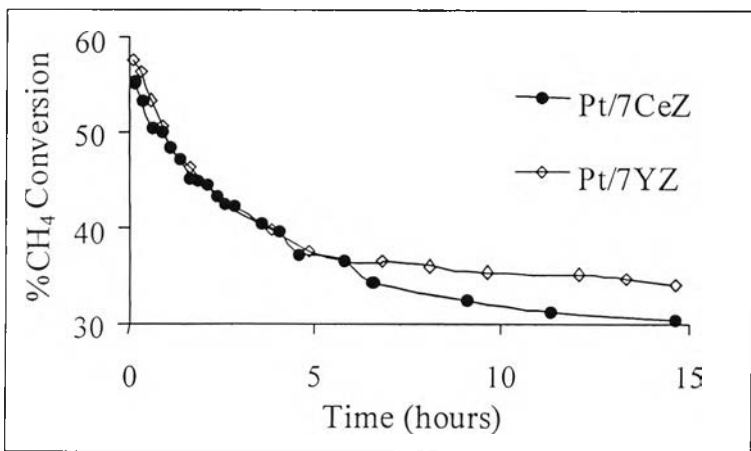
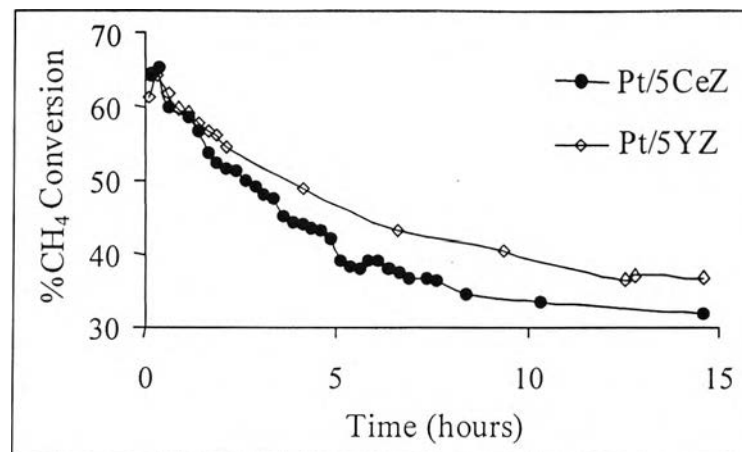
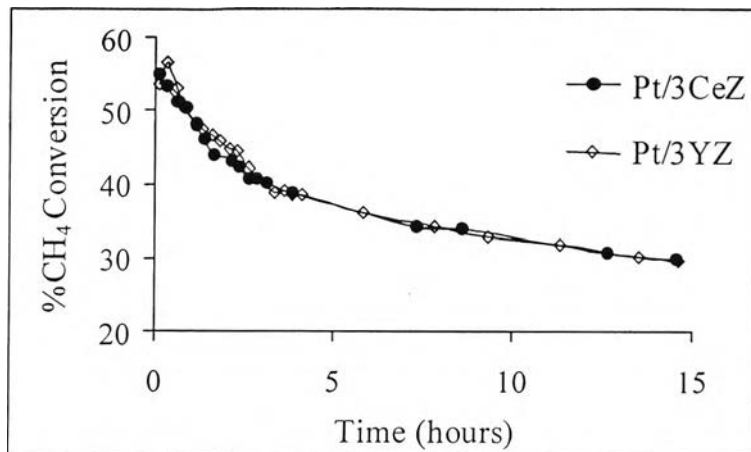
It is interesting to note from the results of both Ce- and Y-promoted catalysts that the rate of catalyst deactivation decreased with increasing promoter concentration. It could be seen from Pt/9CeZ and Pt/9YZ that they had very low deactivation rates and are stable within only 5-6 hours of reaction time. This clearly indicated that the addition of promoters helped

increase the rate of catalyst stabilization. These might be due to oxygen storage properties of both  $\text{CeO}_2$  and  $\text{Y}_2\text{O}_3$ , which could release oxygen to react with carbon deposition on the metal particle as shown in Figure 2.1. Therefore, besides the support and  $\text{CO}_2$  reactant gas, these two promoters are another possible source of oxygen that can promote the cleaning mechanism, and consequently, increase the catalyst life.

