CHAPTER IV
RESULTS AND DISCUSSION

To find the selective catalyst and reaction conditions that preferentially produce high quantity and quality of carbon nanotubes with methane, this study was focused on investigating a series of catalyst materials by systematically varying the metal compositions. Moreover, the effect of synthesis conditions on the carbon nanotube production was studied by varying the reaction conditions. The combination of Raman, TEM, and Temperature Programmed Analysis techniques was used to characterize both qualitative and quantitative of produced carbon. The Raman Spectroscopy was used for systematic screening of the overall types of carbon product and the Transmission Electron Microscope (TEM) was utilized to provide the structure of carbonaceous deposits on catalysts. The Temperature Programmed Analysis was used to confirm the forms of carbon presenting in sample and also provided the amount of total carbon products.

The Raman Spectroscopy of carbon nanotube gives three important modes, namely graphite-like tangential mode (G-band), disordered carbon band (D-band), and the radial A_{1g} breathing mode frequency range (RBM). The tangential modes or G-band locates at around 1570 cm^{-1}, which is the characteristic carbon nanotube and graphite. The latter band at 1350 cm^{-1} (D-band) corresponds to the disorder or amorphous carbon. The analysis of the RBM, which presents at frequency below 300 cm^{-1}, can provide information about the presence of SWNT in the product and also use to estimate the diameter of SWNT.

The TEM technique provides the two-dimensional image of carbon nanotubes. It is then highly suitable for studying structure, diameter and general quality of carbon nanotubes presenting in the carbon products.

The Temperature Programmed Analysis, *i.e.* Temperature Programmed Oxidation (TPO) and Thermal Gravimetric Analysis (TGA), was employed to confirm the types of carbonaceous deposits on spent catalysts. Carbon with different morphology is oxidized at different temperature so examining the oxidation temperature helps in identifying the types of carbon products. It has been reported that the oxidation of amorphous carbon on this type of catalyst under the particular

condition used in this work has a range of 300 to 400 °C, while SWNT and MWNT have shown peaks around 495-530 °C and 600-700 °C respectively (Kitiyanan *et al.*, 2000).

The Temperature Programmed Analysis was also used in this work for quantifying the amount of total carbon products. When the carbonaceous product is oxidized, it generates carbon monoxide or carbon dioxide and its weight is reduced. Quantification of the total lost weight or emitting gas gives a direct measurement of the amount of carbon. If the amount of deposited carbon is high, the sample's weight is accurately monitored and this technique is usually called Thermal Gravimetric Analysis (TGA). If the amount of carbon is low (less than 3% by weight), the evolved carbon monoxide or carbon dioxide is detected and this technique is usually called Temperature Programmed Oxidation (TPO).

4.1 Effect of Methane on the Carbon Nanotube Production

In order to study the effect of methane decomposition on the production of carbon nanotubes, the experiments were conducted over Co-Mo (1:1 mole ratio) on silica supported catalyst with methane. These results were compared with the CoMoCat® process using the Co-Mo/SiO_2 (1:1 mole ratio) and carbon monoxide as the catalyst and feed gas, respectively.

Figure 4.1 shows the Raman spectrum of carbon produced over Co-Mo/SiO_2 (1:1 mole ratio) with methane. From these spectrum, the two main peaks were observed at around 1570 and 1350 cm^{-1}. The peak at 1570 cm^{-1} represents the G-band, which is the characteristic of carbon nanotube and graphite. The peak at 1350 cm^{-1} (D-band) corresponds to the disorder or amorphous carbon. Nevertheless, peak located below 300 cm^{-1} (RBM peak) could not be detected in these spectra. It is indicated that SWNT does not present in this sample.

Figure 4.2 illustrates the TPO profile of carbon produced over Co-Mo/SiO_2 (1:1 mole ratio) with methane. The dominant peak, whose center is around 600 °C, implies the presence of MWNT. The small peak, in the range of 300 to 400 °C, also shows in this profile representing the presence of amorphous carbon. However, peak

at around 550-530 °C, which was previously assigned for SWNT (Kitiyanan *et al.*, 2000), was not detected in this profile. The TPO result is in agreement with the Raman result as reported above. Undoubtedly, it can be concluded that the most of carbon products obtained over Co-Mo/SiO_2 (1:1 mole ratio) with methane are MWNTs.

Figure 4.3 illustrates the Raman spectrum of carbon produced from CoMoCat® process. Both G-band and D-band were investigated in CoMoCat® sample. The RBM peak corresponding to the appearance of SWNTs also shows in this spectrum. The intensity ratio of D-band to G-band (D/G) provides relative amount of disordered carbon to graphite-like carbon. From the spectrum, the relative intensity of D-band is significantly lower than of G-band. This may indicate that the formation of amorphous carbon is less than graphite-like carbon.

The results were confirmed by TPO profile as shown in Figure 4.4. The major peak centered at around 510 °C corresponds to the oxidation of SWNT and the small oxidation peak centered at around 330 °C is ascribed to amorphous carbon. According to both Raman and TPO data, most of products obtained from carbon monoxide over Co-Mo/SiO_2 (1:1 mole ratio) are SWNTs.

Table 4.1 shows the total amount of carbon obtained from CoMoCat® process and from methane decomposition over Co-Mo/SiO_2 (1:1 mole ratio) catalyst. From these results, the amount of total carbon obtained from CoMoCat® process (1.7%) was significantly less than the carbon from methane decomposition over Co-Mo/SiO_2 (24.69%).

Table 4.1 Summary of total carbon yields

Catalyst	Approach	Reaction Temperature (°C)	*Total Carbon Yield (%)
**Co-Mo (1:1)/SiO_2	-	-	1.70
**Co-Mo (1:1)/SiO_2	2	1000	24.69
Co-Mo (2:1)/MgO	1	1000	23.59
Co-Mo (1:1)/MgO	1	1000	41.64
Co-Mo (1:2)/MgO	1	1000	54.27
Fe-Mo (2:1)/MgO	1	1000	31.57
Fe-Mo (1:1)/MgO	1	1000	43.10
Fe-Mo (1:2)/MgO	1	1000	44.95
Co-Mo(1:1)/MgO	2	700	8.75
Co-Mo(1:1)/MgO	2	800	11.76
Co-Mo(1:1)/MgO	2	900	14.47
Co-Mo(1:1)/MgO	2	1000	20.94

* Yield was calculated from TGA result that yield is defined as $(W_{intial} - W_{final})/W_{final} \times 100\%$, where $W_{initial}$ and W_{final} are respectively the weight left at 200 °C and 750 °C.

