# Effect of Support and Reactant on the Yield and Structure of Carbon Growth by Chemical Vapor Deposition

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The effect of catalyst support and reactant on the yield and structure of carbon growth has been investigated in the chemical vapor deposition (CVD) process. Powder Fe and Fe/Al<sub>2</sub>O<sub>3</sub> were the catalysts studied, and CO/H<sub>2</sub>, CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>/H<sub>2</sub> were used as gas precursors. Platelet and fishbone-tubular structures were produced on powder and supported Fe from CO/H<sub>2</sub>, with average diameters of 115 and 45 nm and yields of 28.8 and 17.6 g of C/g of cat. in 8.5 h, respectively. Onionlike carbon was the main structure produced from pure CO on both catalysts. In contrast, from hydrocarbons the highest yield of 2.24 g of C/g of cat. was achieved on Fe/Al<sub>2</sub>O<sub>3</sub>, with predominantly tubular structures produced and average tube diameters close to 21 nm. It is concluded that the reactivity and carbon nanostructures are dictated by the size and crystallographic orientation of the catalyst particles. It has been suggested that the tubular structures were grown by continuous carbon supply directly to the tube, but the fiber structures were grown in a layer-by-layer manner. Controlled synthesis of carbon nanotube, platelet nanofiber, fishbone-tubular nanofiber, and onionlike carbon with high selectivity and yield was demonstrated.

### 1. Introduction

Carbon nanostructures are becoming of considerable commercial importance with a continuous interest growing over the past decades since the discovery of buckminsterfullerene,<sup>1</sup> carbon nanotubes (CNTs),<sup>2-4</sup> and carbon nanofibers (CNFs).<sup>5</sup> Recently, the chemical vapor deposition (CVD) method has emerged as a promising method for nanocarbon synthesis because it is capable of controlling the nanostructure of the carbon deposits and synthesizing in large quantities.<sup>6,7</sup> It is known that nanoparticles of transition metals, such as Fe, Co, and Ni, play an essential role in the carbon growth.<sup>8,9</sup> The gases used in CVD synthesis can be any carbon-containing gas such as methane,<sup>10</sup> ethane,<sup>11</sup> ethylene,<sup>12</sup> acetylene,<sup>8,9</sup> carbon monoxide,<sup>6</sup> and benzene.<sup>2</sup> Factors such as catalyst composition, catalyst support, carbon-containing gases, temperature, and gas partial pressure can have a profound impact on the nanostructure, yield, purity, and crystallinity of the carbon deposits. Research on synthesizing carbon nanostructures is normally focused on varying the composition of the metal particles,<sup>13,14</sup> and the process parameters are also often studied.<sup>15,16</sup>

It is well documented that the catalyst support can have a great impact on the structure of carbon deposits.<sup>12,17–20</sup> It has been shown that the characteristics of CNFs and the product selectivity over supported nickel catalyst can be readily manipulated by the choice of the support material.<sup>12</sup> However, direct comparison of carbon structural differences over catalysts with or without support is not well studied. Anderson et al.<sup>19</sup> demonstrated that major differences in the growth of CNFs can be achieved when the catalysts were used in a supported rather than a powder form. The crystallographic face generation due

to metal—support interactions will result in different catalytic activities and carbon structures. Nevertheless, the metal precursors used by Anderson et al.<sup>19</sup> have very different particle sizes (micrometers vs nanometers), which makes it less reliable for direct comparison.

On the other hand, systematic studies of the influence of gas precursors are much less often performed, but the gas precursors might have profound effects on the resulting carbon nanostructures. Only recently Toebes et al.<sup>7</sup> reported carbon growth from different carbon-containing gases. However, the carbon deposits are always CNFs and the starting metal particle sizes also have large differences. Contradictory views also exist for the impact of the gas precursors: some observed significant differences in CNT formation from different gases,<sup>18</sup> whereas others claimed that the gases are less influential.<sup>21</sup>

In this study we report carbon growth from different carboncontaining gases (CO/H<sub>2</sub>, CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>/H<sub>2</sub>) over supported and powder Fe catalysts. CO and low-molecular-weight hydrocarbons are among the most often used gas precursors, and are known to have completely different activities on Fe catalysts.<sup>22</sup> It will be interesting to study whether different carbon structures will be produced from them, with or without hydrogen. The catalyst precursors used in this study have similar particle sizes in the nanometer range, which will be more suitable for direct comparison. The focus of this study has been to explore how the gas precursors affect the unsupported and supported catalysts differently during carbon growth. It is also our purpose to report some highly selective processes for producing different carbon nanostructures.

