



CHAPTER IV

RESULTS AND DISCUSSION

Catalytic decomposition of carbon-containing compounds is the potential technique for mass production of carbon nanotubes, however carbon fibers, onion-like carbon and amorphous are often simultaneously produced. The selectivity to CNTs depends largely on the carbon source, the operating conditions and catalyst formulation.

In this chapter, the effect of reaction temperature, metal loading and ratio of CO:H₂ in feed gas will be discussed. CO, 4:1, 2:1 and 1:1 CO:H₂ were used as carbon sources and 1, 10, 20 and 30% Fe/Al₂O₃ were used as catalysts. The catalysts were prepared by incipient wetness impregnation method and then calcined at 600°C for 3 hours. Reduction patterns of fresh catalysts were determined by temperature programmed reduction (TPR). From Figure 4.1, the catalysts are reduced through two distinct steps, which are the reduction from Fe³⁺ to Fe²⁺ and from Fe²⁺ to metallic Fe as observed in other report (Zhixin *et al.*, 2005). As expected, the intensity of the peak increases with the amount of iron loading due to more required hydrogen in reduction to metallic iron.

The fresh catalysts were reduced at 600°C for 3 hours with 3:1 Ar:H₂ before cool down to room temperature, and then characterized by XRD. The XRD spectra of the reduced catalyst are shown in Figure 4.2. The peak at $2\theta = 44.7$ degree refers to metal iron. Sharper and higher intensity were observed in higher iron loading sample. Moreover, by applying Scherrer equation, crystallize size can be calculated (Table 4.1). As expected, the crystallize size tends to be larger for higher percent iron loading. However, at 1% Fe, the peak of iron metal cannot be observed, may be due to the short range order of Fe crystal.

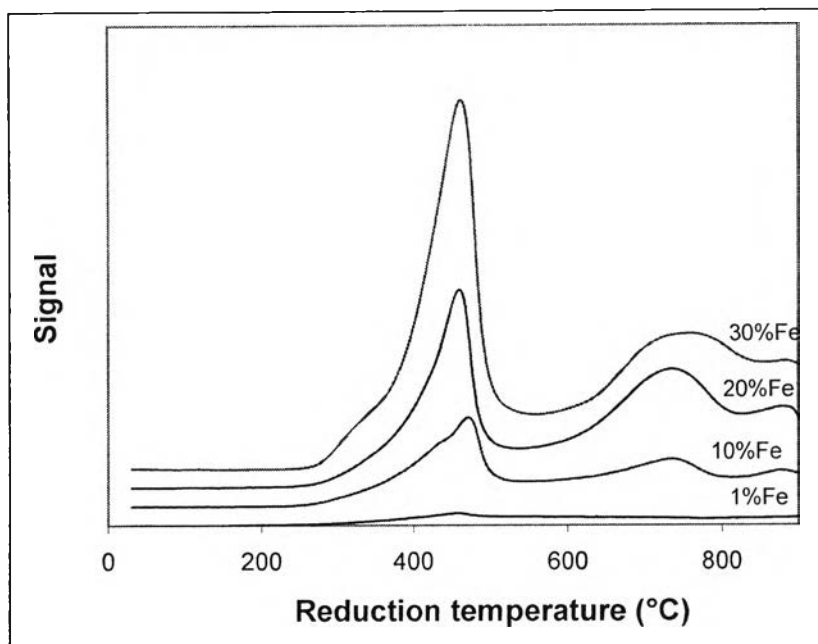


Figure 4.1 TPR profiles of calcined Fe/Al₂O₃ catalysts.

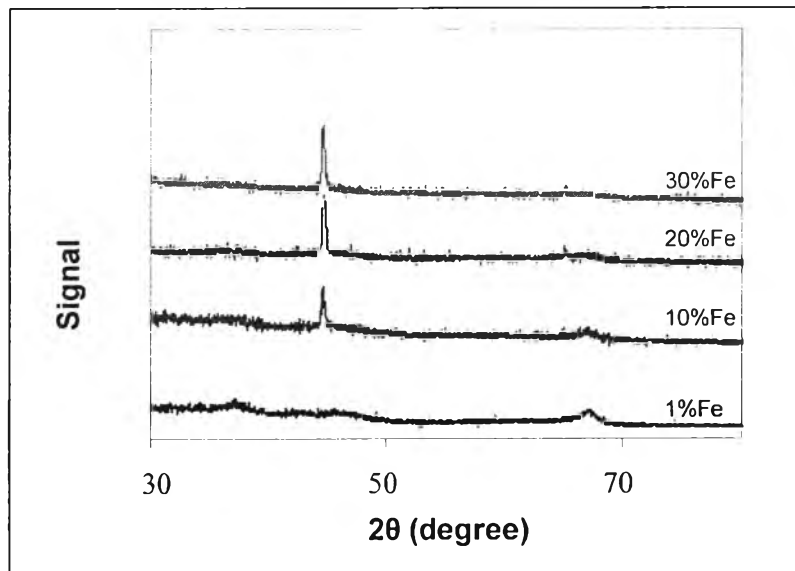


Figure 4.2 XRD spectra of reduced Fe/Al₂O₃ catalysts.

Table 4.1 Crystallize size of iron from different iron loading catalysts calculated by Scherrer equation

%Fe loading	Crystallize size (nm)
10	25
20	36
30	57

4.1 Effect of Reaction Temperature

In this part, the metal loading and the reaction gas were fixed at 20% Fe/Al₂O₃ and 4:1 CO:H₂ respectively. Prior to synthesis, the catalyst was reduced at 600°C for 3 hours. The reaction performed at different temperatures; 400, 500, 600, 700, 800 and 900°C for 2 hours, then cool down to room temperature with argon gas. The deposited carbon was then characterized by XRD, SEM, TPO and TEM.

The detailed structure of the carbon products was distinguished by TEM as seen in Figure 4.3. The results show that the products from 500°C and 600°C are carbon nanofibers, however at 700°C carbon nanotubes are observed instead.

The graphitic plane of graphite is determined by XRD. The X-ray diffraction peak at $2\theta = 26$ degree attributes to the graphitic plane of CNTs and CNFs. XRD spectra of carbon deposited are shown in Figure 4.4. The higher intensity refers to larger diameter due to the more graphitic walls. Therefore the fibers produced at 600°C should be the thickest. For lower reaction temperature the peaks are broader due to lower degree of graphitization. Moreover, no peak can be observed for 400°C reaction temperature. Therefore the product from 400°C should be amorphous carbon.

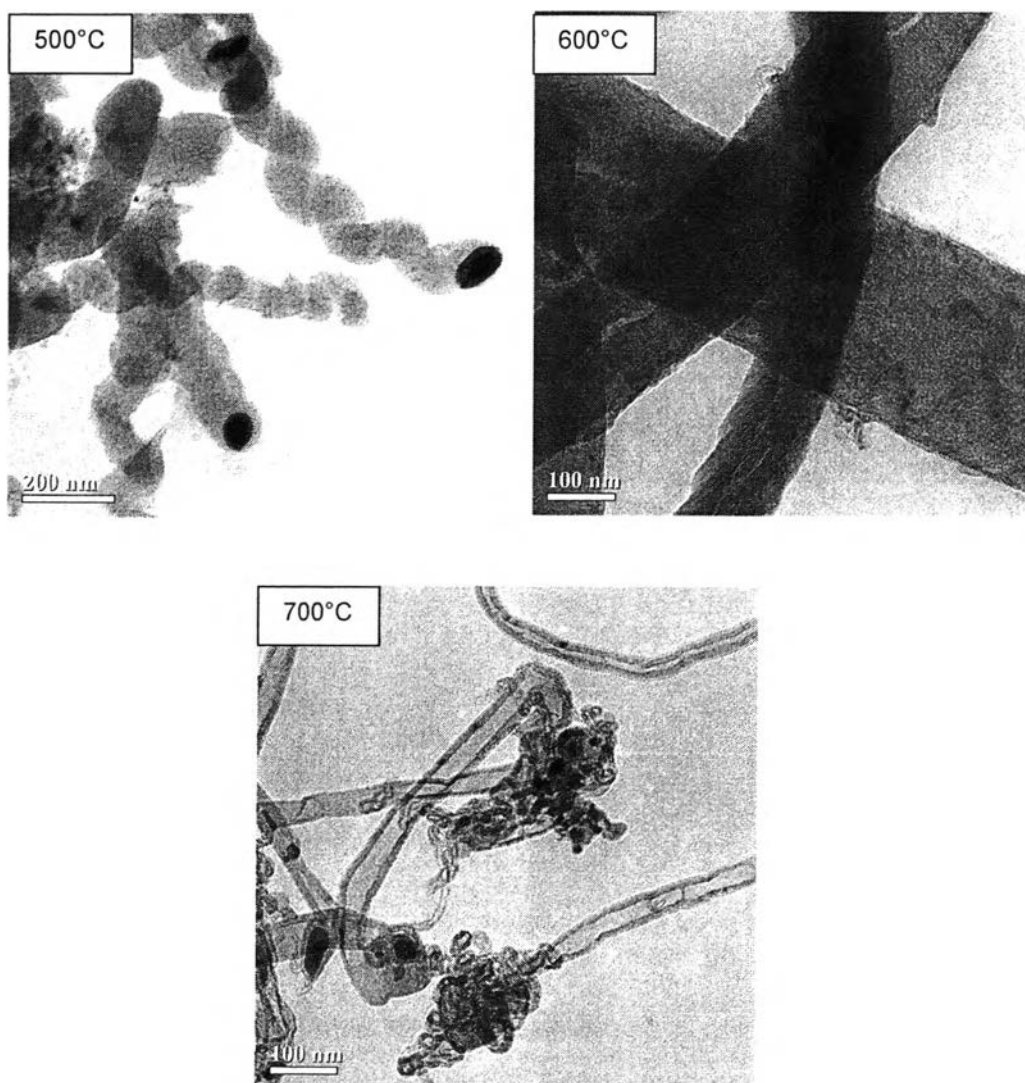


Figure 4.3 TEM images of CNFs and CNTs grown from 4:1 CO:H₂ over 20% Fe/Al₂O₃ catalyst at 500°C, 600°C and 700°C.