** The total carbon yield was obtained by TPO technique.

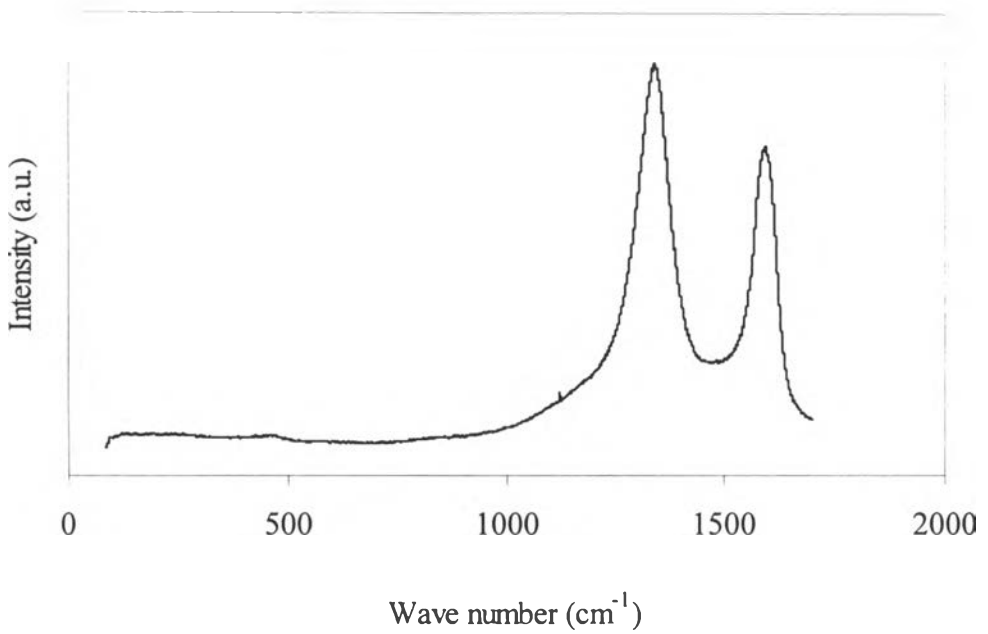

Figure 4.1 Raman spectrum of carbon produced by methane decomposition on Co-Mo/SiO_2 (1:1 mole ratio) catalyst

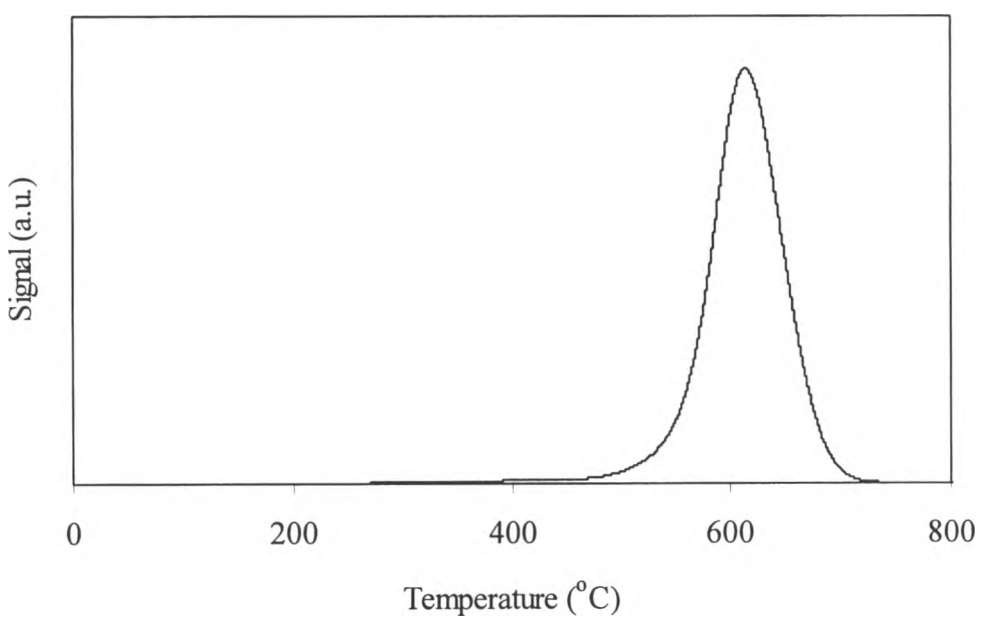

Figure 4.2 TPO profile of carbon produced by methane decomposition on Co-Mo/SiO_2 (1:1 mole ratio) catalyst

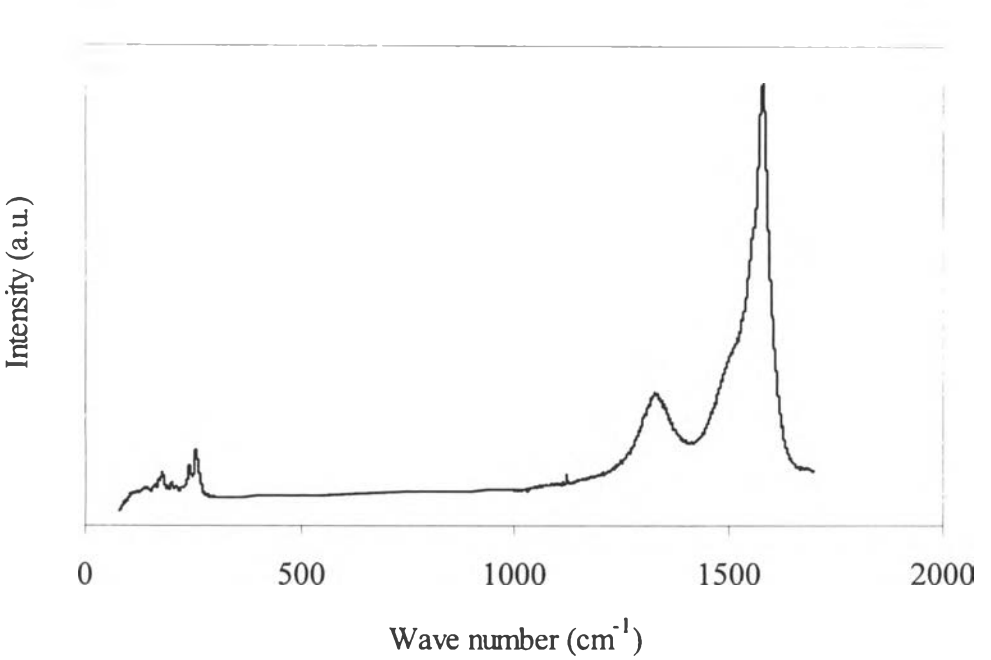

Figure 4.3 Raman spectrum of carbon produced from CoMoCat® process prepared by disproportionation of CO on Co:Mo/SiO_2 (1:1 mole ratio) catalyst