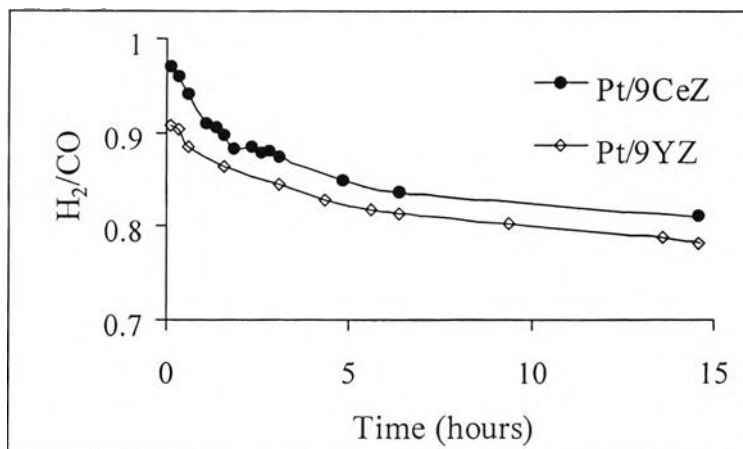
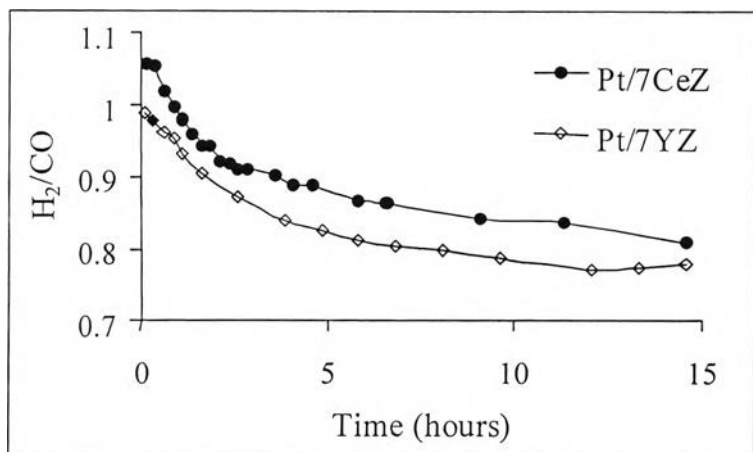
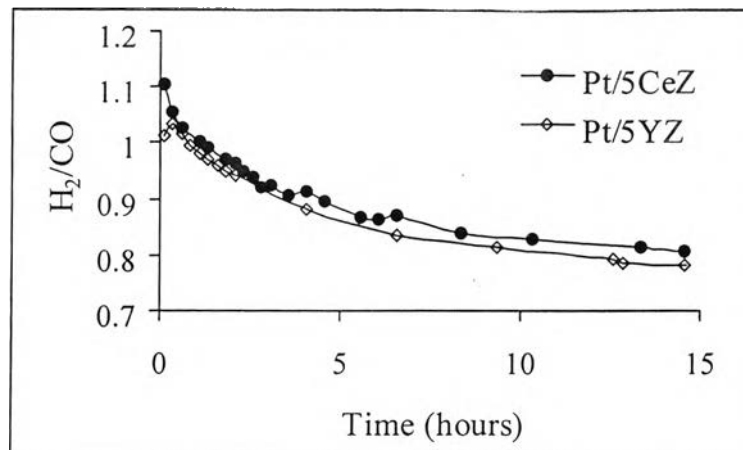
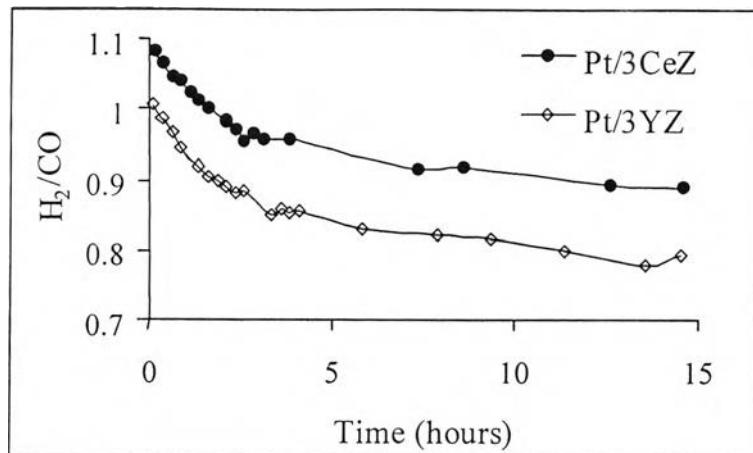
Comparison between Ce- and Y-promoted catalysts from Table 4.1 and Table 4.2 indicates that, when the promoter concentration increased, Y-promoted catalysts had higher surface area. It was found that although the surface area of Pt/3YZ was nearly the same as that of Pt/3CeZ, Pt/7YZ had higher surface area than Pt/7CeZ. The comparisons between Ce- and Y-promoted catalysts in the form of  $\text{CH}_4$  conversions are shown in Figures 4.10. Corresponding to the results from surface area, the result shows that Y-promoted catalysts had higher  $\text{CH}_4$  conversion than Ce-promoted catalysts, especially at high promoter concentrations. However, the results were in contrast to the  $\text{H}_2/\text{CO}$  product ratio, Figure 4.11. It was found that Y-promoted catalysts had lower  $\text{H}_2/\text{CO}$  product ratio than Ce-promoted catalysts. From expectation, lower in  $\text{H}_2/\text{CO}$  product ratio of Y-promoted catalysts might be due to higher consumption of hydrogen via reverse water gas shift reaction (2.7). This led to the conclusion that Y-promoted catalysts had higher trend to produce water than Ce-promoted catalysts.

