# CHAPTER VI

# CATALYTIC PERFORMANCE OF PROMOTERS

## 6.1 Promoters

This part studies and discusses catalytic performance of promoters loaded on Ni/dolomite catalyst. Addition of metallic promoters is used as modifiers for reforming the catalyst. This research used Pt, Co and Fe as promoters. Most metals group VIII, especially noble metal and Ni based catalyst, have been studied for steam reforming, dry reforming, partial oxidation, and reforming of methane (Pompeo et al. 2005, and Rezaei et al. 2008). The addition of metallic noble metals may help the improvement of metallic dispersion, decrease the sintering, and enhance the improvement of thermal stability. Platinum (Pt) is an interesting metal to be used as catalyst for syngas production due to its availability and its relatively low price with respect to rhodium (Pompeo et al.2007). Iron (Fe) has been studied as a catalyst for carbon gasification or hydrogasification and the addition of iron can enhance hydrogen production (Yu et al. 2006). Cobalt (Co) attracted interest as an active metal for the $CO_2$ reforming of methane. The experiment was carried out to study the catalyst preparation methods and catalyst activity of promoters on gas composition product.

## 6.2 Characteristic of catalyst

As mention in Chapter III, the catalysts were prepared by two methods; precipitation and impregnation. The three types of transition metal such as Pt, Co, and Fe 1% were loaded on 10%Ni/dolomite catalyst in equal amount of 1% metal loading. The properties of Ni/Pt/DM, Ni/Co/DM and Ni/Fe/DM catalysts from different preparation method are shown in Table 6.1

### 6.2.1 BET surface area and Chemisorption

The properties of Ni/Pt/DM, Ni/Co/DM and Ni/Fe/DM catalysts from different preparation method were tested by $N_2$ adsorption and hydrogen Chemisorption. The properties of catalyst are shown in Table 6.1

Table 6.1 Properties of catalyst

| Catalyst | Preparation Method | BET [a] ($m^2/g$) | Pore Volume ($cm^3/g$) | Metallic surface area [b] ($m^2/g$ ) | Active particle diameter (nm)[c] |
|---|---|---|---|---|---|
| Ni/Pt/DM | impregnation | 6.74 | 0.046 | 0.92 | 77.66 |
| Ni/Co/DM | impregnation | 5.76 | 0.033 | 0.20 | 364.60 |
| Ni/Fe/DM | impregnation | 11.18 | 0.038 | 0.03 | 2671 |
| Ni/Pt/DM | coprecipitation | 5.33 | 0.038 | 0.06 | 166.34 |
| Ni/Co/DM | coprecipitation | 4.77 | 0.026 | 0.05 | 1532.7 |
| Ni/Fe/DM | Coprecipitation | 8.76 | 0.028 | 0.02 | 2715 |

[a] Calculated from $N_2$ adsorption isotherm

[b] Calculated from hydrogen Chemisorption

[c] Calculated from Pluse Chemisorption

Table 6.1 shows that the catalysts prepared by impregnation method, have a higher surface area of 6.74, 5.76 and 11.18 ($m^2/g$) with the addition of Ni/Pt/DM, Ni/Co/DM and Ni/Fe/DM catalyst, respectively. Metallic surface area of those catalysts prepared by impregnation method is higher than those prepared by the coprecipitation method. Metallic surface area of Ni/Pt/DM, Ni/Co/DM and Ni/Fe/DM impregnation method is 0.92, 0.2 and 0.03 ($m^2/g$), respectively. The coprecipitation method resulted in a less metallic surface area because of metallic active species transformed to less active structure.

Pore volume of the catalysts has similar trend as the surface area depends on the preparation method and types of catalysts loading. Pore volume of Ni/Pt/DM, Ni/Co/DM and Ni/Fe/DM by impregnation method is 0.046, 0.033 and 0.038 ($cm^3/g$), respectively. Adding promoters by coprecipitation method made agglomerated of metal particles, resulting in an increase in crystallize size. Profeti et al. (2008) suggested that addition of noble metal contributed to a decrease in surface area and increase of crystallite size.