#### 2. Experimental Section

**2.1. Catalyst Preparation and Characterization.** The  $Al_2O_3$ -supported Fe catalyst was derived from hydrotalcite precursors, which were prepared by coprecipitation under  $N_2$ 

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protection according to Bhattacharyya et al.<sup>23</sup> FeSO<sub>4</sub> and Al-(NO<sub>3</sub>)<sub>3</sub> were used as metal precursors, while Na<sub>2</sub>CO<sub>3</sub> and NaOH acted as precipitating agents. The molar ratio of Fe/(Al + Fe) is 0.75, resulting in a weight percentage of 76.7% Fe in the reduced catalyst. Fe powder nanoparticles were prepared under N<sub>2</sub> protection according to Kang et al.<sup>24</sup> FeCl<sub>2</sub> and FeCl<sub>3</sub> were used as metal precursors, and NaOH was used as precipitating agent. After precipitation, both catalysts were filtered, washed, and vacuum-dried at 70 °C. The dried catalyst precursors were calcined at 300 °C in 100 mL/min air for 3 h.

The X-ray diffraction (XRD) study was performed using a Siemens D5005 diffractometer equipped with a monochromator. Diffraction was performed with Cu K $\alpha$  radiation at a scan rate of 0.02°/step. Peaks were identified by comparison with standards in a database, and the particle size was calculated from the Scherrer equation. Note that the particle size calculated from the Scherrer equation is a volume-averaged value, and other factors such as lattice strain can also contribute to line broadening. For XRD characterization of the reduced sample, the oxides were reduced to the metallic state in 200 mL/min N<sub>2</sub>/H<sub>2</sub> mixture (50 vol %) for 6 h at 600 °C. Then the samples were cooled to room temperature under flowing N<sub>2</sub> and passivated in 100 mL/min air/N<sub>2</sub> (4 vol % air) for 2 h to prevent bulk oxidation of the metallic particles.

Temperature programmed reduction (TPR) study of the catalysts was carried out with a CHEMBET-3000 TPD/TPR instrument. TPR was performed in 80 mL/min H<sub>2</sub>/Ar mixture (7 vol % H<sub>2</sub>) at a heating rate of 10 °C/min from 30 to 1000 °C, using about 35 mg of catalysts.

**2.2. Carbon Nanostructure Synthesis.** The carbon synthesis was performed in a vertical quartz reactor. In the middle of the reactor there is a porous quartz sinter upon which catalysts can be loaded. For a given reaction, a weighed sample of the catalyst (pellet size 75  $\mu$ m) was reduced in 100 mL/min H<sub>2</sub>/N<sub>2</sub> (25 vol % H<sub>2</sub>) at 600 °C for 6 h. The temperature was raised to 600 °C at 5 °C/min. Following the reduction, the system was flushed for 0.5 h with 100 mL/min helium. Then a desired flow of CO/H<sub>2</sub>, CO, CH<sub>4</sub>, or C<sub>2</sub>H<sub>6</sub>/H<sub>2</sub> was introduced into the reactor. The growth temperature was 600 °C for all syntheses. The gaseous products were analyzed with an online HP5890 gas chromatograph (GC). After the synthesis the products were cooled to room temperature in flowing helium. The amount of carbon synthesized was determined gravimetrically, which is close to the results from GC analysis.

**2.3. Transmission Electron Microscopy (TEM) Characterization.** The structure and diameter of the carbon products were studied by high-resolution TEM. The TEM investigation was performed using a JEOL 2010F electron microscope equipped with a field emission gun. TEM specimens were prepared by ultrasonic dispersion of the slightly ground purified products in ethanol, and then a drop of the suspension was applied to a holey carbon copper grid. The purification was performed by refluxing in concentrated HCl for 1 h, and then in 1 M NaOH for 1 h if the samples were produced from Fe/Al<sub>2</sub>O<sub>3</sub>. The samples were then filtered, washed, and dried.