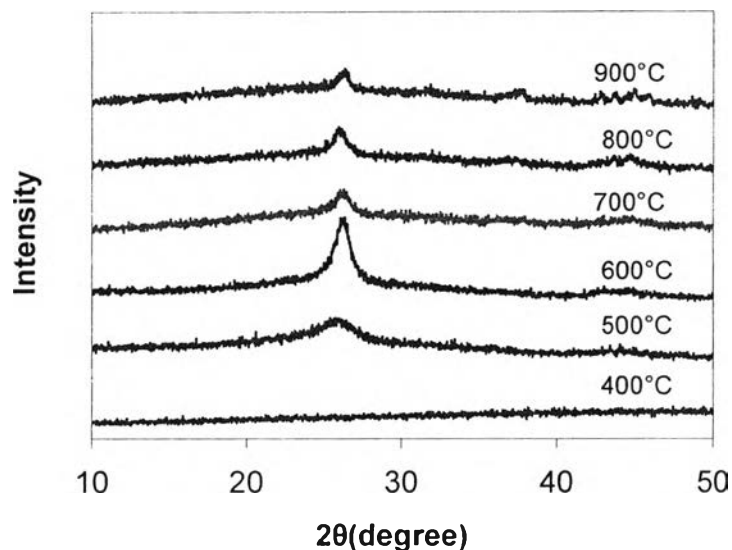


Figure 4.4 XRD spectra of deposited carbon from 4:1 CO:H₂ over 20% Fe/Al₂O₃ at different reaction temperatures.

The SEM images are shown in Figure 4.5. At 400°C reaction temperature, there is no observed CNFs or CNTs. But, CNFs produced at 500°C and 600°C were longer than CNTs that produced at 700°C and 800°C. Moreover, very few CNTs were produced at 900°C may be due to iron agglomeration.

Diameter distribution was statistically obtained by measuring the diameter of the fibers up to 500 points of several nanofibers or nanotubes in SEM. As shown in Figure 4.6, 4.7, 4.8 and 4.9, the narrow diameter distribution is obtained only from 700°C. For other temperature, the diameter distribution is broader.

As shown in Figure 4.10, CNTs' average diameter was smallest at 700°C. The largest diameter of carbon nanofiber is obtained at 600°C which is in agreement with the XRD result.

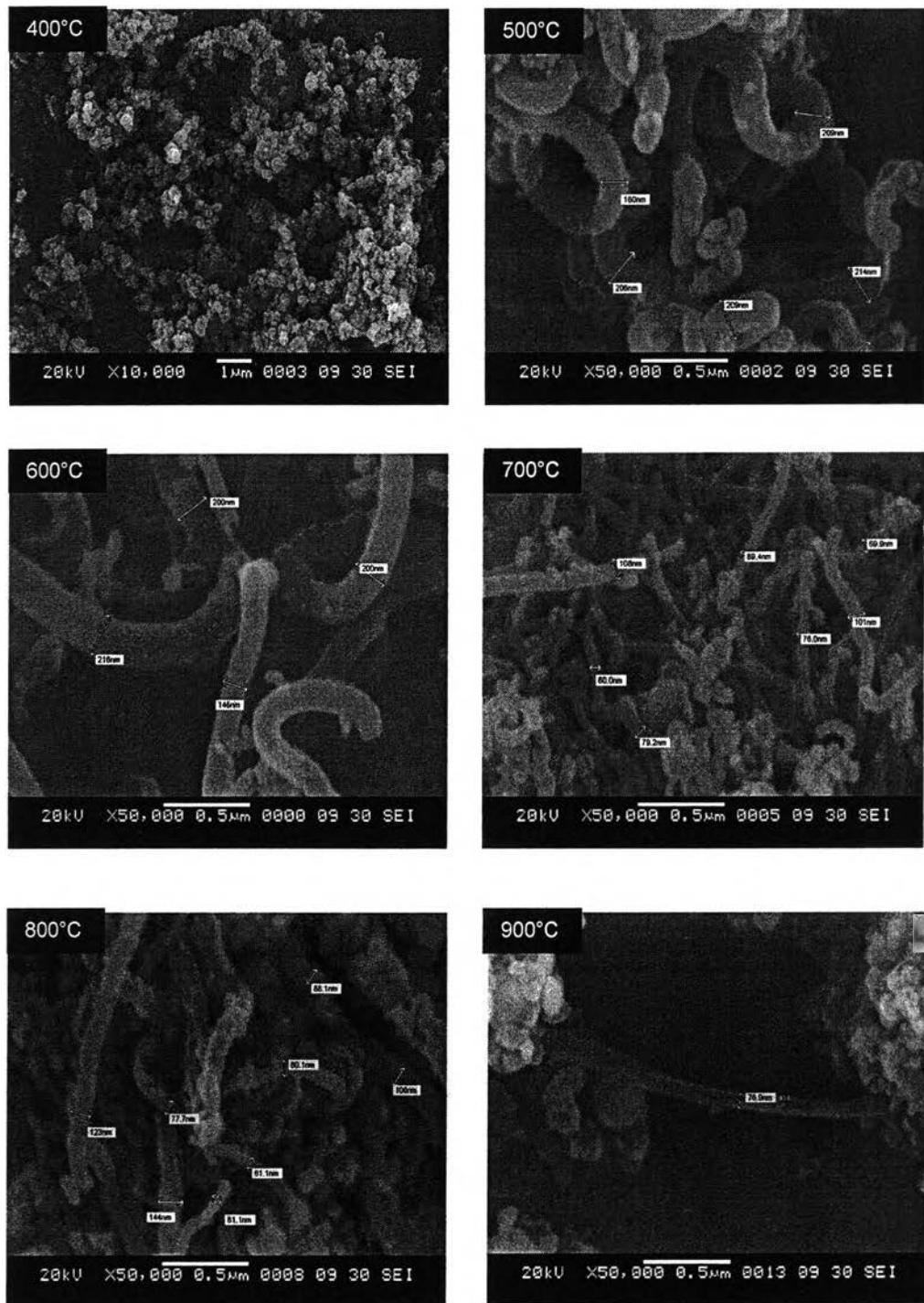


Figure 4.5 SEM images of the deposited carbon from 4:1 CO:H₂ over 20% Fe/Al₂O₃ catalyst at various reaction temperatures.