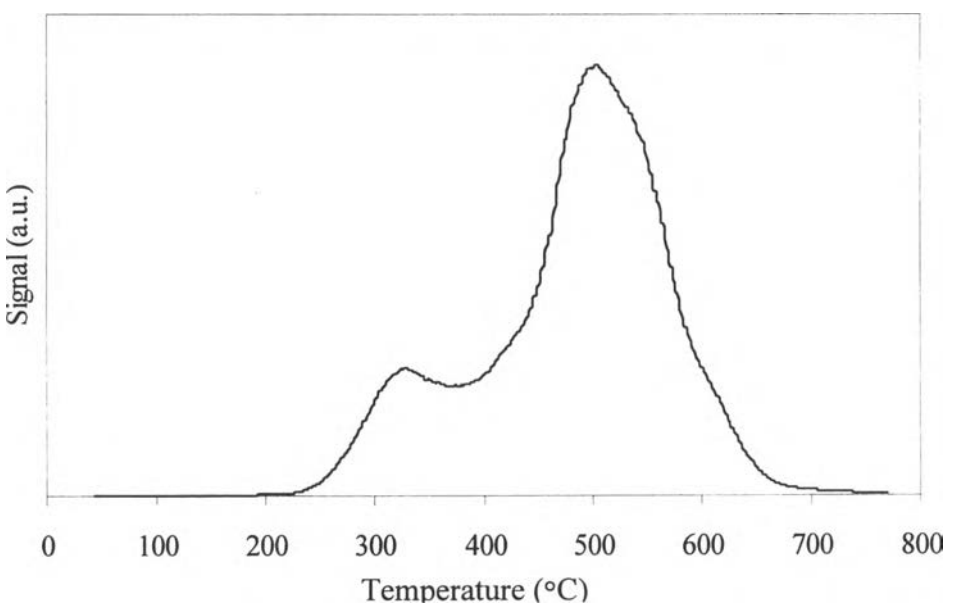

Figure 4.4 TPO profile of carbon produced from CoMoCat® process prepared by disproportionation of CO on Co:Mo/SiO_2 (1:1 mole ratio) catalyst

4.2 Effect of Catalyst Support on the Carbon Nanotube Production

The effect of support on the production of carbon nanotube was studied by comparing between two kinds of support, silica and magnesium oxide. Figure 4.5 illustrates the Raman spectra of carbon produced by methane decomposition on Co-Mo (1:1 mole ratio) over silica and also magnesium oxide supports. From these spectra, they exhibit the same two main peaks. G-band and D-band were observed at around 1570 and 1350 cm^{-1}, respectively. Still, RBM peaks were not detected in these spectra. It can imply that no SWNT exists in the sample. Furthermore, with visual observation, the amount of carbon deposits on Co-Mo/MgO (1:1 mole ratio) catalyst was significantly higher than on Co-Mo/SiO_2 (1:1 mole ratio). Surface area of Co-Mo/MgO (6.45 m^2/g) is considerably less than Co-Mo/SiO_2 (459.5 m^2/g). However, the amount of carbon deposits on Co-Mo/MgO (1:1 mole ratio) catalyst was significantly higher than on Co-Mo/SiO_2 (1:1 mole ratio).

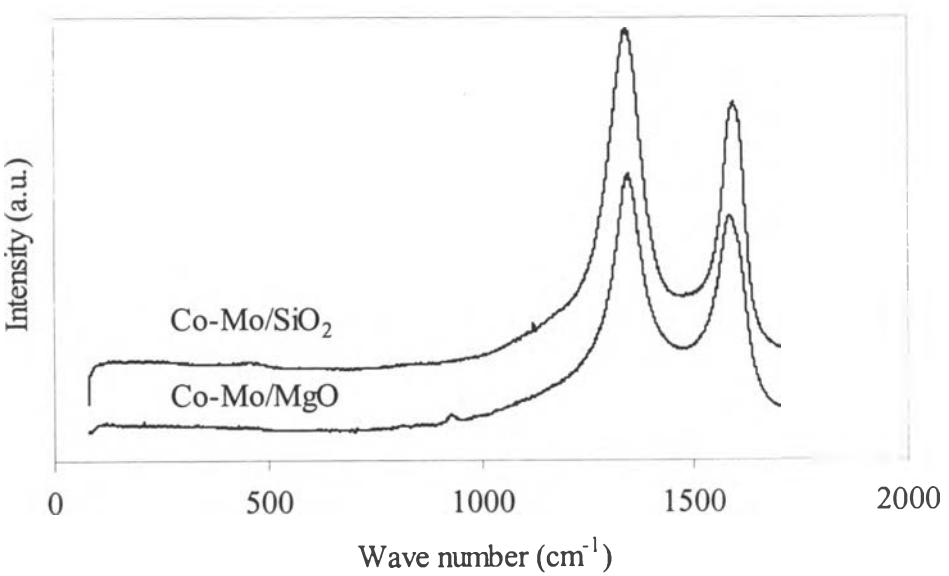

Figure 4.5 Raman spectra of carbon produced by methane decomposition on Co-Mo (1:1 mole ratio) over silica and magnesium oxide supports

4.3 Effect of Co:Mo Mole Ratio on the Carbon Nanotube Production

The effect of Co:Mo mole ratio was studied by varying Co:Mo at 2:1, 1:1 and 1:2 mole ratios on magnesium oxide support and scanning reaction temperature from room temperature up to 1000 °C. Figure 4.6 shows the Raman spectra of carbon produced by methane decomposition on Co-Mo/MgO catalyst at different Co:Mo ratios. From this figure, the presence of both G and D bands were observed at around 1570 and 1350 cm^{-1}, however, the RBM peaks were not detected in these spectra. The calculated of D/G from these spectra were 0.65, 0.55 and 0.42 when Co:Mo were 2:1, 1:1 and 1:2 mole ratios, respectively. These results show that decreasing in Co:Mo ratio resulted in decreasing in the D/G. In other words, the disordered carbon decreased when the Co:Mo ratio decreased. These results are in the same trend with the other report on Co-Mo catalyst (Tang *et al.*, 2001).