#### 3. Results and Discussion

**3.1. Characterization of Fe Catalysts.** The metal precursors for carbon growth are exactly the same for both supported and unsupported catalysts, as verified by the XRD study. The calcined catalysts exhibit the diffraction peaks of magnetite. The particle sizes were calculated by the Scherrer equation from the strongest peak of the (311) plane. For the Fe powder the particle size is 19 nm, while it is 33 nm for the supported Fe (Table 1).

TABLE 1: Diameters of Catalyst Particles and CNTsProduced from Different Gas Precursors

catalyst	$\begin{array}{c} D_{\mathrm{oxide}}^{a} \\ \mathrm{(nm)} \end{array}$	D <sub>Fe</sub> (nm)	D <sub>tube</sub> (nm) (CO/H <sub>2</sub> )	D <sub>tube</sub> (nm) (CO)	D <sub>tube</sub> (nm) (CH <sub>4</sub> )	$\begin{array}{l} D_{\text{tube}} \ (\text{nm}) \\ (\text{C}_2\text{H}_6/\text{H}_2) \end{array}$
Fe <sub>3</sub> O <sub>4</sub>	19	50	116	$32^b$	$22^{b}$	21
Fe/Al <sub>2</sub> O <sub>3</sub>	33	28	45	$27^b$	13	19

 $^{a}D$  means diameter.  $^{b}$  Only a few tubes (about 15) are available for study.



**Figure 1.** XRD patterns for the reduced catalysts: top, Fe/Al<sub>2</sub>O<sub>3</sub>; bottom, Fe powder.



Figure 2. Temperature programmed reduction (TPR) profiles of the iron oxides.

Figure 1 presents the diffraction patterns of the reduced Fe catalysts. The samples exhibit a single Fe phase without the presence of any oxide peaks. However, it is clear that the powder Fe catalyst displays a higher intensity and sharper peak, indicating a larger Fe particle size. Particle sizes calculated by the Scherrer equation from the strongest diffraction plane (110) are 50 nm for Fe powder and 28 nm for Fe/Al<sub>2</sub>O<sub>3</sub>. Therefore, the crystal size is enlarged more than twice for the unsupported Fe compared with the original oxide, implying some sintering effects. In contrast, for Fe/Al<sub>2</sub>O<sub>3</sub> the particle size is about the same, implying that alumina has been effective in stabilizing the Fe particles during the reduction process.

The reduction process was further examined by TPR, which displays a similar profile for both catalysts, as presented in Figure 2. The catalysts are reduced through two distinct steps, indicating the reduction from  $Fe^{3+}$  to  $Fe^{2+}$  and from  $Fe^{2+}$  to metallic Fe.<sup>25</sup> Nevertheless, the peak maximum is always lower for Fe powder compared with Fe/Al<sub>2</sub>O<sub>3</sub> (402 vs 430 °C and 709 vs 846 °C). For powdered Fe the reduction is complete at about 900 °C, whereas the reduction for Fe/Al<sub>2</sub>O<sub>3</sub> is not complete even at 1000 °C. Therefore, the alumina support has impeded the reducibility of Fe, making Fe more stable under



**Figure 3.** Carbon productivity from CO decomposition as a function of reaction time at 600 °C: (a) with hydrogen,  $CO/H_2 = 40/10 \text{ mL/min}$ ; (b) without hydrogen, CO = 40 mL/min.

 TABLE 2: Carbon Productivity<sup>a</sup> and Structures<sup>b</sup> from

 Different Gas Precursors

reactant	productivity,	productivity,	structure,	structure,
	Fe <sub>3</sub> O <sub>4</sub>	Fe/Al <sub>2</sub> O <sub>3</sub>	Fe <sub>3</sub> O <sub>4</sub>	Fe/Al <sub>2</sub> O <sub>3</sub>
CO/H <sub>2</sub>	28.8 (171) <sup>c</sup>	$     \begin{array}{r} 17.6 \ (62)^d \\     1.1^e \\     1.5 \\     2.24 \end{array} $	platelet	F–T
CO	1.8		onion, CNT	onion, CNT
CH <sub>4</sub>	0.37		onion, CNT	CNT, Onion
C <sub>2</sub> H <sub>6</sub> /H <sub>2</sub>	0.45		CNT, F-T	CNT, F–T

<sup>*a*</sup> Carbon productivity after 8.5 h of growth. Units: g of C/g of cat. <sup>*b*</sup> The structure in italics is the dominating form. F–T: fishbone– tubular. <sup>*c*</sup> Value in parentheses gives the productivity after 50.5 h of growth. <sup>*d*</sup> Value in parentheses gives the productivity after 30 h of growth. <sup>*e*</sup> Complete deactivation after 4 h.

reduction atmosphere.<sup>26</sup> The metal-support interaction is evidenced here.