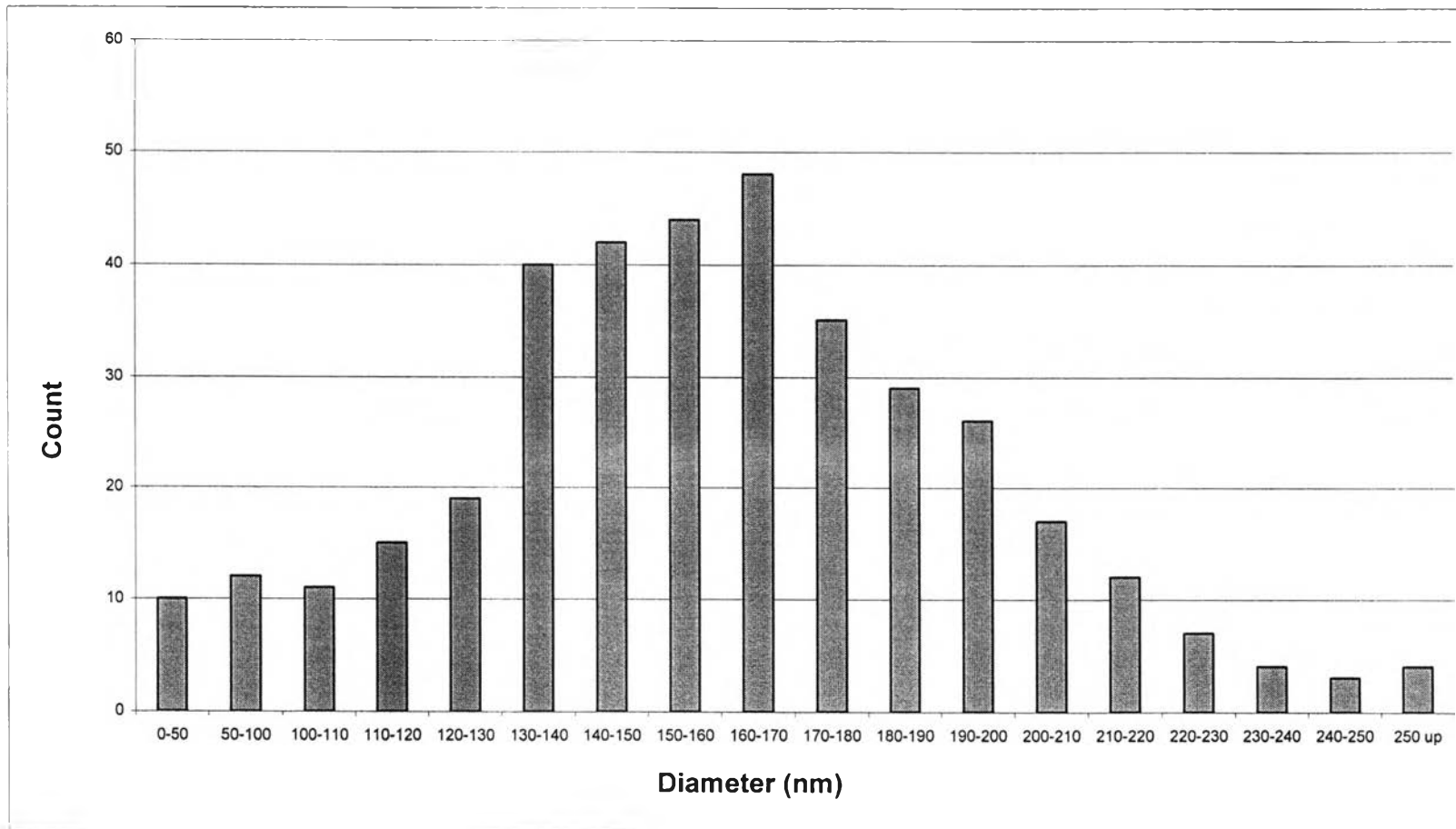


Figure 4.6 Diameter distribution of CNFs grown from 4:1 CO:H₂ over 20% Fe/Al₂O₃ catalyst at 500°C.

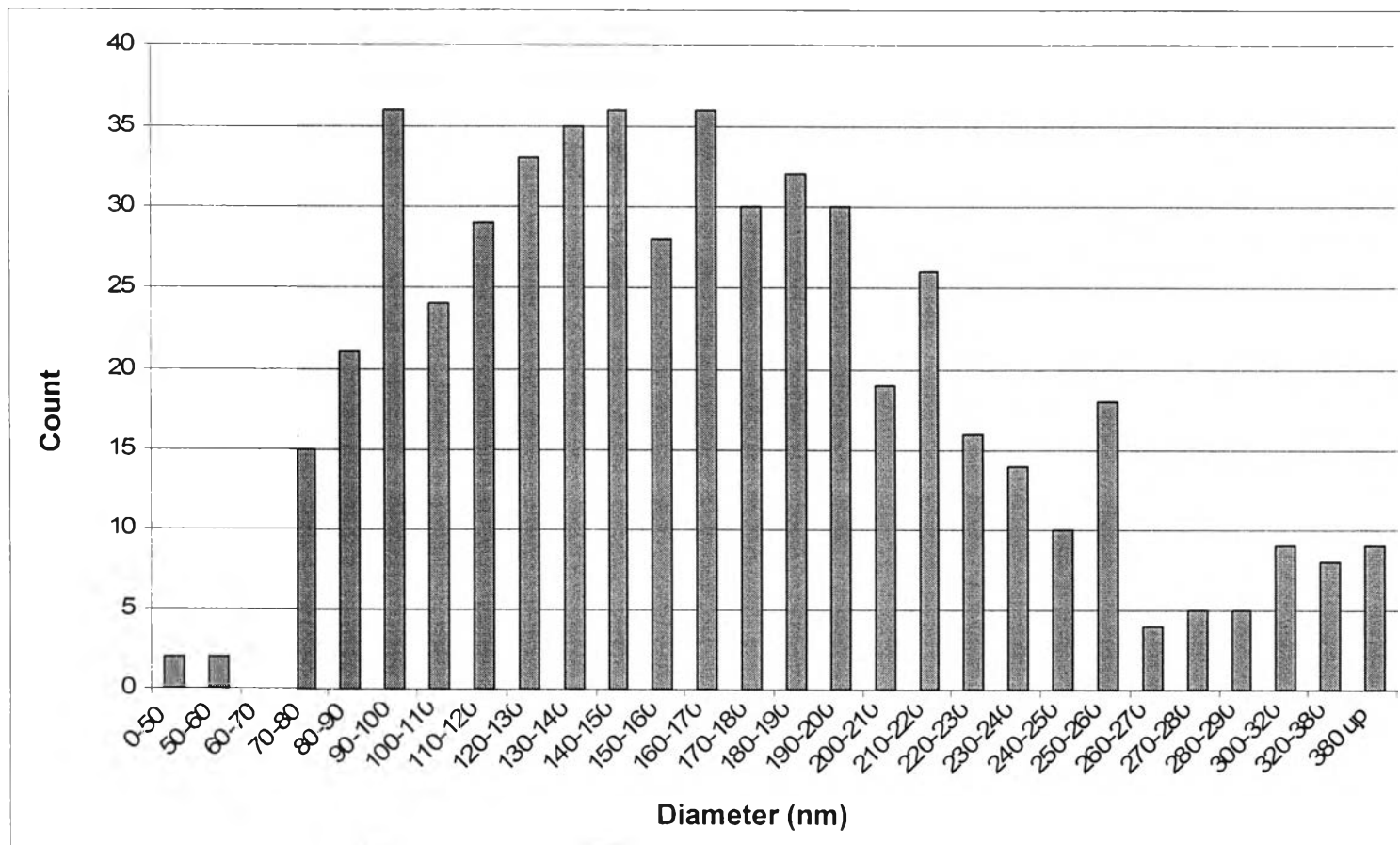


Figure 4.7 Diameter distribution of CNFs grown from 4:1 CO:H₂ over 20% Fe/Al₂O₃ catalyst at 600°C.

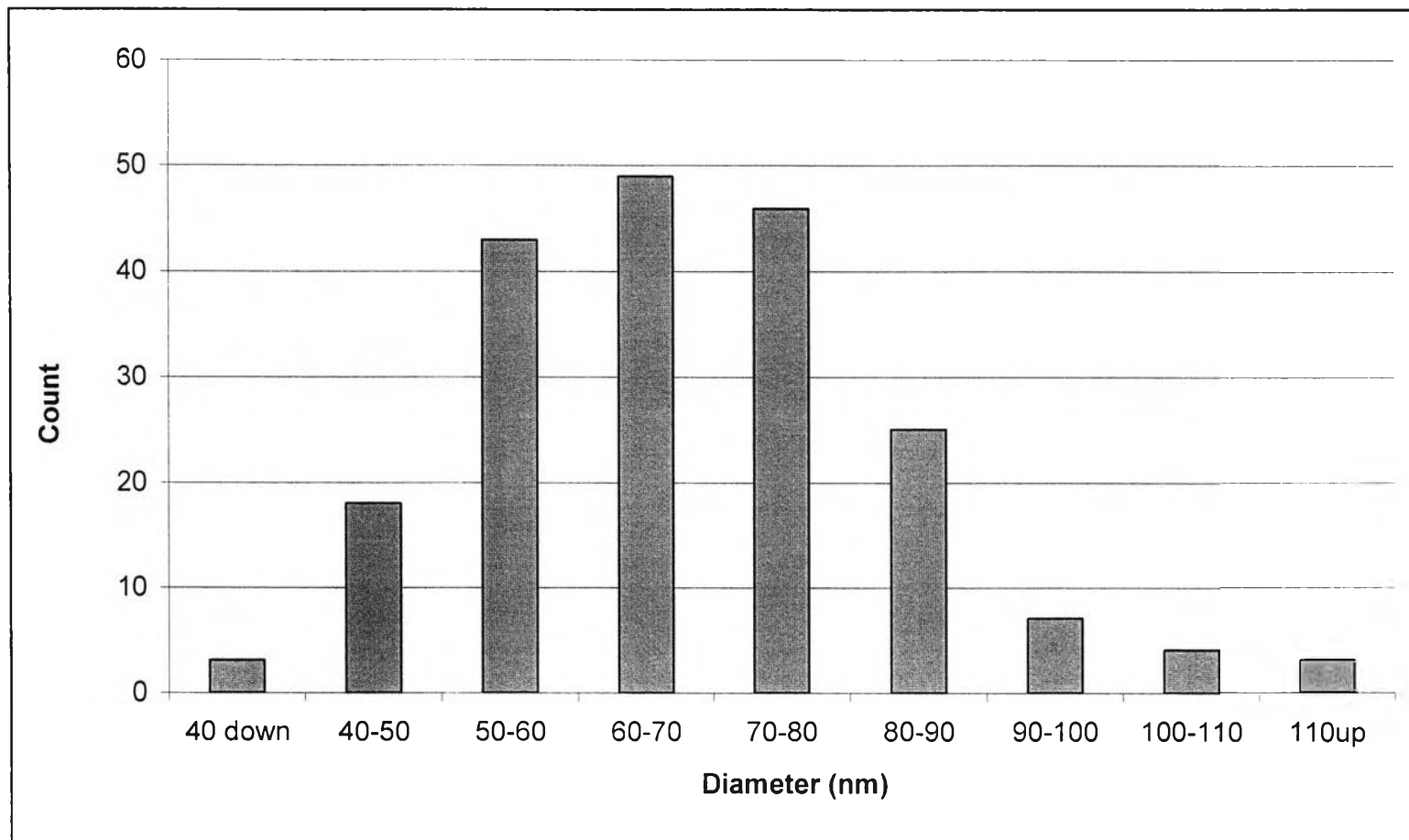


Figure 4.8 Diameter distribution of CNTs grown from 4:1 CO:H₂ over 20% Fe/Al₂O₃ catalyst at 700°C.