### 6.2.2 Catalyst characterization

The XRD patterns of 10% Nickel /dolomite containing the same metal loading 1% of Pt, Co and Fe with two preparation methods are presented in Figure 6.1-6.3. The catalysts were reduced in $H_2$ at 700°C. Figure 6.1 shows XRD pattern of Ni/Pt/DM catalysts prepared by two different methods. The two preparation methods have almost the same XRD patterns. The peak corresponding to $Ni^{\circ}$ is located at $2\theta$ = 44.5 and 51.8°. The addition of a small amount of Pt shows $Pt^{\circ}$ peaks in XRD at $2\theta$ = 40°

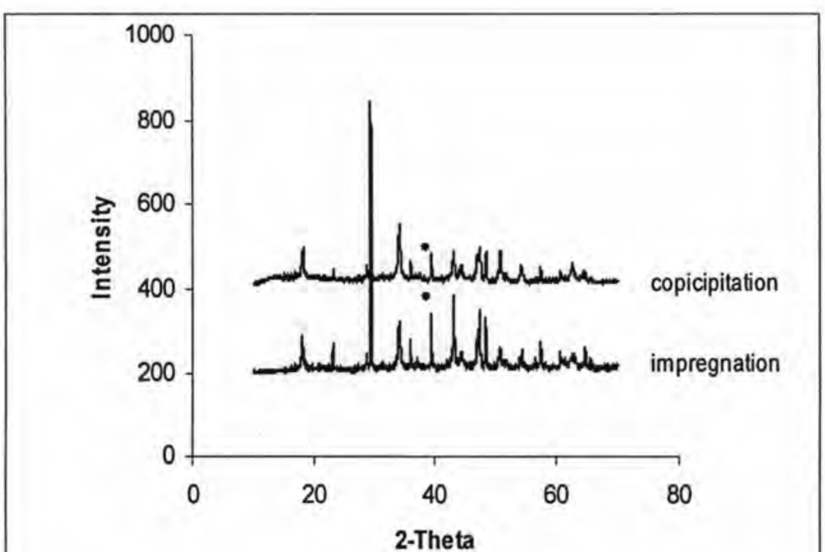



Figure 6.1 XRD pattern of Ni/Pt/DM catalyst ( * Pt )

Figure 6.2 shows XRD pattern of Ni/Co/DM catalyst after reduction of catalyst under $H_2$. The two preparation methods of Ni/Co/DM resulted in the same XRD pattern. The two separate peaks for the metals assigned to $Co^{\circ}$ cubical structure 2θ at $47.5^{\circ}$ and $Ni^{\circ}$ at $44.5^{\circ}$ are observed.

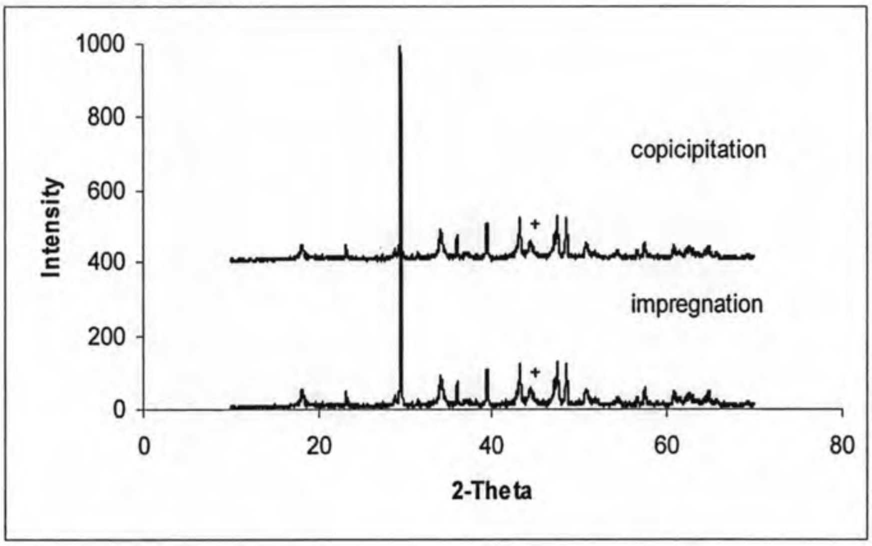



Figure 6.2 XRD pattern of Ni/Co/DM catalyst (+ Co)

Figure 6.3 shows XRD patterns of Ni/Fe/DM catalyst after reduction under $H_2$. The two preparation methods of Ni/Fe/DM appeared to have the same XRD pattern. The two separate peaks for the metals assigned to $Fe^{\circ}$ are observed at 2θ $44.35^{\circ}$ and $Ni^{\circ}$ at $44.5^{\circ}$.