Figure 4.7 illustrates the derivative thermograms of carbon produced by methane decomposition on Co-Mo/MgO catalyst at different Co:Mo ratios. From this figure, the dominant peaks that their centers are around 620 °C correspond to MWNTs and the small peaks that their center are around 370 °C are assigned to amorphous carbon. SWNT oxidation was not detected in these thermograms. These results were confirmed by TEM techniques that the obtained products mostly consist of MWNTs and amorphous carbon. However, no evidence of SWNT was observed in these samples.

Figure 4.8 shows the thermograms of carbon produced from methane decomposition on Co-Mo/MgO catalyst at different Co:Mo ratios. These thermograms were used to calculate the total amount of carbon as described in the experimental section. The total amount of carbons were 23.59%, 41.64% and 54.27% when Co:Mo were 2:1, 1:1 and 1:2 mole ratios, respectively. These results show that decreasing in Co:Mo ratio corresponded with increasing in the total yields of carbonaceous product. These results are in agreement with the published work, Tang *et al.* (2001). In contrast, the total yields of carbonaceous products from published work are significant higher than in this research work.

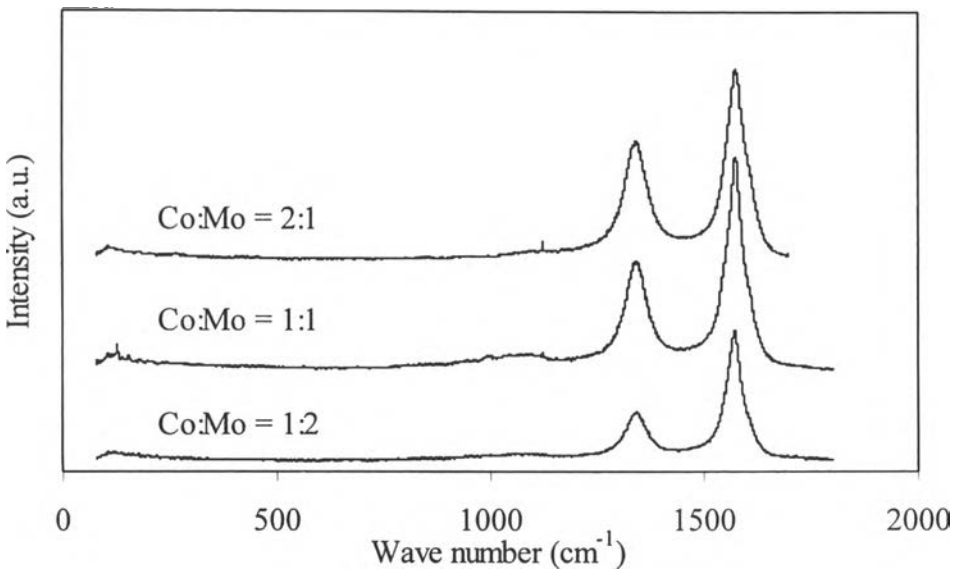

Figure 4.6 Raman spectra of carbon produced by methane decomposition on Co-Mo/MgO catalyst at various Co:Mo ratios

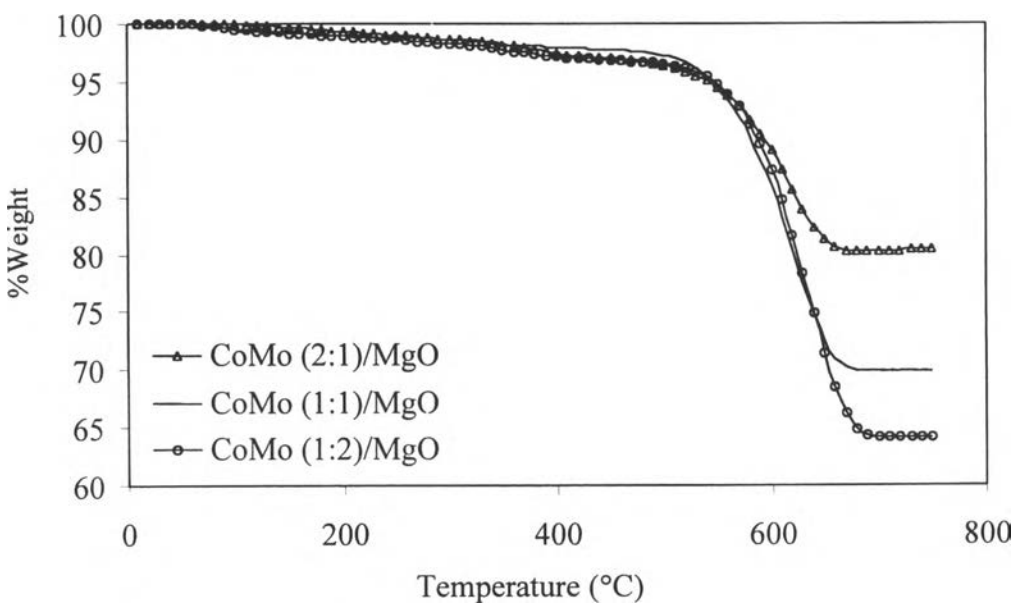

Figure 4.7 Thermograms of carbon produced by methane decomposition on Co-Mo/MgO catalyst at various Co:Mo ratios

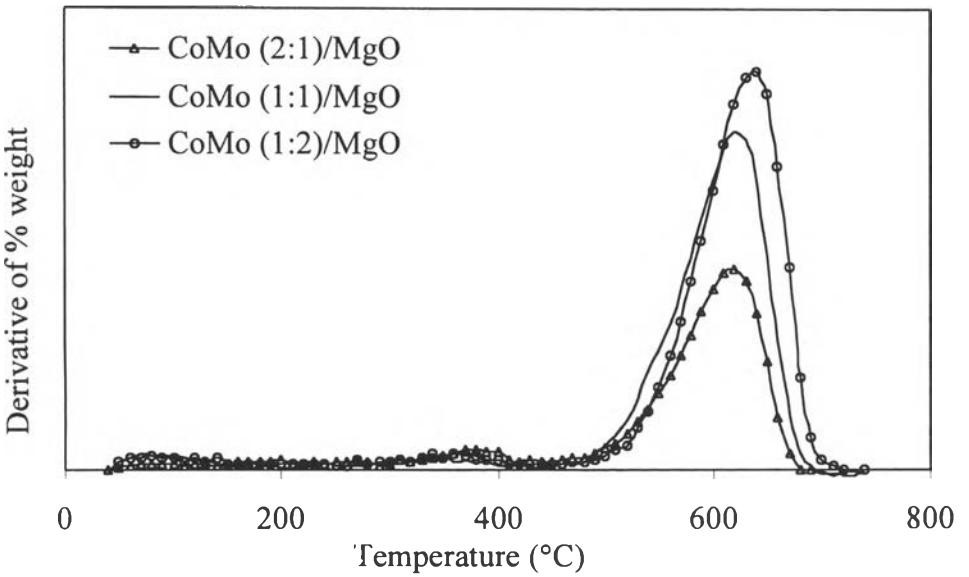

Figure 4.8 Derivative thermograms of carbon produced by methane decomposition on Co-Mo/MgO catalyst at various Co:Mo ratios