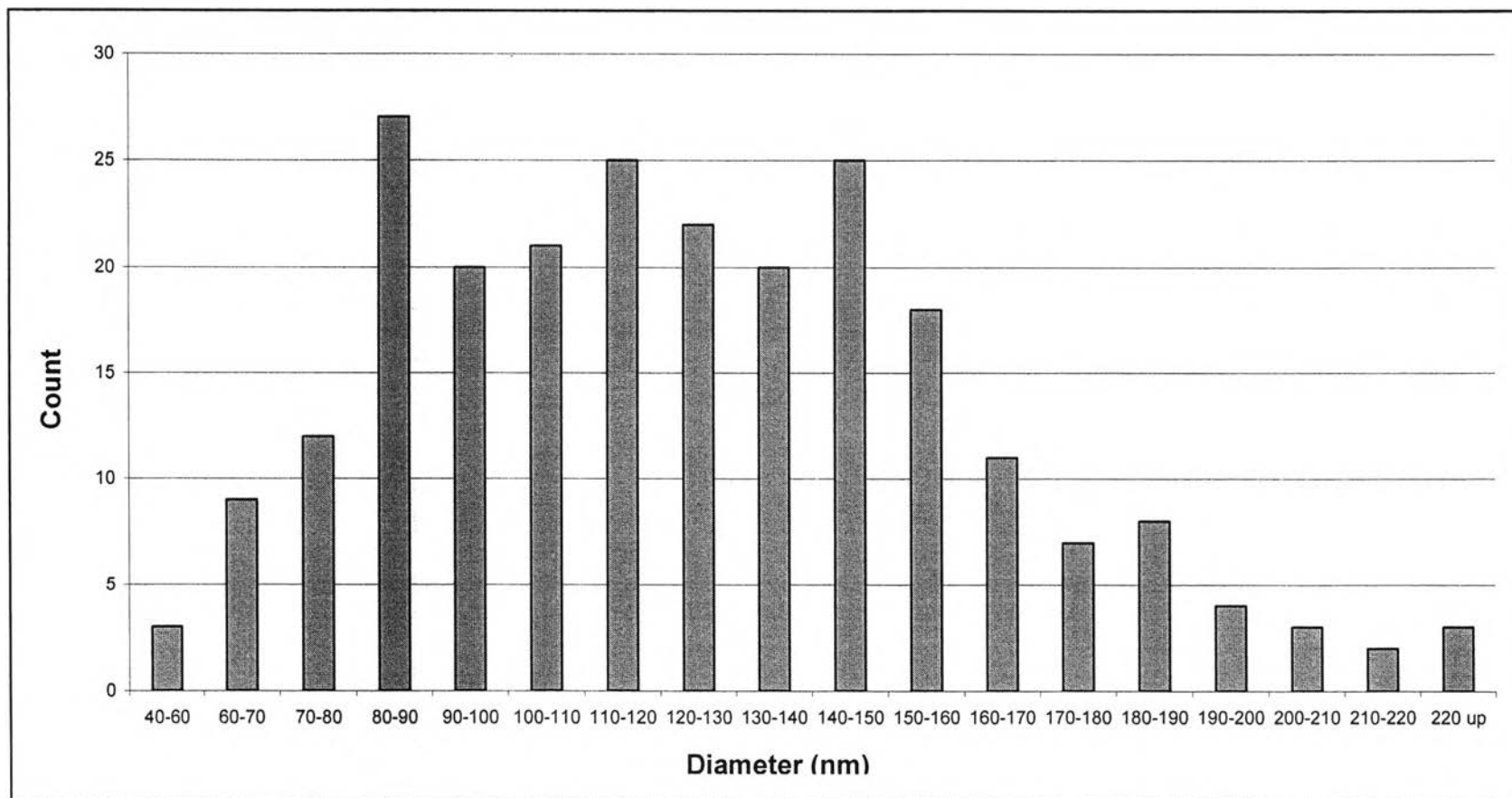


Figure 4.9 Diameter distribution of CNTs grown from 4:1 CO:H₂ over 20% Fe/Al₂O₃ catalyst at 800°C.

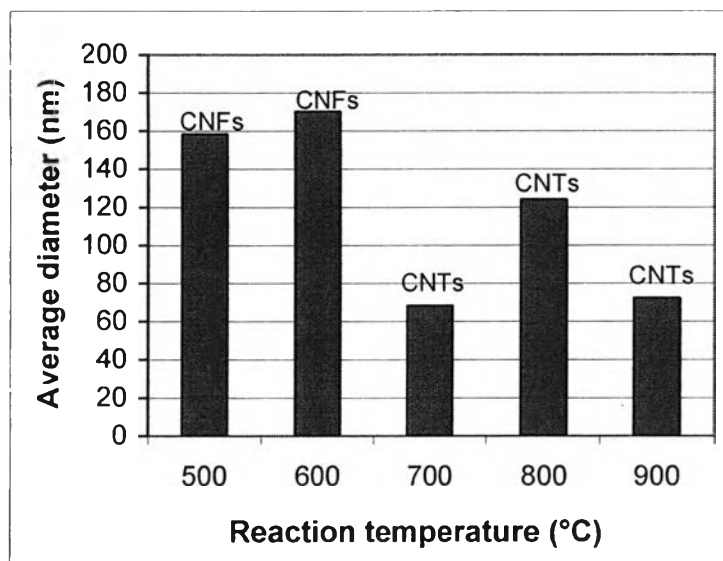


Figure 4.10 Average diameter of CNTs and CNFs produced at various reaction temperatures from 4:1 CO:H₂ over 20% Fe/Al₂O₃.

The temperature programmed oxidation was also used for determining the diameter of carbon nanotubes and carbon nanofibers. Normally carbon nanotubes and carbon nanofibers are oxidized at high temperature (600-700°C). The larger diameter are more difficult to be oxidized due to many layers that prevent the oxygen to oxidize the inner layers. Therefore, the peak was shifted to higher oxidation temperature for the larger diameter. Carbon nanofibers can be oxidized easier than carbon nanotubes due to more exposed edge, so the large CNFs produced from 500°C can be oxidized at lower temperature. Moreover, the oxidation temperature of the deposited carbon from 400°C reaction temperature is very low, which is the oxidation temperature of amorphous carbon in this sample as observed by SEM and XRD.

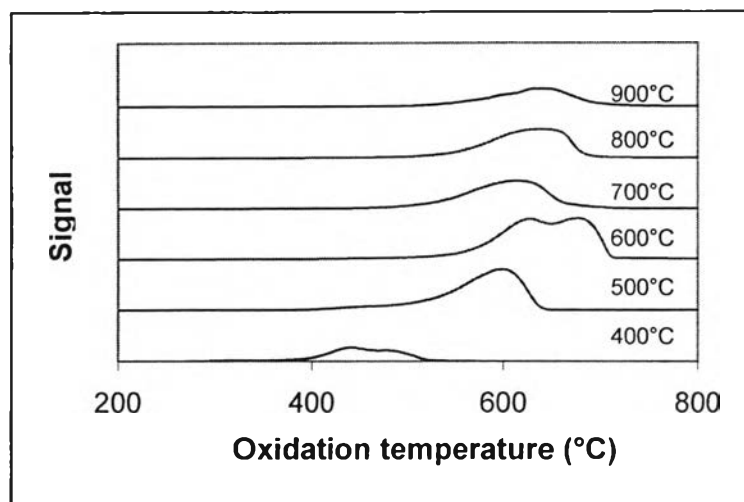


Figure 4.11 TPO profiles of deposited carbon at different reaction temperatures from 4:1 CO:H₂ over 20% Fe/Al₂O₃ catalyst.

Percent deposited carbon in Figure 4.12 was calculated from the area of TPO profile. It was found that up to 600°C the carbon yield increase with the reaction temperature and at reaction temperature above 600°C, higher temperature tends to decrease the carbon deposited.

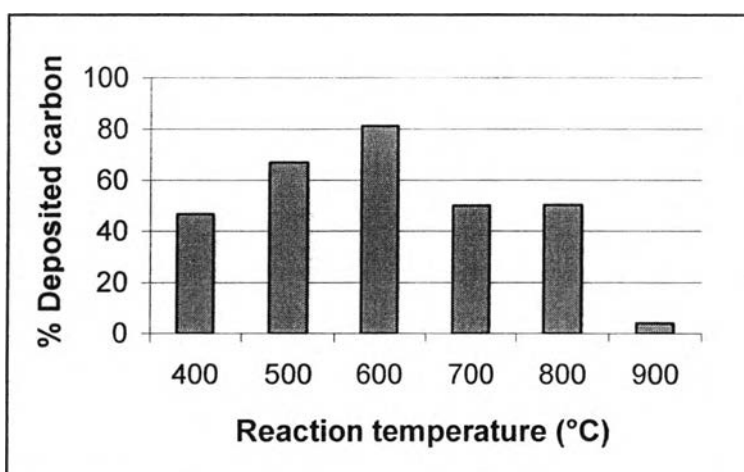


Figure 4.12 Carbon yield of products from 4:1 CO:H₂ over 20% Fe/Al₂O₃ catalyst at different reaction temperatures.