Reverse water gas shift:





**Figure 4.10** CH<sub>4</sub> conversion as a function of time for Ce-promoted catalysts compared with Y-promoted catalysts at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>



**Figure 4.11** H<sub>2</sub>/CO product ratio as a function of time for Ce-promoted catalysts compared with Y-promoted catalysts at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>

### 4.2.3 Effects of Mixed-promoter

#### 4.2.3.1 *Impregnation Catalyst*

Table 4.3 shows the BET surface area and pore volume of mixed-Ce-Ypromoter catalysts prepared by impregnation technique. The results showed that all mixed-promoter catalysts had higher surface area and pore volume than the unpromoted catalyst. Compared to the pure promoted catalysts, the results from the BET surface area of Ce- and Y-promoted catalysts in Tables 4.1 and 4.2 suggest that 7% of promoter loading gave the maximum surface area, while higher loading decreased surface area because of pore blocking effect. For mixed-promoter catalysts, the effect of pore blocking still existed at high amount of promoter, but the maximum capacity of promoter loading increased. It could be seen from Table 4.3 that Pt/5-5im, which had the total promoter loading about 10%, still had high surface area and pore volume. This implied that mixing of Ce and Y together helped improve the loading capacity of each other.

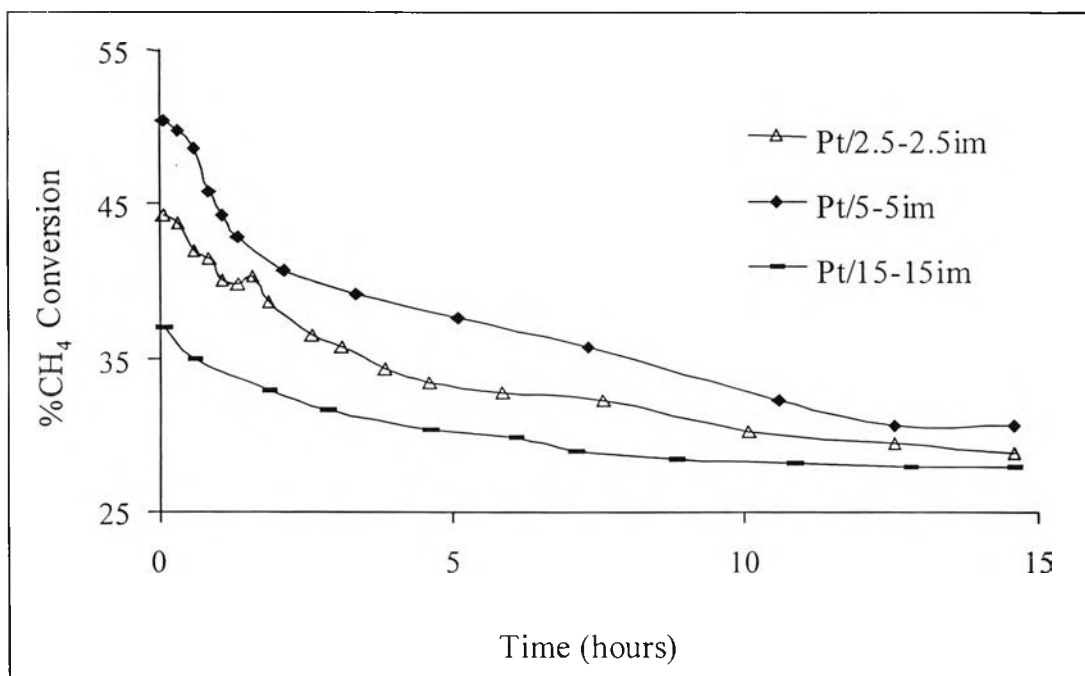
**Table 4.3** BET surface area and pore volume of mixed-promoter catalysts prepared by impregnation technique compared with unpromoted catalyst at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>