**3.2. Carbon Productivity from Different Reactants over the Two Catalysts.** Figure 3a displays the kinetic curve for CO (CO/H<sub>2</sub> = 40/10 mL/min) decomposition at 600 °C. The amount of catalyst used is 0.1 g, so the space velocity is 24 L/g of cat.•h. CO decomposes readily on both catalysts. On Fe powder, no deactivation can be observed even after 50.5 h of growth and the carbon productivity reaches 171 g of C/g of cat. On Fe/Al<sub>2</sub>O<sub>3</sub>, there is some deactivation during the 30 h of growth but the rate of deactivation is extremely low. The productivity during 30 h is about 62 g of C/g of cat. (Table 2).

When hydrogen is removed from the reactant, 0.1 g of catalyst showed little activity for CO decomposition (CO = 40 mL/ min). The catalyst amount was increased to 0.5 g, and the space velocity was 4.8 L/g of cat.•h. The Fe/Al<sub>2</sub>O<sub>3</sub> catalyst deactivated completely after only 4 h. Again the Fe powder shows higher productivity, but after 8.5 h it is close to complete deactivation (Figure 3b). This is in sharp contrast to the catalyst lifetime when hydrogen is added to the feed. The carbon productivity is also much lower, amounting to only 1.8 g of C/g of cat. for Fe powder and 1.1 g of C/g of cat. for Fe/Al<sub>2</sub>O<sub>3</sub> (Table 2).

The significantly long lifetime in the presence of hydrogen can be explained by its gasification effect. During CNT growth, if carbon diffusion cannot keep up with the carbon supply, excessive carbon will build up on the catalyst surface and deactivate the catalyst for further gas decomposition. Hydrogen is beneficial to keep the exposed surface clean of carbon and prevent catalyst deactivation. Consequently, much higher carbon productivity is obtained in the presence of hydrogen.

From CH<sub>4</sub> (40 mL/min) or C<sub>2</sub>H<sub>6</sub>/H<sub>2</sub> (30/50 mL/min) decomposition, very little activity was observed when 0.1 g of catalyst was used. Therefore, the catalyst loading was increased to 0.5 g and the reaction time was maintained for 8.5 h. The space velocities were 4.8 and 3.6 L/g of cat.•h, respectively. The conversion level, and accordingly the rate of carbon growth from the hydrocarbons, was significantly lower than those from CO.



**Figure 4.** TEM images of carbon produced at 600 °C from CO over Fe powder catalyst. (a) High-resolution image shows onionlike structure. The lattice planes of Fe are visible and indicated by the white lines. (b) Low-resolution image shows high selectivity to this structure. (c) High-resolution image shows metal inclusion in some of the CNTs. The structure produced on Fe/Al<sub>2</sub>O<sub>3</sub> is similar.

This is consistent with previous studies because CO is more active toward decomposition over Fe catalysts than hydrocarbons are.<sup>22</sup> In both  $CH_4$  and  $C_2H_6$  the catalysts deactivated, but the deactivation rate was low. The carbon productivity is summarized in Table 2, based on a growth time of 8.5 h.

It is interesting to notice that the reactivity is opposite for CO and hydrocarbons over powder Fe and Fe/Al<sub>2</sub>O<sub>3</sub>. This can be understood from the effect of the catalyst support and particle size. The orientation of the metal particle surface supported on a carrier can be quite different from that of a powder metal particle. As a consequence, the reactivity pattern towards certain gases will be dramatically perturbed. For the Fe/Al<sub>2</sub>O<sub>3</sub> particles, which are smaller and usually more or less spherical/conical, more open, high index planes (step edges) are exposed.<sup>7</sup> These planes are active for dissociation even of CH<sub>4</sub>, the least reactive compound over Fe. A recent study has actually suggested that the decomposition of CH<sub>4</sub> mainly occurs on the step edges.<sup>27</sup> For the powder Fe, which has relatively larger particles, the gas-solid interface is probably dominated by the more stable, low index planes. This means that only the more reactive gases, like CO, are preferred for dissociation. Consequently, CO decomposes readily on both low and high index planes, so the productivity will be higher on the powder Fe because it contains more Fe species. For hydrocarbons, decomposition occurs mainly on high index planes; Fe/Al<sub>2</sub>O<sub>3</sub> is therefore more active. It can be concluded that the catalyst activity is actually dependent on not only the nature of metal-support interaction, but also the nature of the gas precursors.