Table 4.2 Carbon yield, structure and average diameter of CNTs and CNFs at different reaction temperatures

Reaction Temperature (°C)	Structure	% Deposited carbon	Average diameter (nm)
400	amorphous	46.6	no
500	CNFs	66.8	158
600	CNFs	81.2	170
700	CNTs	49.9	68
800	CNTs	50.2	123
900	CNTs	4.0	72

4.2 Effect of Iron Loading

In this study, 1, 10, 20, and 30% Fe/Al₂O₃ were used as catalysts and before the reaction, they were reduced at 600°C by 3:1 Ar:H₂ for 3 hours. The reaction condition was at 700°C in 4:1 CO:H₂ feed gas for 1 hour. The deposited carbon was then characterized by TEM, XRD, TPO and SEM.

The TEM images, as shown in Figure 4.13, demonstrate that the deposited carbon for 20% and 30% Fe/Al₂O₃ catalyst are hollow fibers that have the wall parallel to the axis, moreover, the product from 1% Fe/Al₂O₃ is also similar.

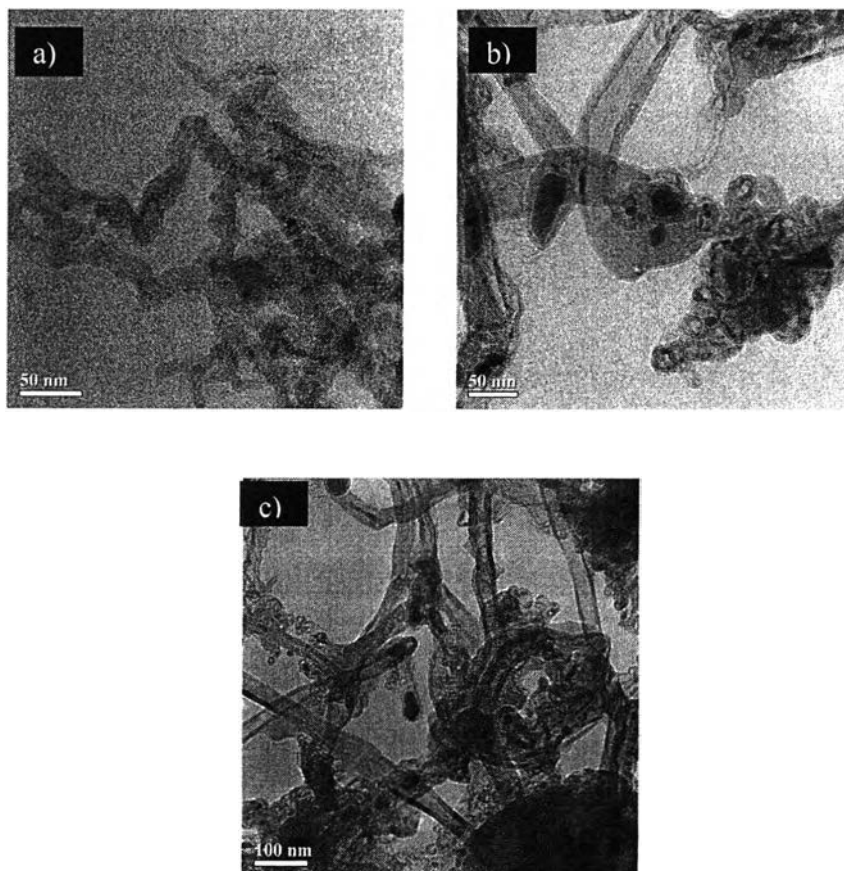


Figure 4.13 TEM images of CNTs grown from 4:1 CO:H₂ at 700°C over a) 1%, b) 20%, and c) 30% Fe/Al₂O₃.

The large-diameter CNTs were obtained from high iron load as seen in Figure 4.14. Diameter distribution and average diameter are shown in Figure 4.15 and 4.16 respectively.

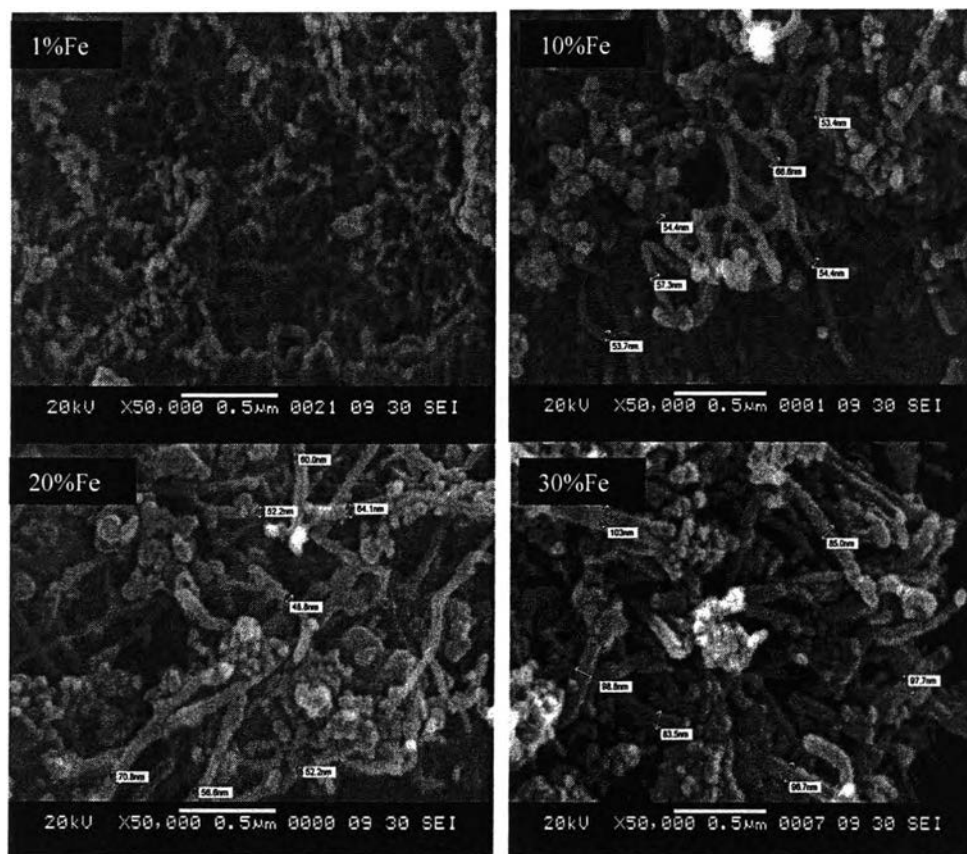


Figure 4.14 SEM images of CNTs grown from 4:1 CO:H₂ at 700°C over 1, 10, 20 and 30% Fe/Al₂O₃ catalysts.