Catalyst	Surface area (m <sup>2</sup> /g)	Pore volume x 10 <sup>-2</sup> (cc/g)
Pt/Z	35.52	1.212
Pt/2.5-2.5im	41.21	1.513
Pt/5-5im	50.13	1.790
Pt/15-15im	42.62	1.561

Figure 4.12 shows the activity of the mixed-promoter catalysts prepared by the impregnation technique at various promoter concentrations. The results showed that, since Pt/5-5im had the highest

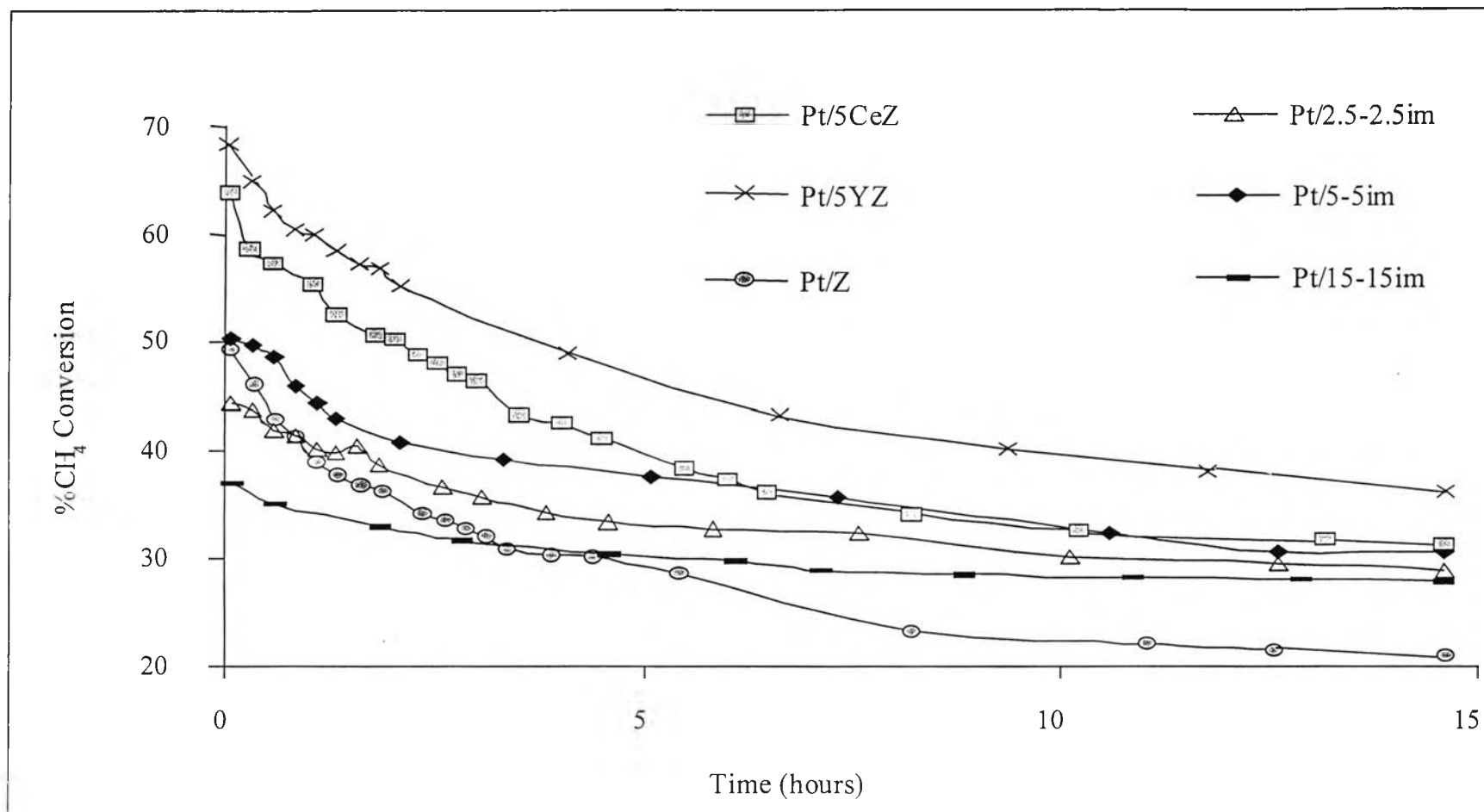


surface area, it had the highest conversion. Moreover, it was found that the higher the promoter loading, the higher the catalytic stability. It could be seen that Pt/15-15im had the lowest rate of deactivation.



**Figure 4.12** CH<sub>4</sub> conversion as a function of time for mixed-promoter catalysts prepared by impregnation technique at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>

Comparison between the activity of the mixed-promoter catalysts with the Pt/Z, Pt/5CeZ, and Pt/5YZ are shown in Figure 4.13. The results indicated that all of mixed-promoter catalysts had higher activity and stability than unpromoted catalyst. Although some of them had lower initial conversion, but within a few hours of reaction time, the conversions were higher. Compared with Pt/5CeZ and Pt/5YZ, although Pt/5-5im had the lower conversion, but it could stabilize within 15 hours of time on stream, while the deactivation of Pt/5CeZ and Pt/5YZ still proceeded.



**Figure 4.13** CH<sub>4</sub> conversion as a function of time for mixed-promoter catalysts prepared by impregnation technique compared with Pt/Z, Pt/5CeZ, and Pt/5YZ catalysts at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>

#### 4.2.3.2 Co-precipitation Catalyst

Table 4.4 shows the BET surface area and pore volume of mixed-promoter catalysts prepared by co-precipitation technique. It was found that the surface area and pore volume increased with increasing promoter concentration. The pore blocking effect was not observed even though the total promoter concentration was about 30%. However, it could not be concluded that co-precipitation catalyst did not have an effect of pore blocking. It could be summarized that the co-precipitation catalyst had higher promoter loading capacity than the impregnation catalyst.

**Table 4.4** BET surface area and pore volume of mixed-promoter catalysts prepared by co-precipitation technique at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>

Catalyst	Surface area (m <sup>2</sup> /g)	Pore volume x 10 <sup>-2</sup> (cc/g)
Pt/5-5co(800)	24.98	0.828
Pt/15-15co(800)	32.46	1.138
Pt/5-5co(600)	61.98	2.082
Pt/15-15co(600)	75.70	2.460

In fact, the co-precipitation catalyst has a well mixed structure between support and promoter because, in this method, both of them dissolve together in solution and may form chemical bonds before precipitating out. On the other hand, for the impregnation catalyst, the promoter solution is physically loaded to the pore of the support, so it has a greater chance to encounter the pore blocking effect.