**3.3. Carbon Nanostructures from Different Reactants over the Two Catalysts.** *3.3.1. Pure CO as Reactant.* Two forms of carbon were deposited on powder Fe from pure CO. One is CNTs, with the graphite sheets completely parallel to the fiber axis with no open edges exposed. The other is the spherical, onion-shaped graphite encapsulating a catalyst particle, as represented in Figure 4a. The iron lattice plane is clearly visible in this high-resolution picture. The onionlike carbon dominates in the product, which is observed from TEM study and is



**Figure 5.** TEM images of filamentous carbon produced at 600 °C from CO/H<sub>2</sub> (40/10 mL/min). (a) High-resolution image shows the platelet structure over Fe powder. (b) High-resolution image shows the fishbone–tubular structure over Fe/Al<sub>2</sub>O<sub>3</sub>. (c) Low-resolution image indicates the large diameters of the platelet structure from Fe powder.

exemplified by the low-resolution TEM image of Figure 4b. The average diameter of the CNTs is about 32 nm, and the dimension of the encapsulated catalyst particle is larger than that of the CNTs. One feature common to carbon growth without hydrogen is the occurrence of Fe inclusions in the growing tube. This effect is shown in Figure 4c. This implies that the metal particles are probably in the fluid state during carbon growth, as suggested by many other studies.<sup>19</sup> The carbon produced from pure CO on Fe/Al<sub>2</sub>O<sub>3</sub> is almost the same as those on the powder Fe: CNTs and onionlike carbon, with the latter dominating. The average diameter of the CNTs on Fe/Al<sub>2</sub>O<sub>3</sub> is about 27 nm, slightly smaller than those on the powder Fe (Table 1).

The synthesis of onionlike carbon has brought about a growing interest due to its use for many applications.<sup>28</sup> For example, carbon encapsulation of metal nanoparticles can protect ferromagnetic particles from oxidation, making it an interesting magnetic medium. In this study we disclosed a route that is highly selective to this structure.

3.3.2. CO/H<sub>2</sub> as Reactants. Significantly different carbon structures were produced from the CO/H2 mixture over the two catalysts, as shown in the high-resolution TEM images of Figure 5a, b. On Fe powder, the so-called "platelet" structure is produced, with very straight graphite sheets stacked perpendicular to the fiber axis and surfaces consisting primarily of edge sites (Figure 5a). The excellent crystallinity of this platelet structure is demonstrated on this high-resolution image. The interlayer distance is 0.3353 nm, close to that of natural graphite. The filaments have a large diameter distribution from 35 to 366 nm, as shown in the low-resolution TEM image (Figure 5c). The average diameter estimated from more than 150 fibers gives a value of 116 nm (Table 1). After carbon growth, although the particles can be of various shapes, the particle at the tip of each filament always adopts plane facets and has very large sizes, close to the diameter of the fibers. On these plane facets the continuous stacking of graphite sheets took place. The large diameter and flattening of the resulting particles imply that the particles have undergone a wetting and spreading action during carbon growth, as suggested by Baker et al.<sup>29</sup> The particles are

probably completely mobile during the growth, due to the uptake of a large amount of carbon in the metal.

The platelet structure with a distinctively large diameter has been reported from early studies.<sup>30,31</sup> Moreover, the product selectivity in our process estimated from TEM is significantly higher than a previous report of 50%, which synthesized this platelet structure from CO and Fe(CO)<sub>5</sub>.<sup>31</sup> It is not clear if platelet filaments with smaller diameters can be synthesized; for energetic reasons probably only particles large enough can exhibit plane facets.