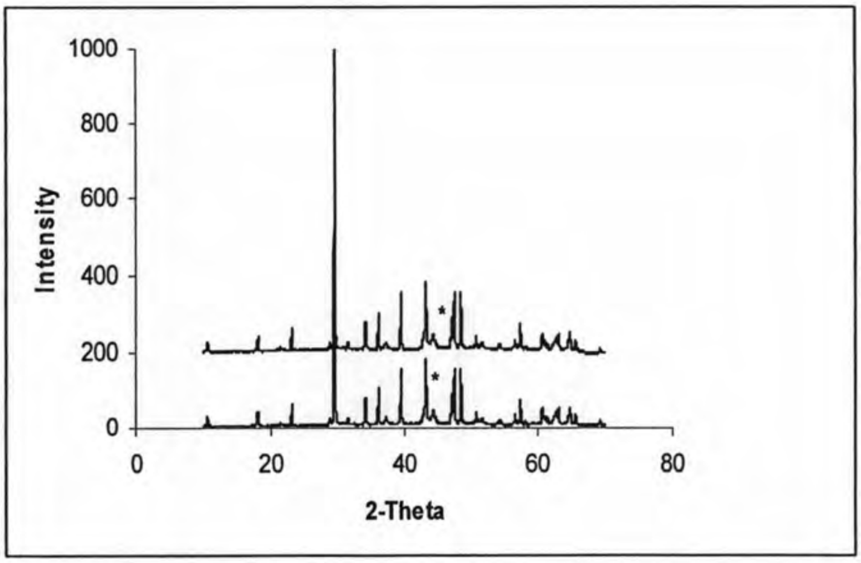
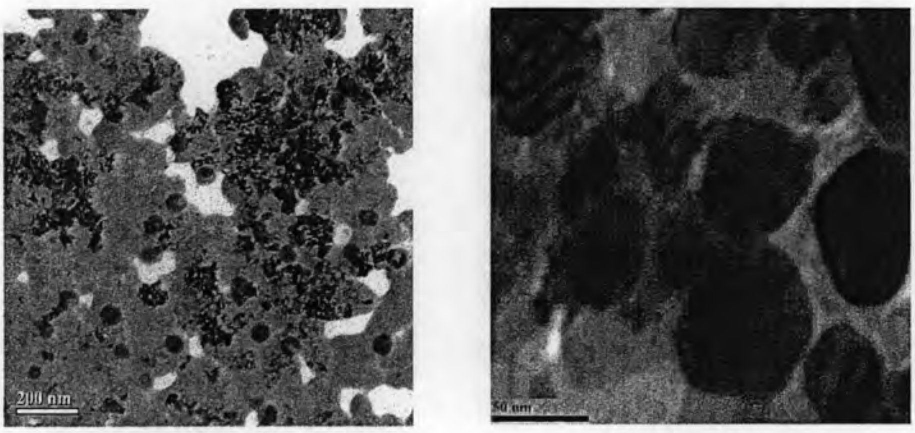



Figure 6.3 XRD pattern of Ni/Fe/DM catalyst (* Fe)

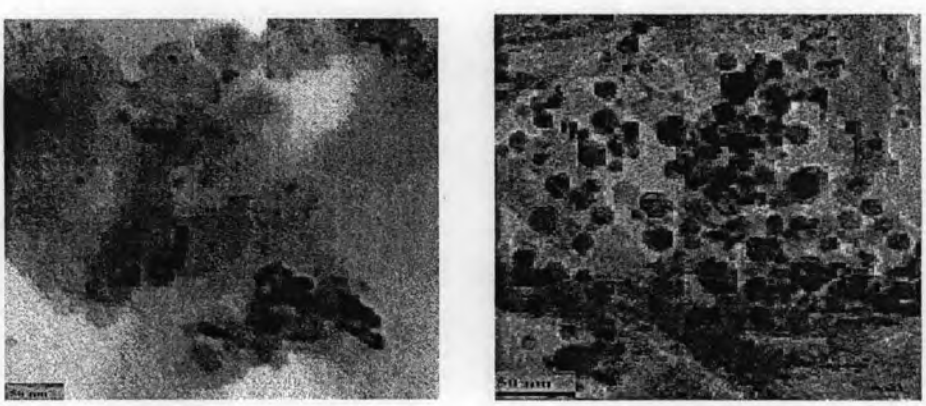
### 6.3 The morphology of the catalysts

The morphology of the catalysts was observed by Transmission electron microscopy (TEM) after the catalysts were reduced in $H_2$ at 700$^{\circ}$C for 2 hour. The TEM images of 10% Ni/dolomite containing the metal loading 1% of Pt, 1% of Co and 1% of Fe with different preparation method are presented in Figure 6.4- 6.6. The black dots represent particles in different crystallite.