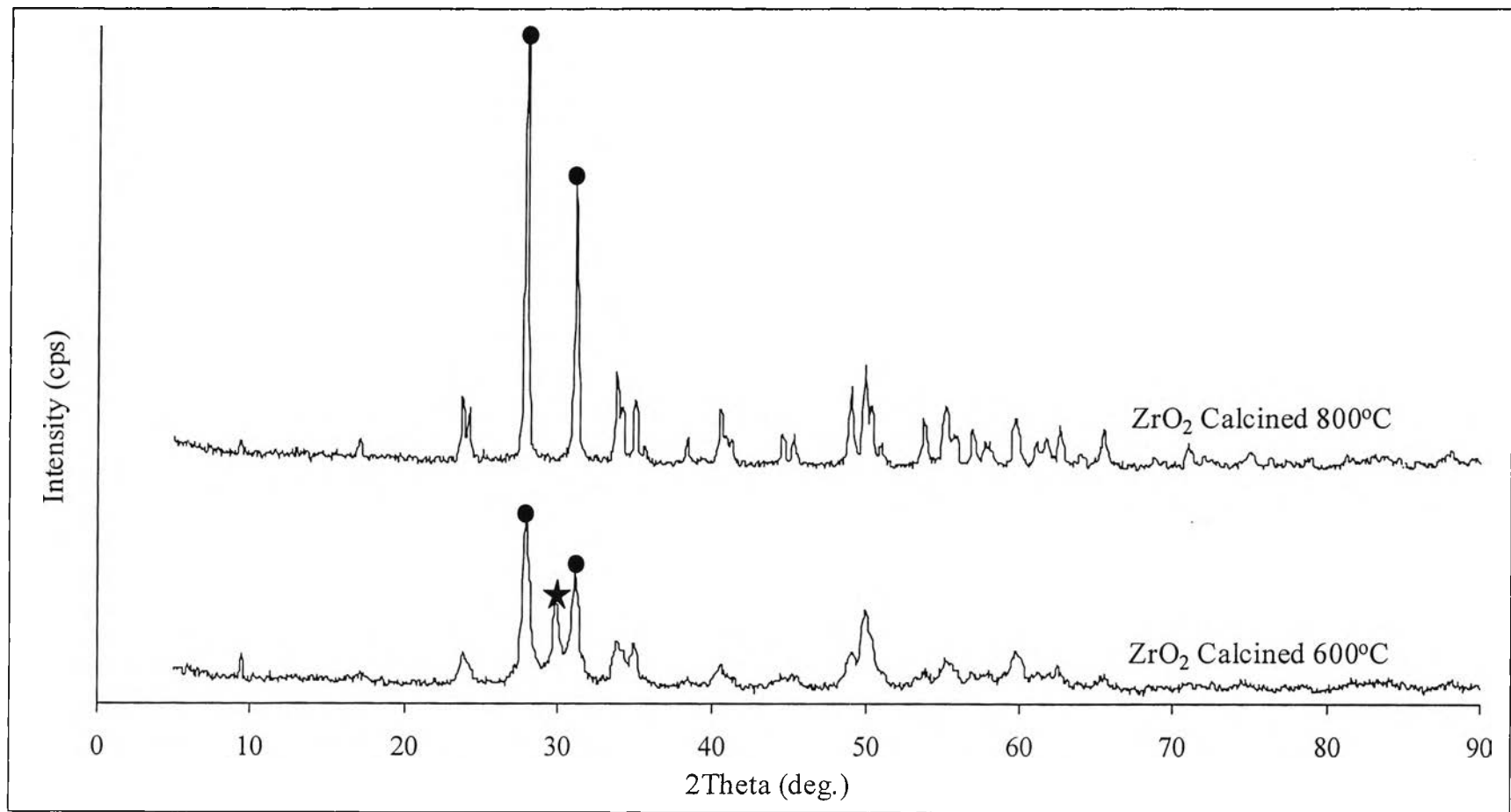
The effect of calcination temperature was also studied for the co-precipitation catalysts. As seen in Table 4.4, the co-precipitation catalysts when calcination at 800°C resulted in very low surface area and pore

volume. On the other hand, when the calcination temperature was decreased to 600°C, the surface area and pore volume of the catalysts increased, significantly. The XRD patterns in Figure 4.14 showed almost completely monoclinic form of ZrO<sub>2</sub> after calcination at 800°C, while the tetragonal form was observed after calcination