On Fe/Al<sub>2</sub>O<sub>3</sub>, the carbon deposits exhibit exclusively fishbone-tubular structure: the graphene sheets are stacked at a small angle to the fiber axis with some edges exposed, and there is always a hollow core (Figure 5b). This fishbone-tubular filament has diameters in the range of 10-60 nm, with an average diameter of 45 nm. Hence, a much narrower diameter and diameter distribution were formed from the Al<sub>2</sub>O<sub>3</sub>-supported catalyst. This suggests that presence of the Al<sub>2</sub>O<sub>3</sub> support makes the particles less mobile, again characteristic of the metalsupport interaction. The stacking of the graphite sheets at an angle to the fiber axis is probably dictated by the surface orientation of the Fe particles, which in turn is determined by the metal-support interaction, and the interaction between metal and reactants. It has been observed by many high-resolution electron microscopy studies that the graphite sheets will have their basal planes predominantly parallel to the planes of the catalyst particles during carbon growth.<sup>27,32</sup> This occurs because the interfacial free energies are the smallest.<sup>33</sup> The occurrence of a central hollow core can be attributed to the deformation or faceting of the supported metal particle that alters the relative rate of carbon diffusion and nucleation.34

The strikingly different carbon nanostructures produced from CO and CO/H<sub>2</sub> can be explained by several effects induced by hydrogen. First, hydrogen is believed to influence the surface orientations of the catalyst by lattice restructuring, which consequently influences the carbon deposit structure.13,35-37 Second, for both the platelet and fishbone-tubular structure, energetically costly edges are exposed. This is made possible by H<sub>2</sub>, because H<sub>2</sub> will satisfy the valence of open-edged planes, and without H<sub>2</sub> edges do not form. The phenomenon has been nicely illustrated by Nolan and co-workers.35-37 When no hydrogen is present on the surface of the particle, carbon is deposited as closed shells or as parallel tubes. Third, H<sub>2</sub> is beneficial for keeping the catalyst surface clean of carbon, so there will be more chances to nucleate CNTs or CNFs instead of onionlike carbon. Dong et al.<sup>38</sup> suggested that the presence of hydrogen also provides the additional energy needed for the nucleation of CNTs instead of onionlike carbon.

3.3.3. CH<sub>4</sub> as Reactant. From CH<sub>4</sub> decomposition the carbon deposited on the powder Fe also gives onionlike carbon and CNTs (Figure 6a). The onionlike carbon occupies a large part of the product but is not as dominating as those formed from pure CO decomposition, as observed from TEM study. The average tube diameter is about 22 nm. For those produced on Fe/Al<sub>2</sub>O<sub>3</sub>, the majority of the product is CNTs with uniform diameter distribution, though not completely free of onionlike carbon (Figure 6b). From this low-resolution TEM image it is obvious that the size of CNTs is always smaller than the dimension of the onionlike carbon. The CNTs have a few graphite layers (<10) only and good crystalline nature, as exemplified in the high-resolution image of Figure 6c. The average diameter is 13 nm, even smaller than the original Fe catalyst, suggesting particle fragmentation. Particle fragmentation is a common phenomenon during carbon growth, and is



**Figure 6.** TEM images of carbon produced at 600 °C from CH<sub>4</sub> (40 mL/min). (a) Low-resolution image shows mainly onionlike carbon from Fe powder. (b) Low-resolution image shows mainly CNTs from Fe/Al<sub>2</sub>O<sub>3</sub>. (c) High-resolution image shows the CNTs consist of very few graphene sheets from Fe/Al<sub>2</sub>O<sub>3</sub>.

likely caused by germination of dissolved carbon atoms in the bulk of the catalysts.  $^{36}$ 

The dominance of onionlike carbon on the powder Fe catalyst can be explained by energetics. It was demonstrated both theoretically and experimentally that, for large particles, the formation of onionlike carbon is favored over CNT formation, since growing a tube over large particles would be energetically more costly.<sup>39,40</sup> Nerushev et al.<sup>41</sup> also reported that, for C<sub>2</sub>H<sub>2</sub> and C<sub>60</sub> decomposition over SiO<sub>2</sub>-supported Fe films, nanotubes do not form from C<sub>60</sub> if the Fe particle sizes are too large. Because the reduced Fe powder catalyst has relatively larger particles than Fe/Al<sub>2</sub>O<sub>3</sub>, onionlike carbon is formed preferentially.