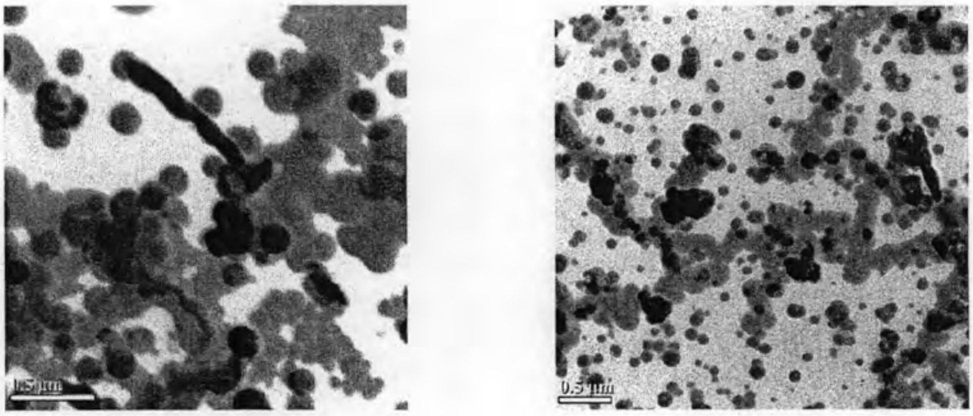

(a) (b)

Figure 6.4 TEM images of 10%Ni1%Co/DM (a) impregnation (b) coprecipitation



(a) (b)

Figure 6.5 TEM images of 10%Ni1%Pt/DM (a) impregnation (b) coprecipitation



(a) (b)

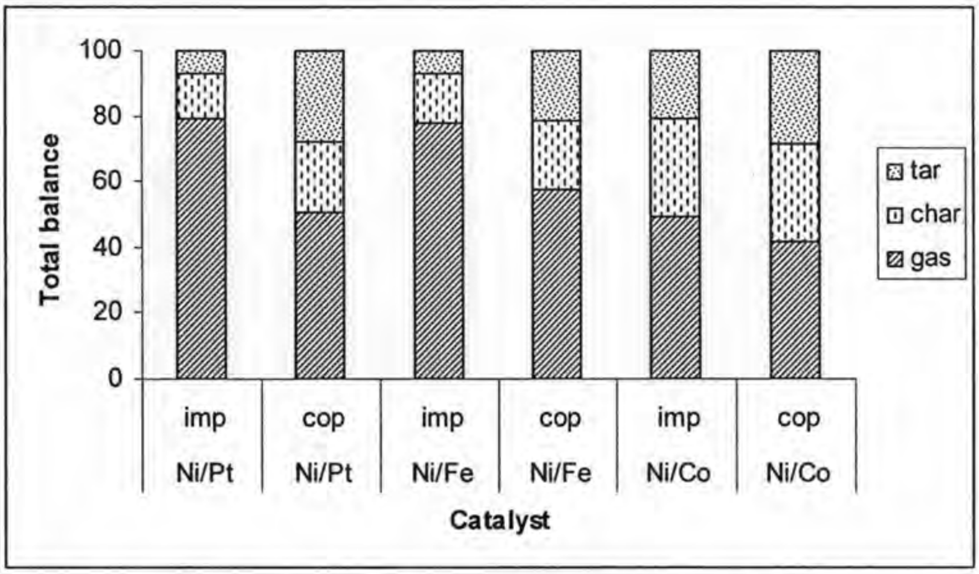
Figure 6.6 TEM images of 10%Ni1%Fe /DM (a) impregnation (b) coprecipitation

**6.4 Catalytic performance of promoters**

In this part investigations were carried out to determine catalytic performance of promoters loaded on Ni/dolomite catalyst. The purpose of this part is to study the effects of critical parameters such as catalyst preparation method, effect of promoters on gas composition and coke formation.

**6.4.1 Effect of catalyst preparation**

The activity of promoters was studied to compare effect of catalyst preparation method on carbon balance, as shown in Figure 6.7. The experimental was performed at the temperature of 800 °C, (S/C) ratio of 0.95, fluidization flow rate at 300 ml/min, using coconut shell as a biomass and feed rate of 1.76 g/min. A comparative study of Ni/Pt/DM, Ni/Fe/DM, and Ni/Co/DM catalysts are presented as a function of catalyst preparation technique.