at 600°C. This meant that the crystallographic form of ZrO<sub>2</sub> prepared by co-precipitation technique was changed from tetragonal to monoclinic in the temperature range of about 600-800°C.

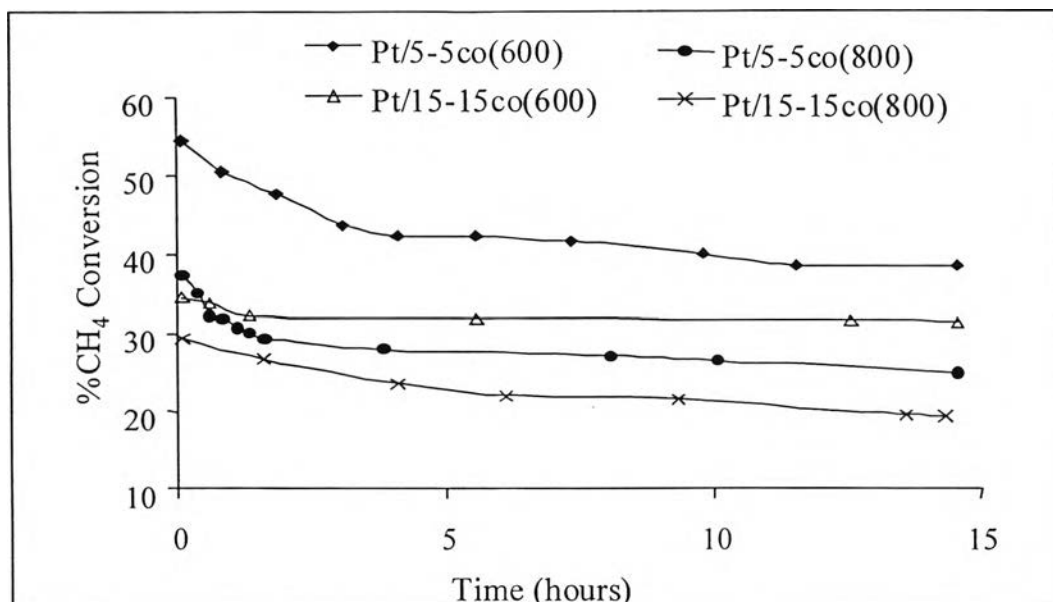
The CH<sub>4</sub> conversions of mixed-promoter catalysts prepared by co-precipitation technique calcination at 600°C and 800°C as a function of time are shown in Figure 4.15. Corresponding to the surface area, the results showed that co-precipitation catalysts calcination at 600°C had higher activity and stability than those calcination at 800°C.