4.4 Effect of Fe:Mo Mole Ratio on the Carbon Nanotube Production

The effect of various formulations was further studied over Fe-Mo/MgO at 2:1, 1:1 and 1:2 Fe:Mo mole ratios. Figure 4.9 shows the Raman spectra of carbon produced over Fe-Mo catalyst at different Fe:Mo mole ratios. The calculated D/G from these spectra were 0.29, 0.45 and 0.53 when Fe:Mo were 2:1, 1:1 and 1:2 mole ratios, respectively. In contrast with the effect of Co:Mo mole ratio, the lower Fe:Mo ratio resulted in the higher D/G or the greater amount of amorphous carbon.

When considering the Raman spectra in RBM range (Figure 4.10), Raman spectrum of carbon produced with Fe:Mo at 2:1 mole ratio shows a broader peak in the range of 157 to 267 cm^{-1}. This implies the presence of SWNTs in this sample. The peaks presented in these ranges could correspond to SWNT diameters in the range of 0.88 to 1.56 nm. TEM technique was further used to confirm the presence of SWNTs on this sample that exhibits the bundles of SWNT (Figure 4.11). Nevertheless, the intensity of RBM peak of carbon produced with Fe:Mo (2:1 mole ratio) is significantly lower than G-band. Consequently, it can indicate that carbon produced over Fe:Mo (2:1 mole ratio) consists of mostly MWNTs and much less amount of SWNTs.

The results were further confirmed by TGA, as displayed in Figure 4.11. There is a small weight loss below 200 °C that possibly accounts for the sample moisture. The peak around 370 °C corresponds to the oxidation of amorphous carbon and the major peak centered around 620 °C can be assigned to the oxidation of MWNTs. The calculated amounts of total carbonaceous product over Fe-Mo/MgO catalysts are summarized in Table 4.1. The carbon contents obviously increased when mole ratio of Fe to Mo decreased, as in case of Co-Mo/MgO. The weight gained on Fe:Mo (2:1 mole ratio) catalyst is only 31.57% and 43.10% for Fe:Mo (1:1 mole ratio) catalyst. However, the total carbon deposits were slightly increased to 44.95% when performed the reaction with Fe:Mo (1:2 mole ratio).

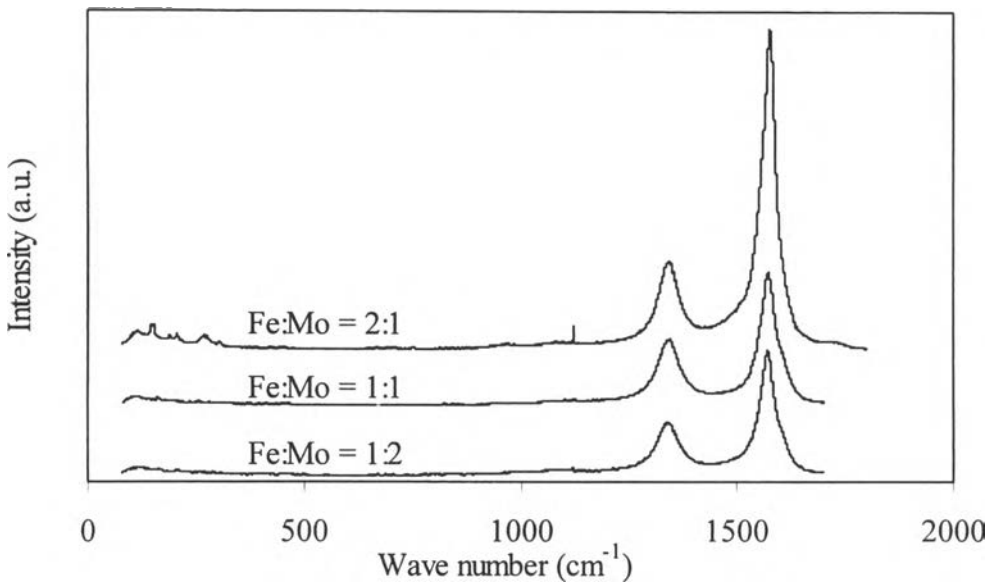

Figure 4.9 Raman spectra of carbon produced by methane decomposition on Fe-Mo/MgO catalyst at various Fe:Mo ratios

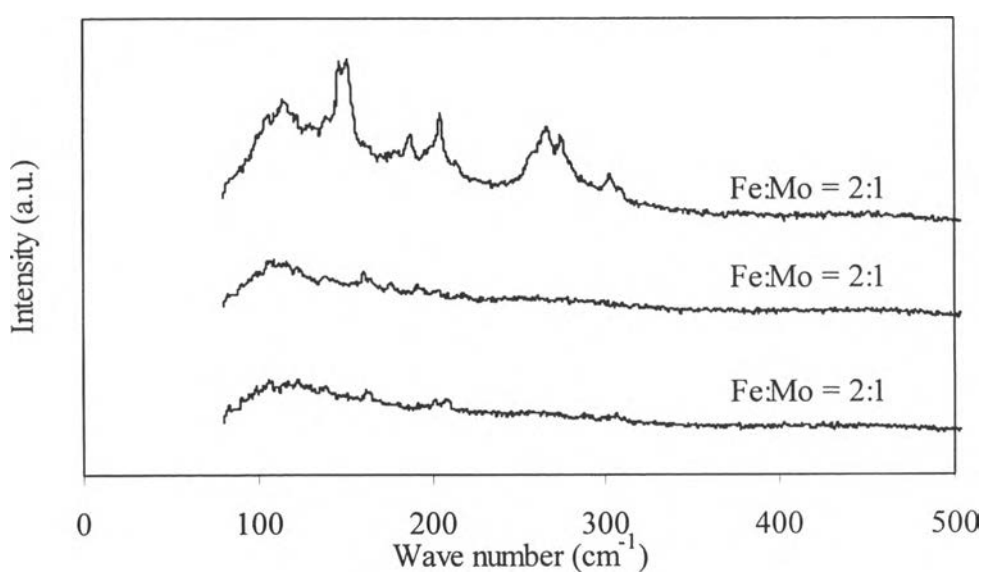

Figure 4.10 Raman spectra at RBM range of carbon produced by methane decomposition on Fe-Mo/MgO catalyst at various Fe:Mo ratios