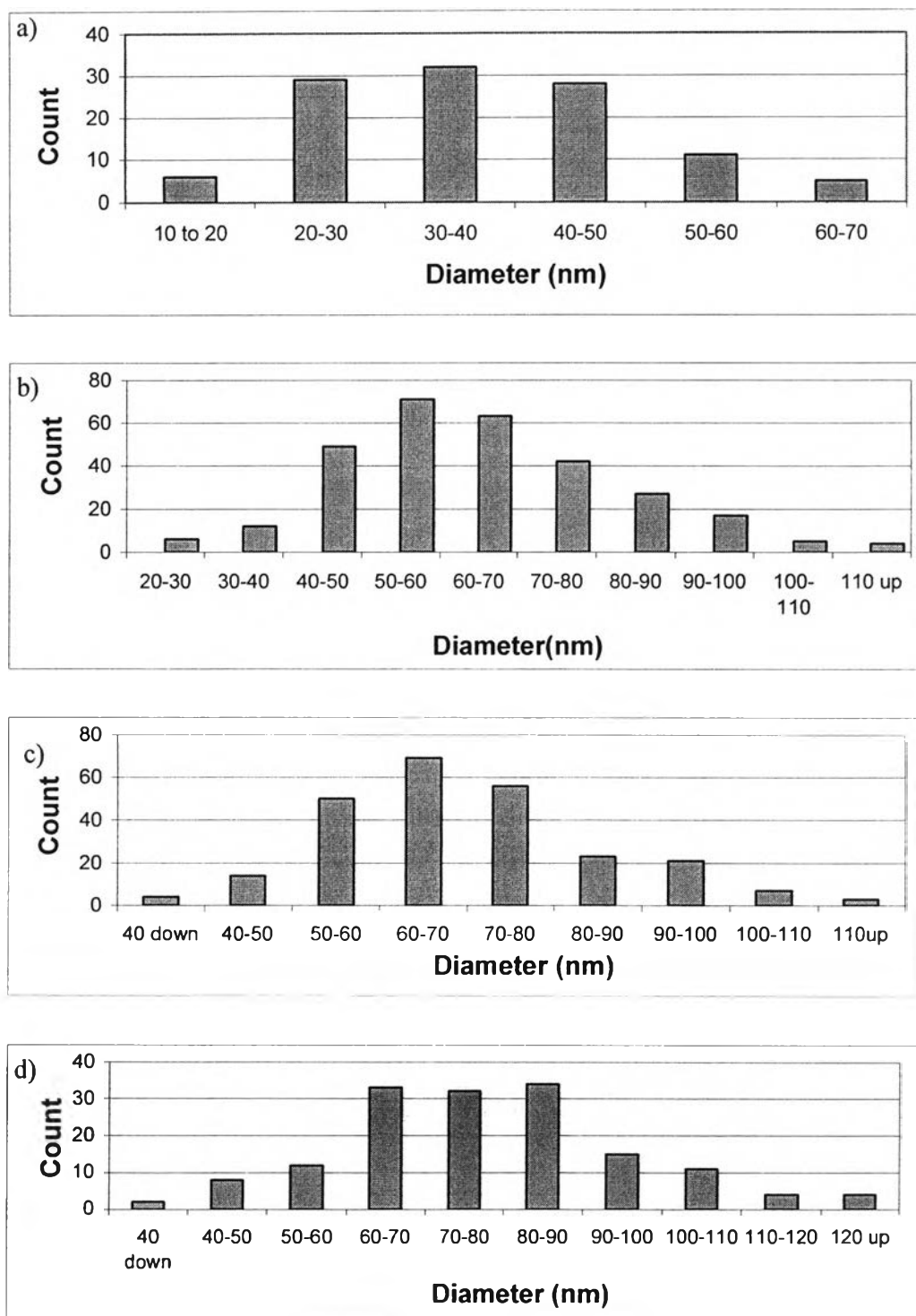


Figure 4.15 Diameter distributions of CNTs grown from 4:1 CO:H₂ at 700°C over a) 1%, b) 10%, c) 20% and c) 30% Fe/Al₂O₃ catalyst.

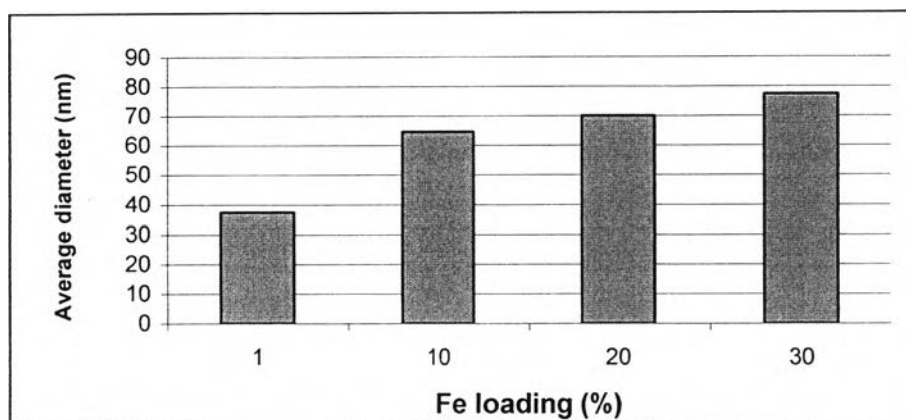


Figure 4.16 Average diameter of CNTs grown from 4:1 CO:H₂ at 700°C over various Fe loading catalysts.

The SEM results correlate well with TPO and XRD results. The higher oxidation temperature from TPO refers to the thicker CNTs wall. From TPO profile in Figure 4.17, the oxidation temperature shift to higher temperature when iron loading increase, proving that larger CNTs diameter is produced from higher iron loading.

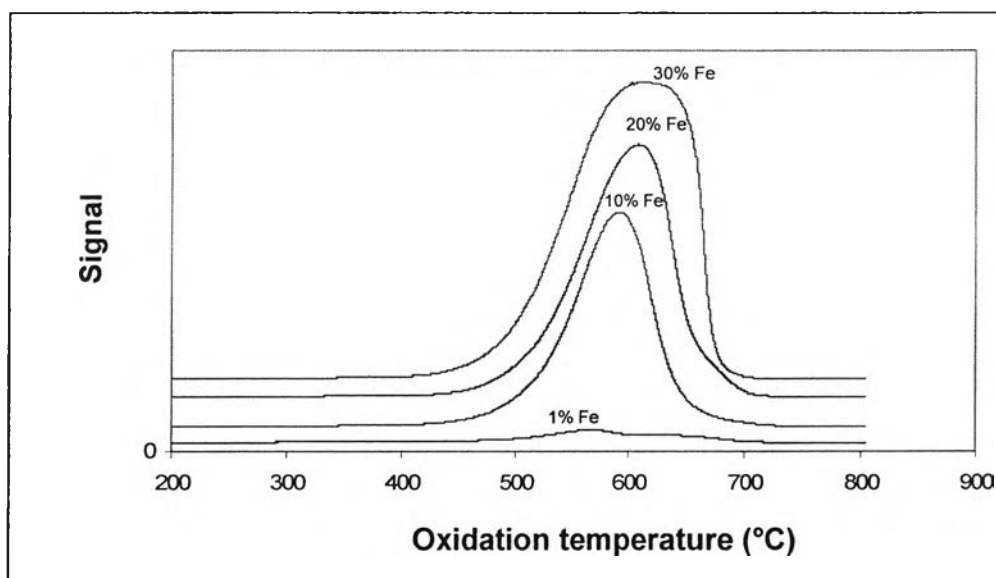


Figure 4.17 TPO profiles of deposited carbon produced from 4:1 CO:H₂ at 700°C over different Fe loading catalysts.

The XRD results in Figure 4.18 are in agreement with the TPO and SEM. The peak at $2\theta = 26$ degree refers to the graphic plane of CNTs. The higher intensity of the peak is due to the thicker wall. In Figure 4.18 the higher intensity was observed when higher iron loading was used and this means larger CNTs diameter was formed.

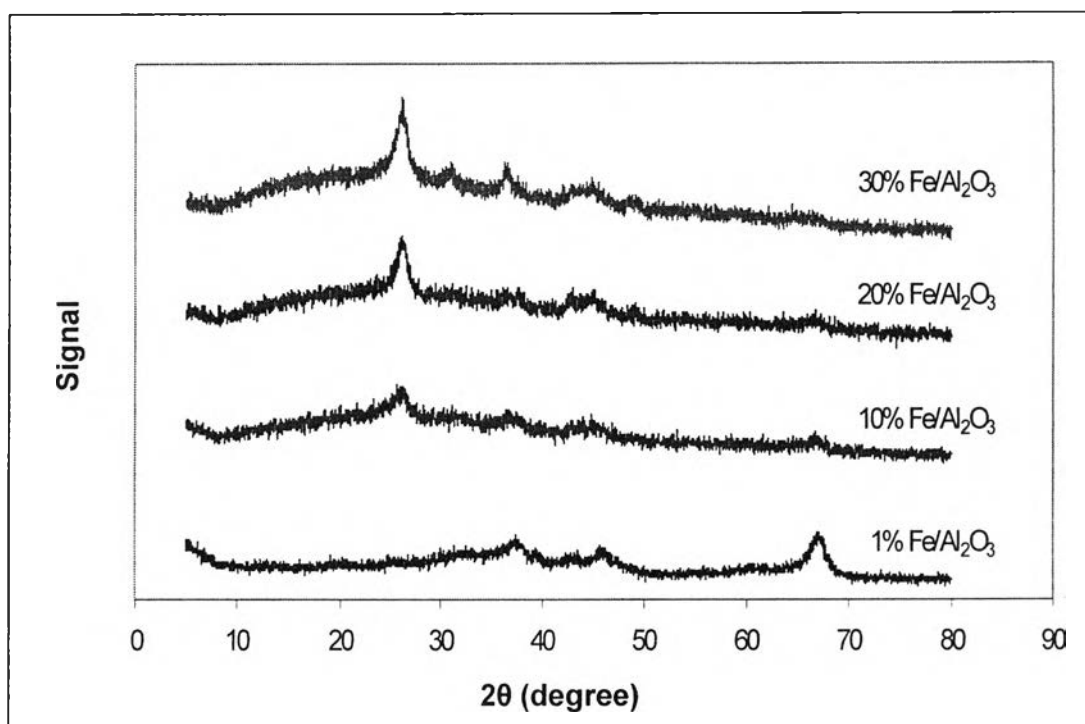


Figure 4.18 XRD spectra of the CNTs grown from 4:1 CO: H₂ at 700°C over different Fe loading catalysts.

The higher iron loading yield larger iron crystallize size as seen in Table 4.3, that may be the reason for the larger CNTs diameter.

Table 4.3 Summary of carbon yield and average diameter of CNTs grown from 4:1 CO:H₂ at 700°C over different Fe loading catalysts

Fe loading (%)	Crystallize size of Fe(nm)	CNTs' average diameter (nm)	% Deposited carbon
1	-	37	1.6
10	25	64	31.9
20	36	70	43.6
30	57	77	57.2

From the mechanism demonstrated in Figure 4.19 (Nagy *et al.*, 2004), there are four steps for CNTs growth; the hydrocarbon decomposition, the carbon diffusion, the cap formation and the growth of CNTs. In the cap formation step, it is reasonable to demonstrate that the larger iron particle can form the larger cap that make the CNTs diameter larger.