Comparison of the mixed-promoter catalysts prepared by the impregnation and co-precipitation techniques is shown in Figure 4.16. It could be seen that the co-precipitation catalysts had higher activity and stability than impregnation catalysts where Pt/5-5co(600) had the highest activity and Pt/15-15co(600) had the highest stability. This meant that the well-mixed structure of support and promoter of the co-precipitation catalyst increased the capacity of metal loading, leading to high catalytic activity. The rate of oxygen released from the support and promoter to promote the cleaning mechanism might increase, so the co-precipitation catalyst had high stability.

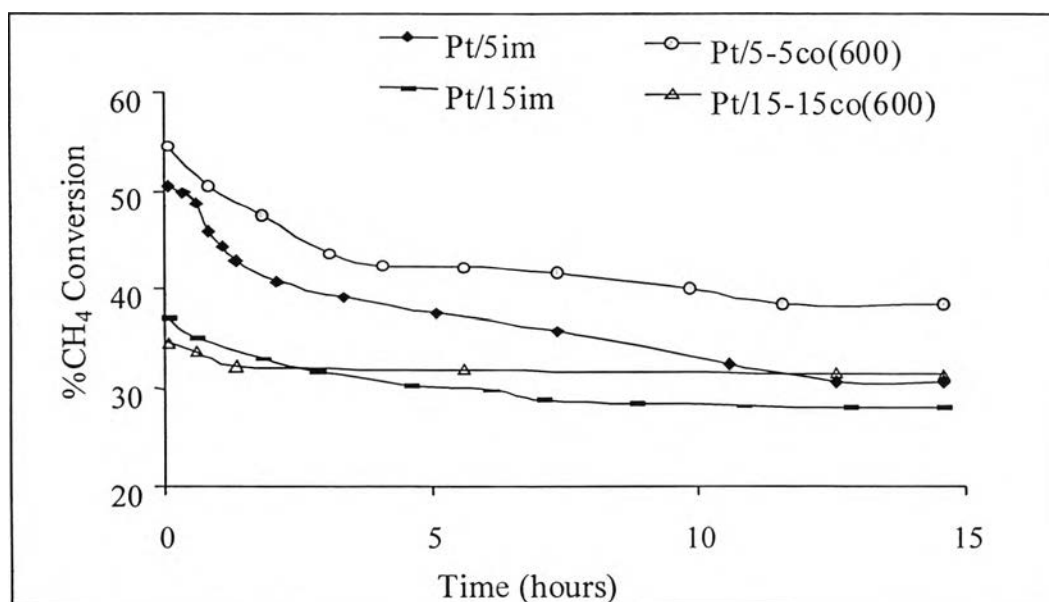
The results from the unpromoted catalyst, single promoted catalysts, and mixed-promoter catalysts are shown in Figure 4.17. The results suggested that Pt/5YZ had the highest initial conversion, but after about 10 hours of reaction the conversion of CH<sub>4</sub> by Pt/5-5co(600) catalyst remained high. Therefore, these two catalysts were good candidates for the dry reforming reaction.