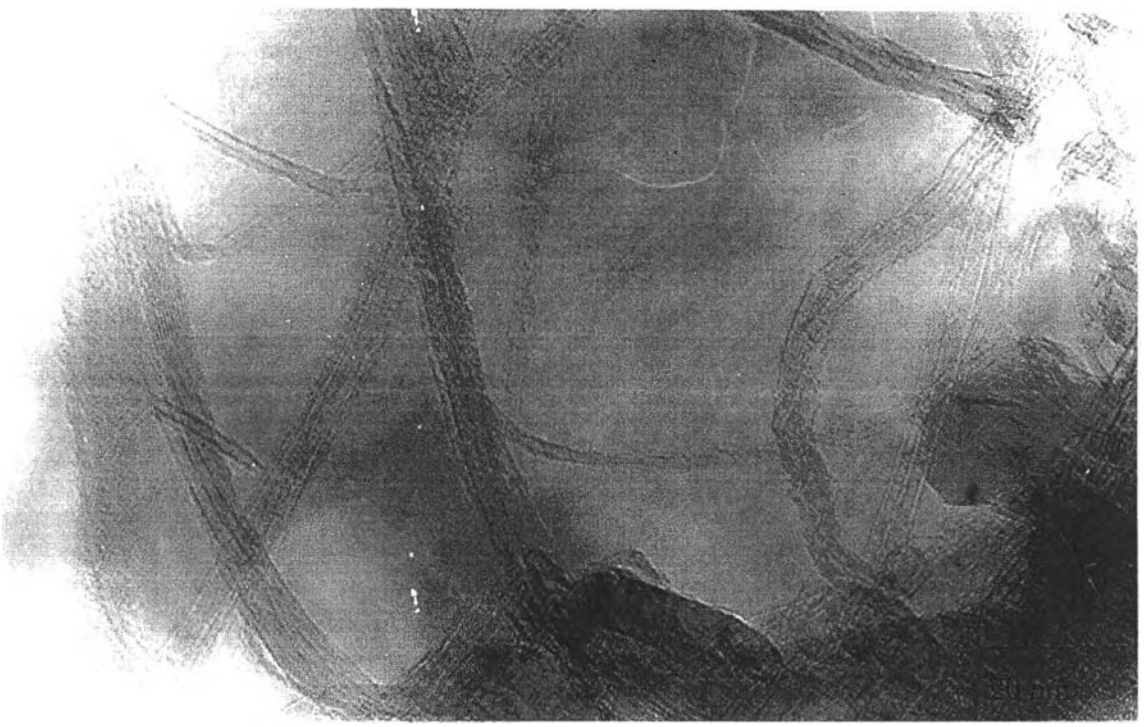

Figure 4.11 TEM image showing a mixture of SWNTs in bundle form and MWNTs produced by methane decomposition on Fe-Mo/MgO catalyst, at 2:1 mole ratio

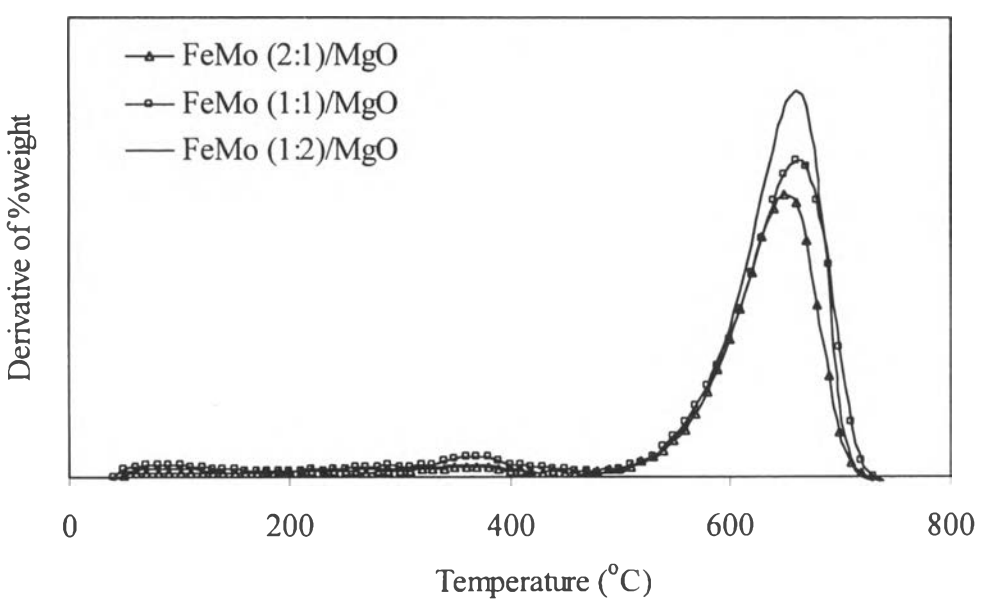

Figure 4.12 Derivative thermograms of carbon produced by methane decomposition on Fe-Mo/MgO catalyst at various Fe:Mo ratios