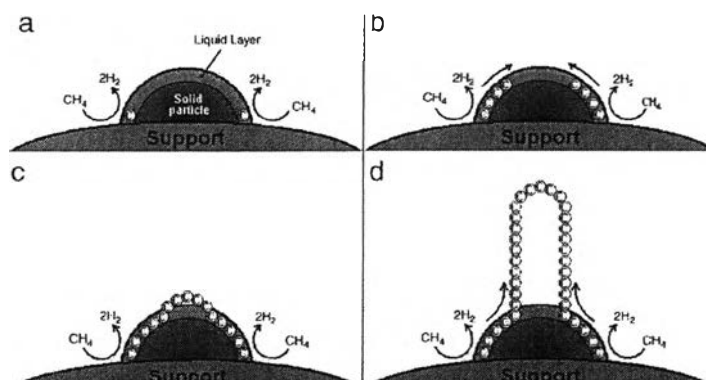


Figure 4.19 Schematic view of the nucleation of a cap of SWNT (a) Hydrocarbon decomposition. (b) Carbon diffusion in the surface layer. (c) Supersaturation of the surface and formation of the cap (d) Growth of a SWNT (Nagy *et al.*, 2004).

The carbon yield was calculated from the TPO. The deposited carbon increases with higher iron loading due to more active site.

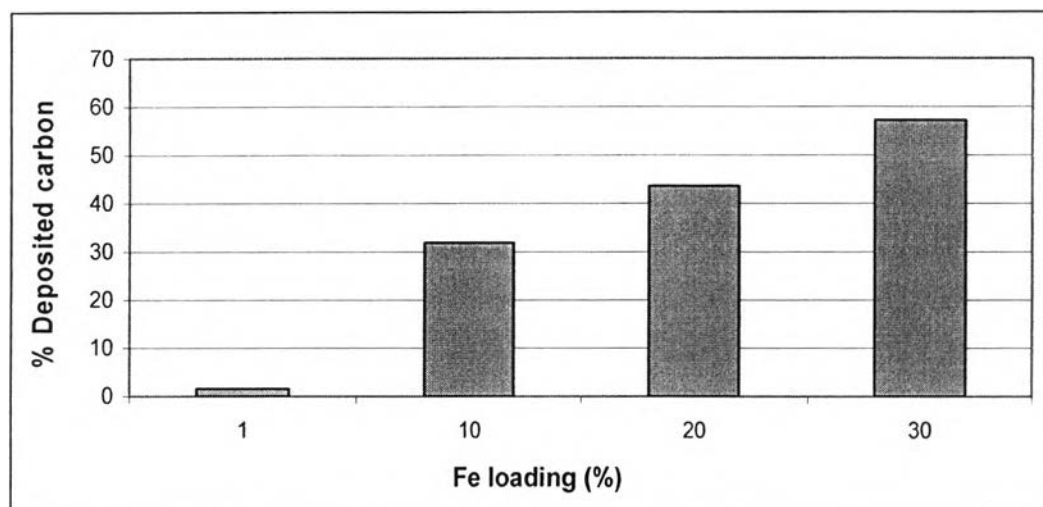


Figure 4.20 Percent deposited carbon from 4:1 CO:H₂ at 700°C over 1, 10, 20 and 30% Fe/Al₂O₃ catalyst.

4.3 Effect of CO and H₂ ratio in feed gas

In this part, the effect of hydrogen fraction in the feed gas will be discussed. The catalyst was a 10% Fe/Al₂O₃ that was reduced at 600°C with 3:1 Ar:H₂ for 3 hours prior to the reaction. The different feed gas compositions including 1:1, 2:1, 4:1 CO:H₂ and pure CO were used. The reaction temperature and time were fixed at 700°C and 1 hour, respectively. The deposited carbon was then characterized by XRD, SEM and TPO.

Major XRD peak at $2\theta = 26$ degree demonstrates the graphitic structure of the samples. The higher intensity possibly shows the thicker of CNTs' wall. In Figure 4.21, the product from pure CO have very small peak at $2\theta = 26$ degree, however the higher peak intensity was observed when hydrogen was added into the system. This hints that very thin graphitic layers were produced from pure CO and the thicker layers were formed when hydrogen fraction is increased.

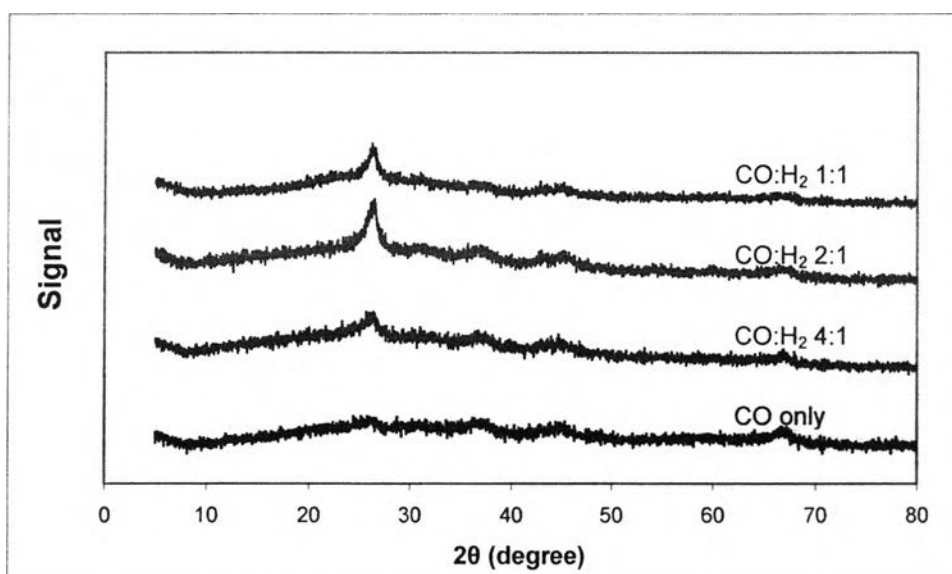


Figure 4.21 XRD spectra of CNTs grown from different CO: H₂ ratios on 10% Fe/Al₂O₃ at 700°C.

The results from TPO correlate well with XRD. The thicker graphitic walls are more difficult for oxygen to access to. Therefore the thicker CNTs are oxidized at higher temperature. From Figure 4.22, higher oxidation temperature of the product was observed when hydrogen is added to the system. It shows that the larger-diameters CNTs were obtained from the products of higher hydrogen fraction in feed.

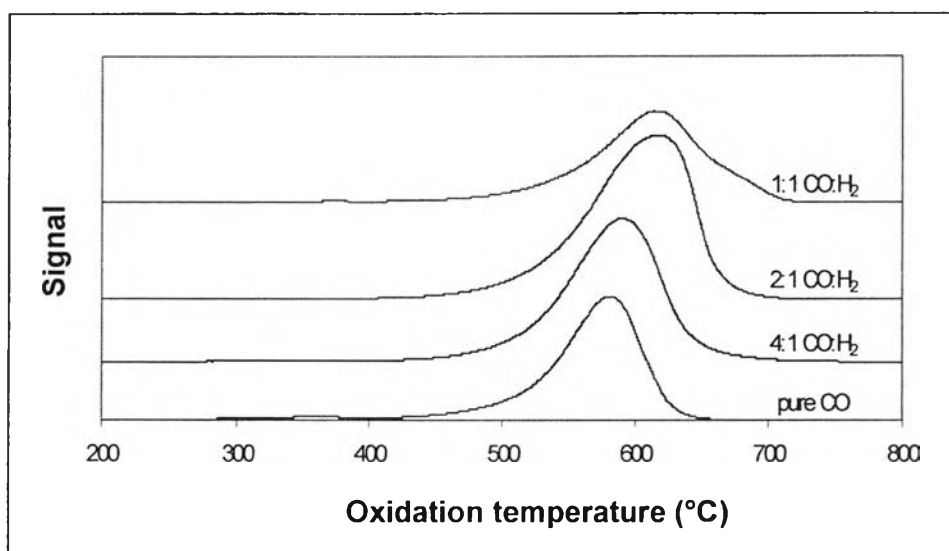


Figure 4.22 TPO profiles of the product from different CO:H₂ ratios on 10% Fe/Al₂O₃ at 700°C.

The SEM images (Figure 4.23) show that large-diameter CNTs can be observed only in the sample that hydrogen is involved in the gas feed. Larger-diameter CNTs can be observed when hydrogen fraction was higher, which is in agreement with the XRD and TPO results. The diameter distribution and average diameter are shown in figure 4.24 and 4.25 respectively.