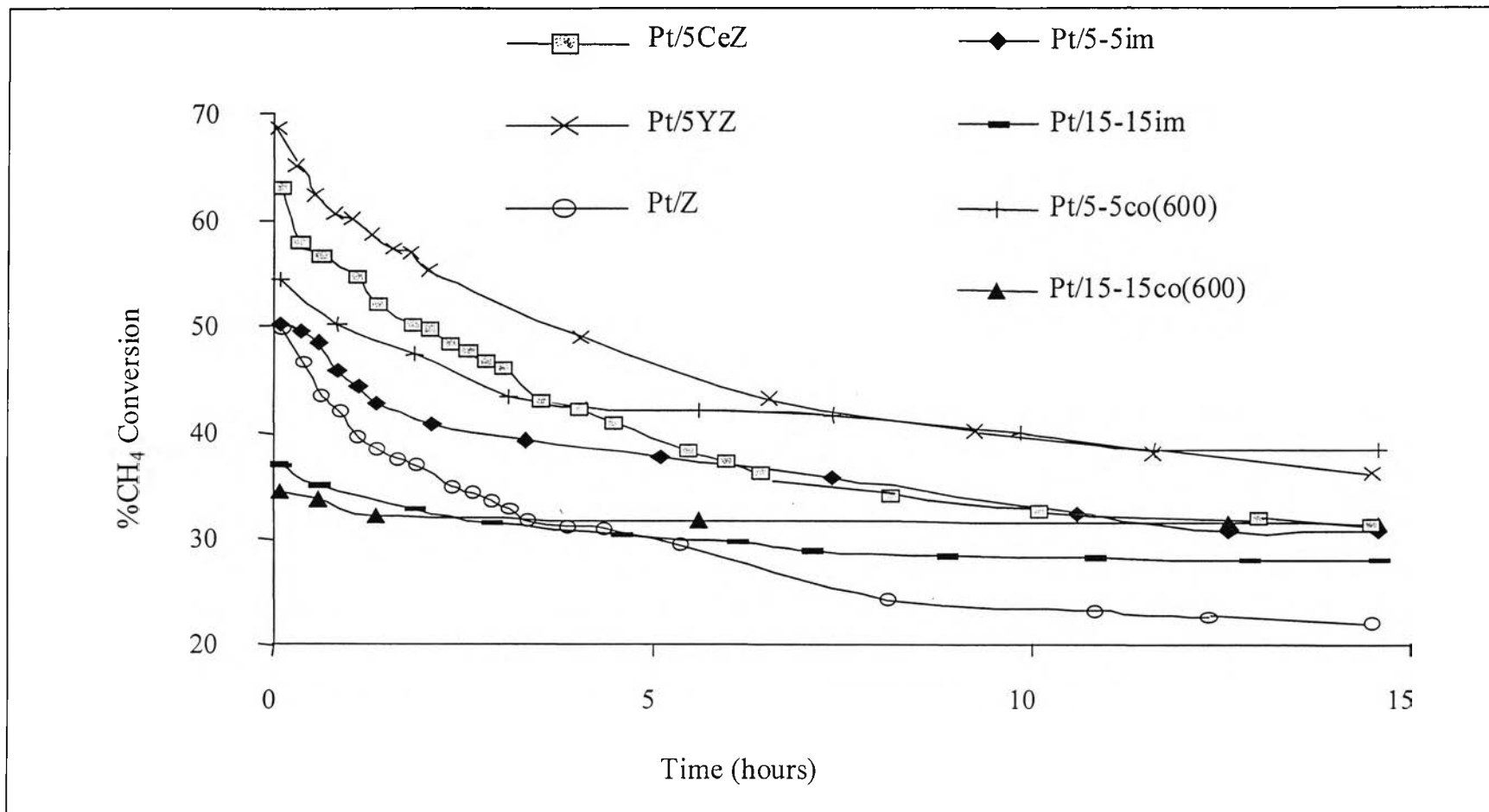
**Figure 4.14** XRD patterns for ZrO<sub>2</sub> prepared by co-precipitation technique calcination at 600°C and 800°C; tetragonal form (★), monoclinic form (●)



**Figure 4.15** CH<sub>4</sub> conversion as a function of time for mixed-promoter catalysts prepared by co-precipitation technique at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>



**Figure 4.16** CH<sub>4</sub> conversion as a function of time for mixed-promoter catalysts prepared by impregnation technique compared with co-precipitation technique at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>



**Figure 4.17** CH<sub>4</sub> conversion as a function of time for mixed-promoter catalysts compared with Pt/Z, Pt/5CeZ, and Pt/5YZ catalysts at CH<sub>4</sub>/CO<sub>2</sub> ratio of 2/1 and GHSV of 477500 h<sup>-1</sup>