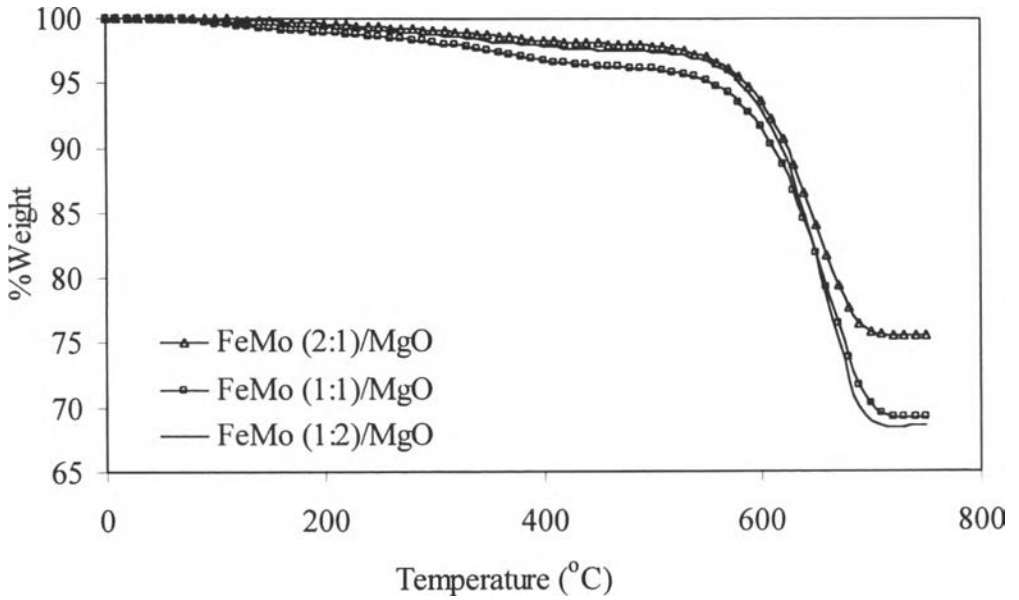

Figure 4.13 Thermograms of carbon produced by methane decomposition on Fe-Mo/MgO catalyst at various Fe:Mo ratios

4.5 Effect of Reaction Temperature on the Carbon Nanotube Production

The effect of reaction temperature on the carbon nanotube production was investigated by varying the operating temperatures from 700 to 1000 °C over Co-Mo/MgO catalyst (1:1 mole ratio) with methane. The Raman spectra of these samples are illustrated in Figure 4.14. From the Raman results, the D-band and G-band are mainly presented. The calc0ulated of intensity ratio of D-band and G-band (D/G) were 0.91, 0.86,0.61 and 1.09 when Co-Mo/MgO were treated at 700, 800, 900 and 1000 °C, respectively. These results show that D/G decreased when the reaction temperature increased, except at 1000 °C. This indicates that the formation of carbon nanotube by methane favors to occur at high temperature, however, at higher temperature (*i.e.*, 1000 °C), methane is probably self-pyrolyzed and then may lead to the generation of amorphous carbon.

From the Raman results, particularly in the range of RBM (Figure 4.15), only Co-Mo (1:1 mole ratio) treated at 900 °C shows a sharp peak at 183 cm^{-1}. It implies the presence of SWNTs in this sample, however, the intensity of RBM peak is significantly lower than G-band. Consequently, it possibly means that carbon products consist of very little amount of SWNTs. The presence of SWNTs on this sample was further confirmed by TEM (Figure 4.16). The image shows that carbons produced at 900 °C consist of the minor amount of SWNTs and major products are MWNTs and graphite.

Figure 4.17 shows the thermograms of carbon produced from methane decomposition on Co-Mo/MgO (1:1 mole ratio) catalyst at different reaction temperatures. These thermograms were used to calculate the total amount of carbon as described in the experimental section. The total amount of carbon were 8.75%, 11.76%, 14.47 and 20.94% when reaction temperatures were 700, 800, 900 and 1000 °C, respectively. The amount of carbon deposited on catalyst increased with increasing operating temperature, which is possibly due to the thermodynamic of methane decomposition and rate of carbon deposition. As mentioned earlier, methane can self-pyrolyzed at high temperature and the rate of reaction is also increased with temperature. From the TGA results, it is clearly seen that the sample

reacted at 1000 °C exhibit a significant amount of total carbon product, but the amount of amorphous carbon is greater than the amount of carbon nanotube.

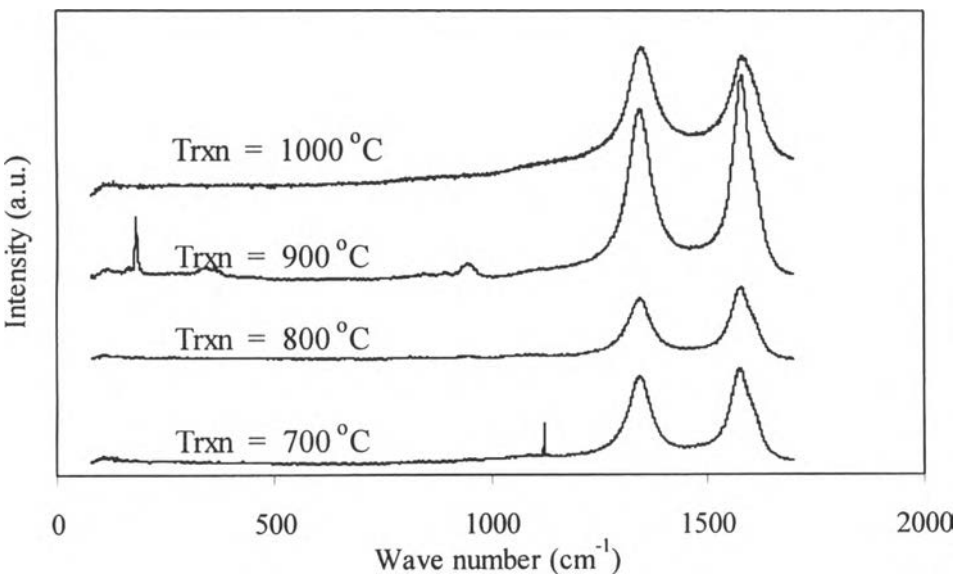

Figure 4.14 Raman spectra of carbon produced by methane decomposition on Co-Mo/MgO (1:1 mole ratio) catalyst at various reaction temperatures