(imp= impregnation method, cop= coprecipitation method)

Figure 6.7 Effect of catalyst preparation methods on carbon balance

(Condition; temperature of 800 °C, (S/C) ratio of 0.95, flow rate of nitrogen of 300 ml/min, coconut shell feed rate of 1.76 g/min)

The catalyst preparation by impregnation method yielded higher percentage of carbon conversion to gas. As can be seen from Figure 6.7, catalyst prepared by impregnation method gave $C_{conv}$ to gas of 79.19%, 78.12% and 49.53%, when using Ni/Pt/DM(imp), Ni/Fe/DM(imp) and Ni/Co/DM(imp), respectively. However, in the cases where the catalysts were prepared by coprecipitation method, the activity $C_{conv}$ were 50.51%, 57.46% and 41.82% when using Ni/Pt/DM (cop), Ni/Fe/DM(cop) and Ni/Co/DM(cop) as catalysts, respectively.

### 6.4.2 Effect of promoters on gas composition

After the analysis on the effect of preparation method was completed, the effects of promoter types were investigated by considering the catalytic performance on product gas composition. The experiments were performed at the temperature of 800 °C, steam to carbon ratio (S/C) of 0.95 by using three types of impregnated catalysts: 10%Ni/1%Pt, 10%Ni1%Fe and 10%Ni1%Co. The results can be understood through evaluation of catalyst activity on gas composition and carbon balance.

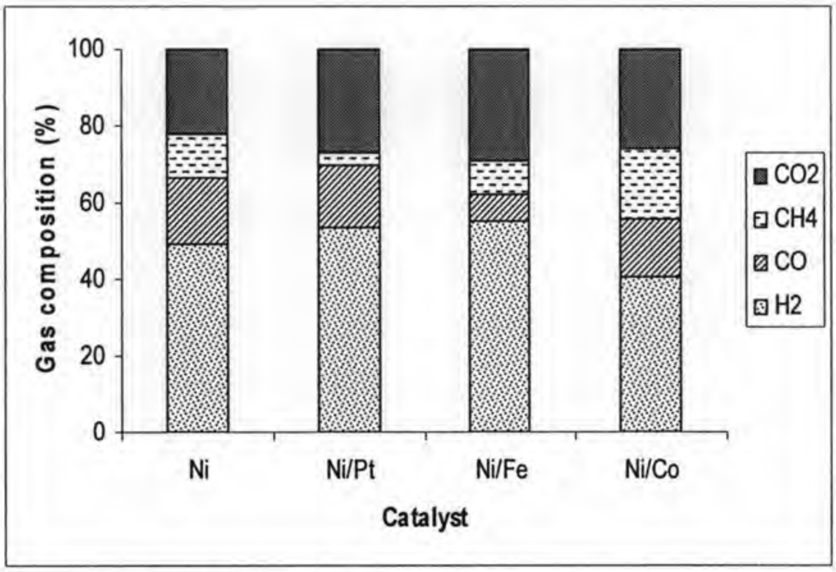



Figure 6.8 Effect of promoters on gas composition

(Condition; temperature of 800 °C, (S/C) ratio of 0.95, flow rate of nitrogen 300 ml/min, coconut shell feed rate of 1.76 g/min)