Two more points are worth taking into consideration. First, the main carbon structures formed over Fe/Al<sub>2</sub>O<sub>3</sub> from decomposition of CO and CH<sub>4</sub> are different. This is because CH<sub>4</sub> decomposition occurs only significantly on high index planes of the particles. Accordingly rapid nucleation of carbon over the whole surface is less likely. In fact, it has been observed by in situ TEM studies that, if step edges act as the centers for gas decomposition and graphene growth, the reshaping of the metal nanoclusters assists the alignment of graphene layers into a tubular structure.<sup>27</sup> In contrast, CO decomposition occurs at a high rate simultaneously on the whole surface of the particle, and then carbon quickly forms an onionlike structure without nucleating CNT.14 Second, CH<sub>4</sub> decomposition will generate hydrogen, but only closed form carbon structures have been produced from pure CH<sub>4</sub>. This is due to the low hydrogen concentration as a result of the low conversion of CH<sub>4</sub> in this study. This implies that hydrogen must be present over a threshold amount to change the closed structure to the open type.

3.3.4.  $C_2H_6/H_2$  as Reactants. Homologues will lead to similar structured carbon.<sup>42</sup> CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are homologues, and similar carbon structures are expected from these two gases. To study the effect of H<sub>2</sub> on hydrocarbon decomposition, a large amount of H<sub>2</sub> has been added for C<sub>2</sub>H<sub>6</sub> decomposition. A low-resolution image shows that carbon grown from C<sub>2</sub>H<sub>6</sub>/H<sub>2</sub> on Fe powder



**Figure 7.** TEM images of carbon produced at 600 °C from  $C_2H_6/H_2$  (30/50 mL/min) over Fe powder catalyst. (a) Low-resolution image shows uniformly distributed CNTs. (b) High-resolution image shows the coexistence of CNTs (T) and fishbone-tubular (F-T) structure. The structure produced on Fe/Al<sub>2</sub>O<sub>3</sub> is similar.



Figure 8. Diameter distribution of CNTs produced from decomposition of  $C_2H_6/H_2$  (30/50 mL/min) over Fe catalysts at 600 °C. For each analysis, 150 tubes have been selected.

catalyst consists mainly of a tubular structure (Figure 7a). The onionlike carbon is negligible. These CNTs are of very good quality with a uniform diameter distribution and good crystalline nature. Careful examination by high-resolution TEM revealed that a few of the tubes have their graphite sheets stacked in a very small angle to the tube axis (Figure 7b). The carbon deposited on Fe/Al<sub>2</sub>O<sub>3</sub> displays no big difference from those on the Fe powder: tubular and a few fishbone–tubular structures. The product also has very good quality, free of any onionlike carbon. Therefore, the addition of hydrogen also creates favorable conditions for the nucleation of CNTs for hydrocarbons. The existence of some fishbone–tubular filaments can also be ascribed to the addition of H<sub>2</sub>.

Figure 8 presents the diameter distribution of CNTs over the two catalysts, obtained from about 150 tubes in TEM study. It is obvious that the CNTs from both catalysts have their diameters centered around 20 nm. The CNT diameter from Fe/Al<sub>2</sub>O<sub>3</sub> is more skewed to smaller dimensions, while the tube diameter over the powder Fe is skewed to larger sizes. The average diameter is 19 nm for Fe/Al<sub>2</sub>O<sub>3</sub> and 21 nm for Fe powder (Table 1). The similar average CNT diameter implies that probably an optimum particle size exists for CNT growth. This notion has been put forward for CNT growth from methane decomposition on both Ni- and Fe-based catalysts.<sup>20,43</sup>

Numerous studies have proposed that the unsupported catalysts produce fibers with much larger diameters than the supported ones.<sup>12,13,19,44</sup> This has been attributed to the inability to control the initial size of the individual particles in the powder catalysts.<sup>44</sup> Nevertheless, one important finding from this investigation is that the above statement is not always true. The final diameter of carbon fibers formed on catalysts with or without support is strongly dependent on the reactant. Powder catalysts can also be a good candidate for synthesizing uniform

CNTs with high quality, provided that a "milder" atmosphere such as low active hydrocarbons are used for carbon growth.