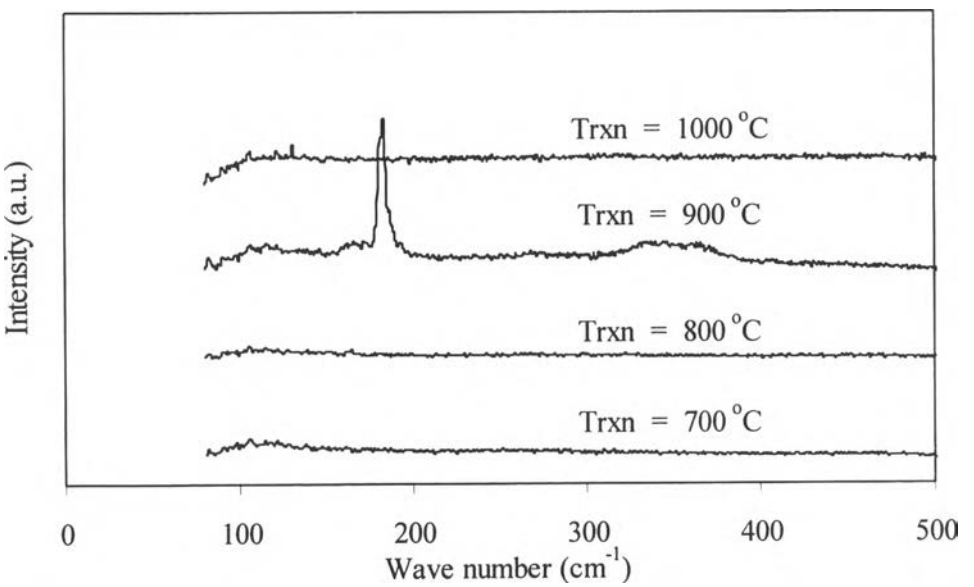

Figure 4.15 Raman spectra at RBM range of carbon produced by methane decomposition on Co-Mo/MgO (1:1 mole ratio) catalyst at various reaction temperatures

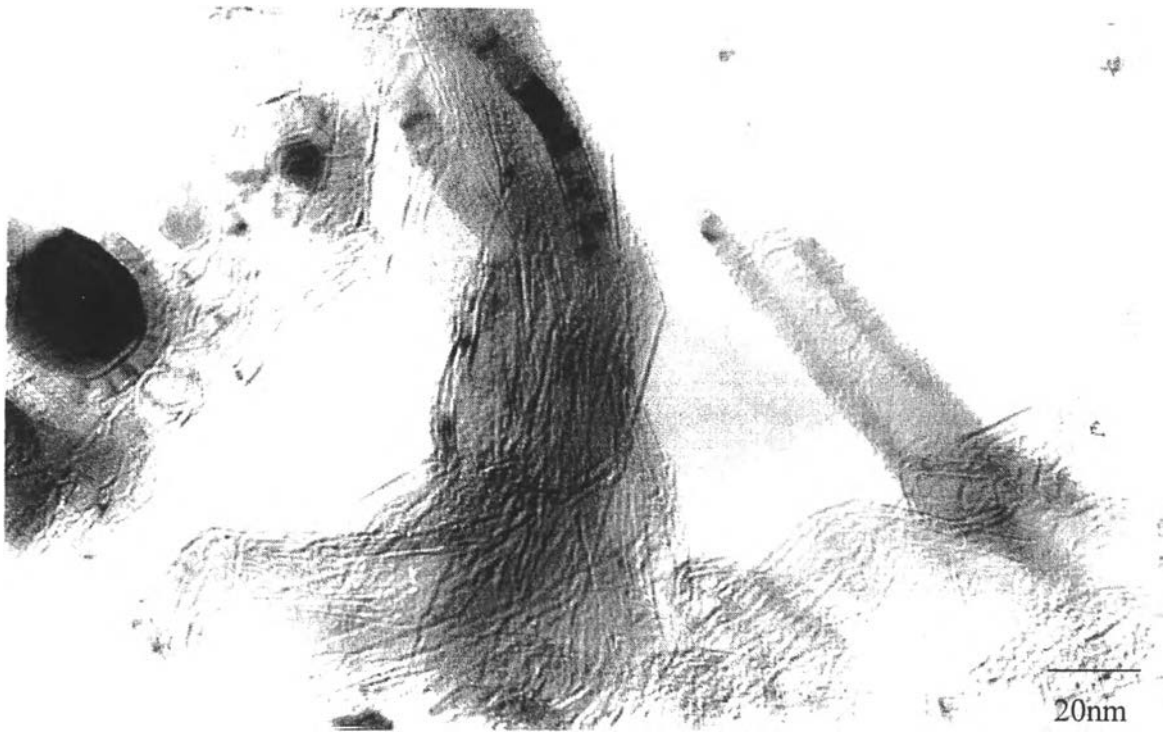

Figure 4.16 TEM image showing a mixture of SWNTs and MWNTs produced by methane decomposition on Co-Mo/MgO (1:1 mole ratio) catalyst at 900 °C

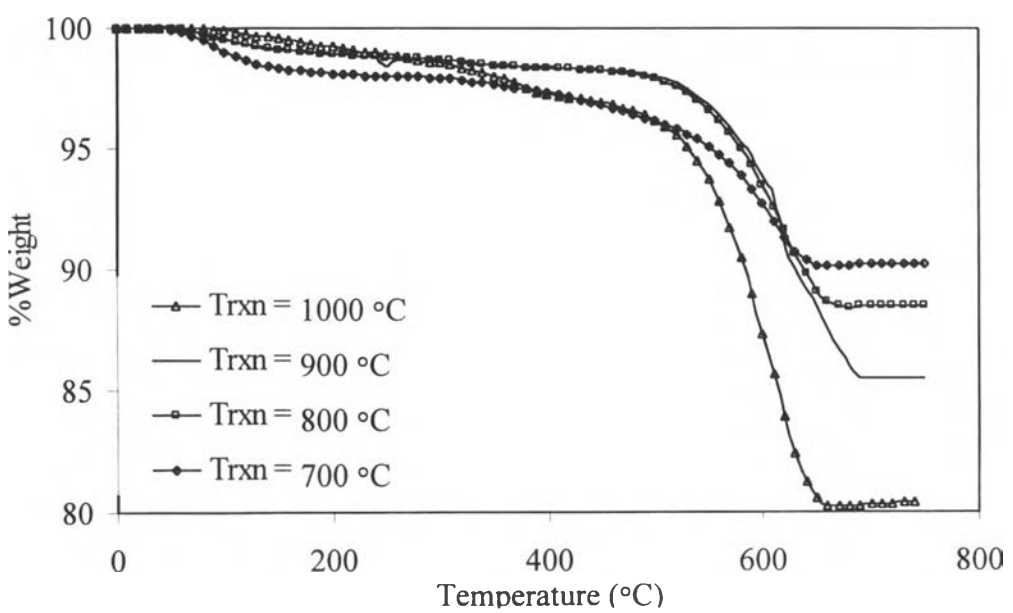

Figure 4.17 Thermograms of carbon produced by methane decomposition on Co-Mo/MgO (1:1 mole ratio) catalyst at various reaction temperatures