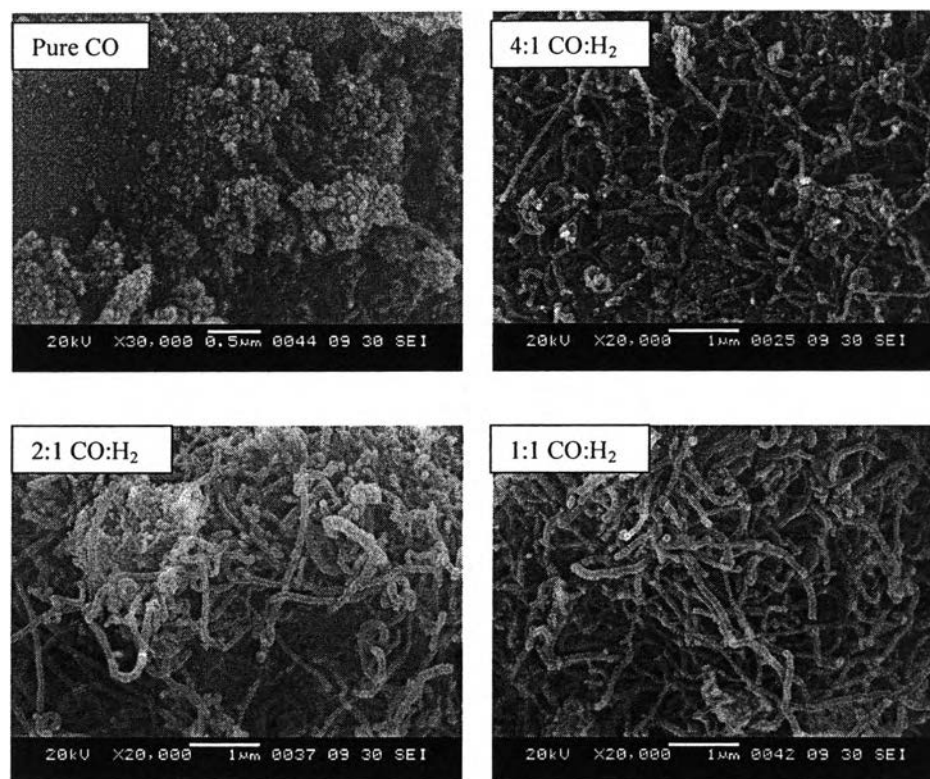


Figure 4.23 SEM images of deposited carbon from pure CO, 4:1, 2:1, and 1:1 CO:H₂ over 10% Fe/Al₂O₃ catalyst at 700°C.

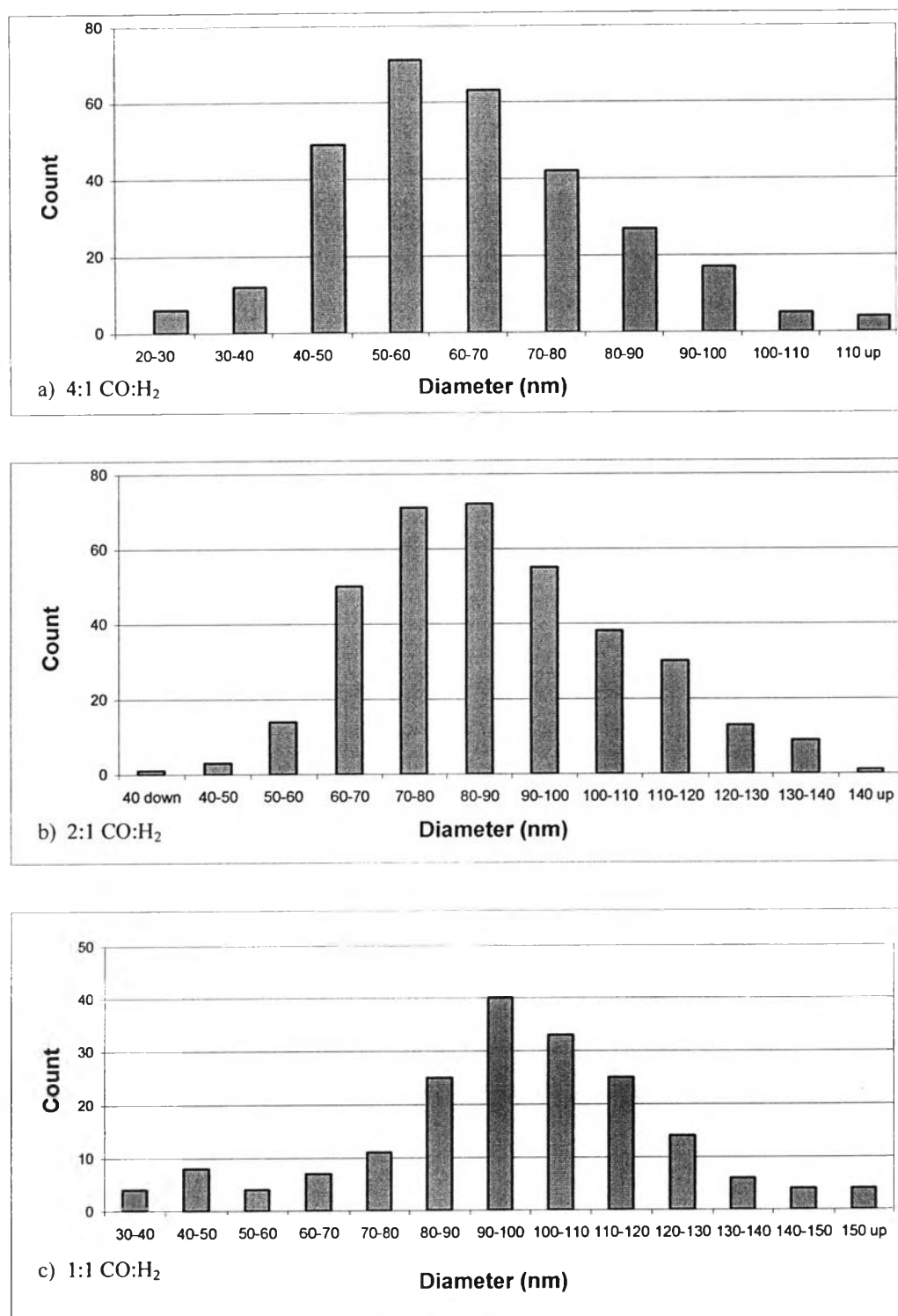


Figure 4.24 Diameter distributions of CNTs grown from a) 4:1, b) 2:1 and c) 1:1 CO:H₂ at 700°C over 10% Fe/Al₂O₃ catalyst.

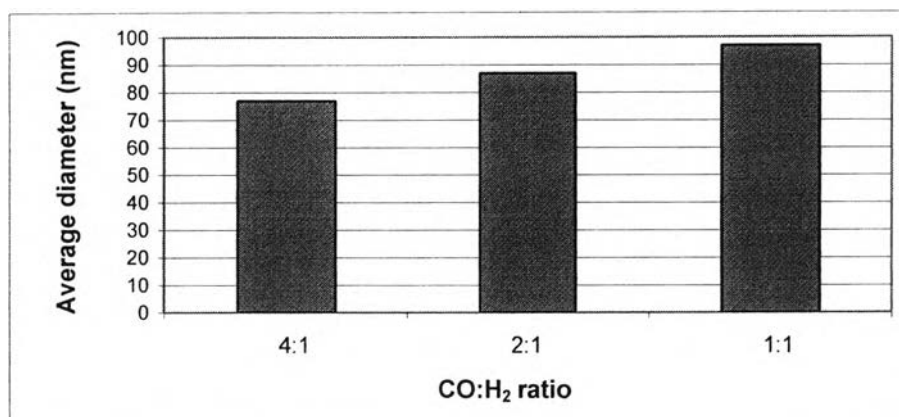


Figure 4.25 Average diameter of CNTs grown from 4:1, 2:1 and 1:1 CO:H₂ over 10% Fe/Al₂O₃ catalyst at 700°C.

Moreover, high hydrogen fraction yielded more deposited carbon as seen in Figure 4.26. The maximum carbon yield was found at 2:1 CO:H₂.

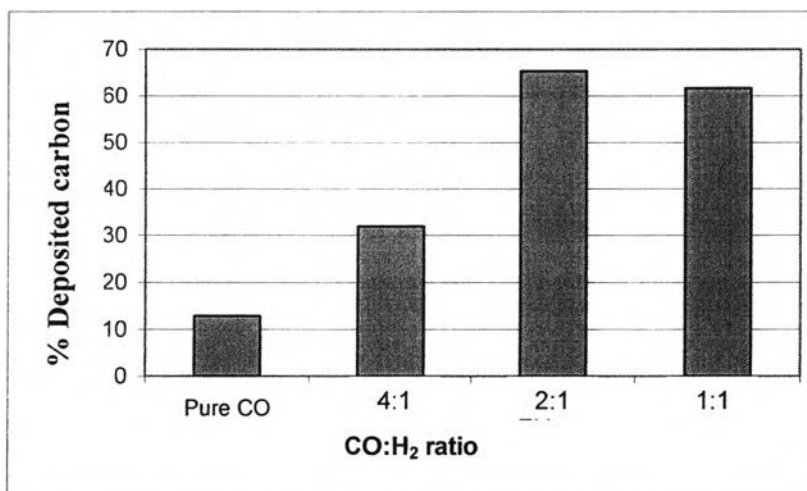


Figure 4.26 Carbon yield of product from pure CO, 4:1, 2:1 and 1:1 CO:H₂ over 10% Fe/Al₂O₃ catalyst at 700°C.

Table 4.4 Summary of carbon yield and average diameter of CNTs from different CO:H₂ ratios

CO:H ₂	% Deposited carbon	Average diameter (nm)
Pure CO	12.86	-
4:1	31.88	64
2:1	65.00	87
1:1	61.65	97

The different structure and carbon yield from pure CO and CO/H₂ is due to many effects (Zhixin *et al.*, 2005). First, hydrogen is believed to influence the surface orientation of the catalyst by lattice restructuring, which consequently influences the carbon deposit structure. Dong *et al.* (2002) suggested that the presence of hydrogen also provides the additional energy needed for the nucleation of CNFs instead of on-ionlike carbon. Moreover, hydrogen may help clearing up the amorphous carbon, which might then enhance CNFs and CNTs formation and possibly prevent catalyst deactivation. However, higher concentration of H₂ is not always preferred. Pham-Huu *et al.* (2002) showed that, for ethane decomposition on supported Ni catalyst, too high hydrogen fraction led to a slight decrease in the carbon yield.