It is further interesting to correlate the carbon growth rate with the final diameter of the carbon filaments (Tables 1 and 2). It turns out that the higher the carbon growth rate, the larger the diameter of the carbon filaments, thus the resulting catalyst particles (CO vs hydrocarbons). This can be understood by the dissolution of carbon in Fe particles, which will lead to a semiliquid state of the system, at a temperature far below the melting point of Fe.<sup>45</sup> It is reasonable to say that carbon dissolves in the metal with a higher concentration when the growth is faster. This leads to the higher mobility of the metal particles to form larger filaments.

**3.4. Growth Mechanism.** Various models for filamentous carbon formation have been proposed.<sup>39,46,47</sup> It is normally accepted that carbon growth involves surface carbon decomposition, carbon diffusion, and then precipitation. However, different views exist on how different carbon nanostructures nucleate, and especially on how carbon fibers grow. Based on previous available models and the experimental observations in this study, a mechanism can be proposed to explain the growth of all carbon structures.

The Fe particles initially decompose the carbon-containing molecules on the catalyst surfaces and lead to the formation of surface carbon. The formation of surface carbon could probably go through an intermediate iron carbide phase.<sup>45,48</sup> Then carbon dissolves and diffuses on the surface or through the bulk of the metal particles. When carbon supersaturation is reached, carbon segregation will occur. Carbon atoms will move towards the surface and combine to form an initial graphene layer, as suggested by B.Nagy et al.<sup>47</sup> This early stage of carbon nucleation on the particle surface is probably common for both CNTs and CNFs. Carbon will deposit in various structures afterward, depending on the crystallographic faces of the resulting catalyst particles, which is a function of the metal—support interaction, the gas precursors, and particularly hydrogen.

For CNT growth, the initial nucleated graphene layer may detach from the particle surface and form a fullerene-like cap.<sup>39,47</sup> This cap is always chemisorbed to the catalyst particles during the growth. This will avoid the growth of any open edges, which would expose energetically costly dangling bonds.<sup>39</sup> Newly arrived carbon atoms will nucleate additional graphite layers beneath the initial cap and in the inward direction,<sup>39,45</sup> or move toward the graphene—metal interface and be incorporated into the graphite sheets. This contributes to the lengthening of the tube.

The growth of CNFs is possible in the presence of hydrogen: the initial nucleated graphene layer will be directly segregated as graphite sheets instead of the formation of a fullerene-like cap. Hydrogen probably initiates the segregation of the graphene layer.<sup>28</sup> The exposure of energetically costly dangling bonds of the released graphite sheets is possible because hydrogen can saturate the dangling bonds. Newly arrived carbon atoms will nucleate additional graphene layers, and CNFs then grow in a layer-by-layer manner, which contributes to the lengthening of the fibers. This accounts for the growth of both platelet and fishbone—tubular structures.

If there is not enough energy to nucleate CNTs or CNFs, for example over large particles, carbon will deposit as a film encapsulating the particles and form an onionlike structure. The size of the catalyst particle is also influenced by the metal support interaction and the reactants. In all cases surface carbon encapsulation surely occurs at some rate, which finally deactivates the catalysts.

#### 4. Conclusions

The carbon yield and nanostructure have been studied on powder and alumina-supported Fe catalysts from the decomposition of different carbon-containing gases. Opposite reactivity was demonstrated for CO or hydrocarbon decomposition over the two catalysts. Completely different or similar structures were synthesized depending on the nature of the gas precursors. It is reasoned that the reactivity and the structure of carbon deposits are dictated by the size and crystallographic faces of the catalyst particles, which are in turn a direct consequence of the strength of metal-support interaction, and are further influenced by the reactants during carbon growth. Hydrogen plays an essential role in the processes by surface reconstruction, keeping the catalyst surface clean of carbon, and satisfying dangling bonds. Based on the experimental results and existing CNT growth models, a mechanism is proposed to illustrate the growth of all carbon nanostructures. Earlier studies have suggested that powder catalysts generate larger diameter fibers than the supported ones. The findings from this study point out that it is not always true, because the final diameter of the fibers is also reactant dependent.

Finally, a major factor to emerge from this investigation is the development of processes to synthesize relatively large quantities of CNTs, fishbone-tubular fibers, platelet fibers, and onionlike carbon encapsulating magnetic particles, all with high quality and selectivity. The findings here are important for realizing controlled synthesis of different carbon nanostructures for their applications in various fields.

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