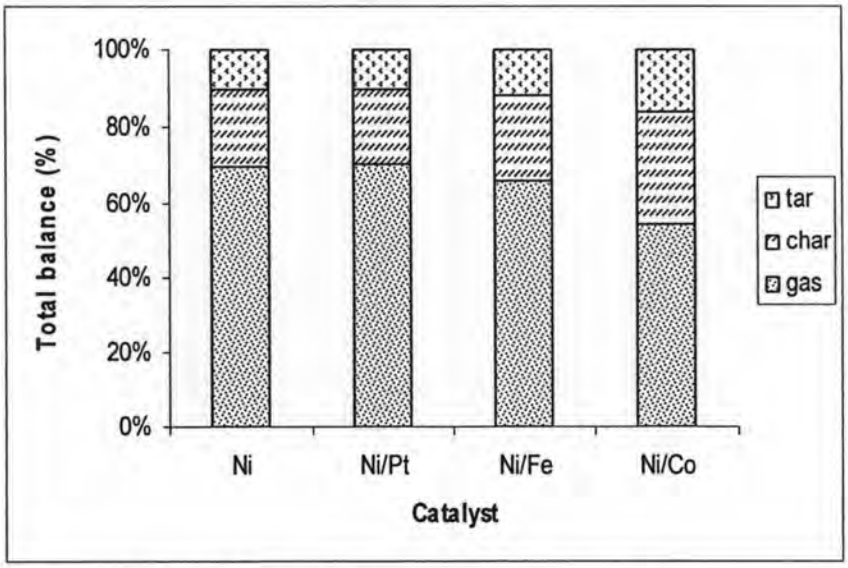



Figure 6.9 Effect of promoters on carbon balance

(Condition; temperature of 800 °C, (S/C) ratio of 0.95, flow rate of nitrogen 300 ml/min, coconut shell feed rate of 1.76 g/min)

Figure 6.8 shows effects of promoters on gas composition and carbon balance. The addition of Pt enhances the performance in the steam gasification of coconut shell in terms of carbon conversion to gas yield as shown in Figure 6.9. The Ni/Pt/DM catalyst promoted steam reforming and methane reforming and increased in $H_2$, CO and $CO_2$ contents. The following equations explain;

$$C + H_2O \rightarrow CO + H_2 \quad (6.1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (6.2)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (6.3)$$

The effect of using iron(Ni/Fe/DM) as a catalyst was that in $H_2$ and $CO_2$ production was increased by catalyzes water gas shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (6.4)$$

The result show similar trends as the observations of Yu et al. (2006), which found the significant enhancement of hydrogen production during the gasification of Victorian brown coal in the presence of iron. The Ni/Co/DM catalyst promoted methanation and reforming of methane which increased in $CH_4$ and $CO_2$ contents can be illustrated following reaction;

$$C + 2H_2 \rightarrow CH_4 \quad (6.5)$$

$$CH_4 + H_2O \rightarrow CO_2 + 3H_2 \quad (6.6)$$

The gaseous products were increased with the use of catalysts as the following orders: Ni/Pt/DM (72.34%), Ni/DM (70.34%)>Ni/Fe/DM (68.12 %) >Ni/Co/DM (54%).

**6.4.3 Coke formation analysis**

The primary source of deactivation of catalyst is the formation of coke deposition on the surface. Thus, it is essential to measure the amount of coke to compare the carbon resistance of the catalysts. The purpose of this section is to design an excellent catalyst which would result in a less amount of coke formation.

Table 6.2 Coke formation by thermogravimetric (TG/DTA) analysis of various catalysts after reactions

| Catalyst | Coke amount [a]( %) |
| --- | --- |
| Ni/DM | 16.5 |
| Ni/Pt/DM | 6.5 |
| Ni/Fe/DM | 8.3 |
| Ni/Co/DM | 9.3 |

[a](g of coke/g of sample)x 100

The carbon deposition was analyzed by TGA in air. At the temperature range of 600 $^{\circ}$C represented the weight loss of the carbon deposited on the surface. From Table 6.2, it can be seen that the amount of coke formation of catalyst was as following: Ni/Pt/DM< Ni/FeDM< Ni/Co/DM< Ni/DM. As reported in previous study (Chen et al., 1997), three kinds of deposited coke have been found in steam reforming process. Carbon deposition proceed via the formation of carbide species by Boudouard reaction ($2CO \rightarrow CO_2 + C$) and $CH_4$ decomposition ($CH_4 \rightarrow 2H_2 + C$). The type and the nature of coke formed depends on the metal and in some case on the support used.

### 6.5 Conclusions

1. Catalyst preparation significantly changes the values of the BET surface area, pore volume, metallic surface area, crystallize size and morphology of a catalyst. Impregnation method gave higher BET surface area and metallic surface area than coprecipitation method because of agglomeration of metal particles, resulting in an increase in crystallize size

2. Adding small amount of promoters affects the gas composition. The results implied that different promoters play significant role in gasification reaction. The Ni/Pt/DM catalyst promoted steam reforming and water- gas shift reaction and increased $H_2$, CO and $CO_2$ contents. Effect of using iron as a catalyst catalyzed water gas shift reaction

and increased $H_2$ and $CO_2$ production. The Ni/Co/DM catalyst promoted methanation and reforming of methane which increased $CH_4$ and $CO_2$ contents.

3. The effect of noble metal on its stability to coke formation is shown as follow: Ni/Pt/DM< Ni/Fe/DM< Ni/Co/DM< Ni/DM. The addition of metallic noble metals may help the improvement of metallic dispersion, decrease the sintering, and enhance the improvement of thermal stability.