Catalytic Vapor Decomposition of Methane over Nickel Catalyst: Growth Rate and the Corresponding Microstructures of Carbon Nanofibers

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Time-resolved intrinsic reaction rate of catalytic vapor deposition of methane into carbon nanofibers (CNFs) and hydrogen on supported Ni catalysts was determined under different reaction temperatures (773–973 K) and feed compositions ($P_{H_2} = 0\text{--}0.29$ atm, $P_{CH_4} = 0.28\text{--}0.71$ atm) and the microstructure of the produced CNFs was characterized by Raman and TEM. The results showed that, increasing the reaction temperature, methane partial pressure and decreasing hydrogen partial pressure increased the initial reaction rate but generally led to fast catalyst deactivation. A high carbon yield per unit catalyst was obtained as a compromise between initial reaction rate and catalyst deactivation rate. The microstructures of the produced CNFs had a close relationship with the initial reaction rate. The CNFs produced with high initial rate tended to have a small angle between the graphene layers and the growth axis, thin diameter and a hollow core. This phenomenon can be used for monitoring and controlling the CNFs synthesis process.

Introduction

The history of carbon nanofibers (CNFs) can be traced back to 1889 when the method for synthesis of filamentous carbon by hydrolysis of a mixture of methane and hydrogen in an iron crucible was reported (Ermakova *et al.*, 2001). Carbon nanofibers (CNFs) have unique chemical stability, electrical conductivity, mechanical strength and textural/surface properties (De Jong and Geus, 2000), which make them good candidates for absorbents and catalysts and therefore are the subject of numerous studies especially in the latest few decades. Possible use of carbon nanofibers in super capacitor or fuel cell as part of the electrodes is also a hotspot of research (Xing, 2004).

Catalytic decomposition of methane over Ni catalysts is an effective method for CNFs synthesis and also an alternative route of hydrogen production from natural gas (Takenaka *et al.*, 2002, 2003a, 2003b). This reaction is moderately endothermic:

This reaction is also of research interest for inhibition of

carbon growth in steam or dry reforming of methane process. Comprehensive studies (Chen *et al.*, 2005; Suelves *et al.*, 2005; Lazaro *et al.*, 2007; Biris *et al.*, 2008) have been conducted for many years to elucidate the effect of catalyst particle size and operating variables, such as temperature and feed concentration, on the carbon growth rate and microstructure of the CNFs. Information compiled from these experiments reveals that the growth of CNFs is a complex process, and all the variables can alter the CNFs structure. Despite the large number of publications devoted to the mechanism of carbon nucleation and growth, up to now few researches have been conducted to investigate the changes of intrinsic reaction rate and microstructure with growth condition, which are needed in process development and design for large scale production.

In this paper, CNFs were grown on Ni (20%)/ γ - Al_2O_3 catalyst with different particle sizes and at different temperatures and feed concentrations. The rate of carbon growth was recorded as a function of time and the microstructure of the CNFs was characterized. The relationship between the reaction rate and microstructures of the as grown CNFs is established and the reason account for this relationship is also addressed.

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Table 1 Influence of temperature of nickel oxide calcination on textural parameters of the catalysts

Calcination temperature [K]	BET surface area [cm ² /g]	Total pore volume [cm ³ /g]	Micropore volume [cm ³ /g]
773	194.4	0.36	0.007
873	171.2	0.45	0.006
973	160.0	0.39	0.004

1. Experimental

The Ni (20%)/ γ -Al₂O₃ catalysts used for direct cracking of methane were synthesized by deposition–precipitation using urea as precipitant. Nickel nitrate and urea were dissolved in water and mixed with an aqueous alumina suspension, which was then heated in a water bath to 363 K. The solution was mechanically agitated at 363 K for 10 h, and was then filtrated under vacuum. The obtained precipitate was dried overnight in air at 393 K. The catalysts with different Ni particle sizes were obtained by calcinating the precipitate at 773, 873 and 973 K for 3 h.

The specific surface area of the catalysts was characterized by nitrogen adsorption at 77 K on ASAP 2010 (USA). The X-ray powder diffraction (XRD, Rigaku Corp.) pattern was recorded by D/Max 2550 VB/PC diffractometer equipped with a Cu K α radiation source ($\lambda = 0.154056$ nm) and operated at a voltage of 40 kV and a current of 100 mA. The crystal size of Ni was determined by H₂ chemisorption at 313 K on Autochem II 2920 (Micromeritics Instrument Corp.). The reducibility of NiO was studied by temperature programmed reduction (TPR) on Autochem II 2920 (Micromeritics Instrument Corp.). HRTEM images were obtained by a JEM 2010 electron microscope (JEOL Ltd.). Laser Raman spectra were obtained on an inVia+Reflex spectrometer with an Ar+ tuned at 514 nm and a delivering power of 1–100 mW at the sample (Renishaw plc.).

The catalytic vapor deposition process was studied at 823–973 K and atmospheric pressure, using a quartz tubular reactor of 8 mm i.d. In each experiment, 0.02 g Ni (20%)/ γ -Al₂O₃ catalysts, with an average size of 74 μ m and in the oxide state, were loaded and reduced in situ at 873 K in a 50 mol% H₂/Ar mixture at a total flowrate of 30 mL/min. After that, the sample was set to the specified reaction temperature in Ar and then a feed consisting of CH₄, H₂ and Ar was introduced, the total flow rate of which was 105 mL/min for all experiments. Some preliminary tests were also carried out and the results indicated that both internal and external diffusion limits could be ruled out under the reaction conditions used in this article. The concentrations of effluent gases were analyzed by an on-line quadruple mass spectrum (Questor, ABB Corp.). CH₄, Ar and H₂ concentrations were determined at $m/z = 16$, 40 and 2 and recorded at a time interval of

Table 2 Particle sizes of the catalysts with different calcination temperature and the corresponding yields of CNFs

Calcination temperature [K]	773	873	973
D_{Ni} [nm]	39.6	68.3	76.5
CNFs yield [g-c/g-cat]	5.7	6.1	4.2

Fig. 1 XRD patterns of catalysts calcined at 773 K (bottom), 873 K (middle) and 973 K (top). Peaks marked with (\$) are characteristic of NiO structure; peaks marked with (#) are characteristic of spinel phase.

0.1 s. The yields of CNFs were calculated from the conversion of methane. After each experiment, the produced CNFs were discharged and weighed. It was found that the difference between the calculated yields and the weighed yield was within $\pm 3\%$.

2. Results and Discussion

2.1 Influence of calcination temperature

By applying different temperatures for calcination, one can have different nickel particle sizes. **Table 1** shows the decreasing specific surface area of NiO calcined at 773, 873 and 973 K respectively and **Figure 1** shows the X-ray powder diffraction patterns of the three samples. The average sizes of the NiO crystallites, as calculated by Debye–Scherrer equation, are 11.0, 19.4 and 22.7 nm, respectively. Figure 1 indicates that the crystalline phases of the catalysts are almost identical at these temperatures.

The crystal size of the Ni was characterized by hydrogen chemisorption and the result was shown in **Table 2**. The particle size increases with the increase of calcination temperatures, which are consistent with XRD characterization results.

Figure 2 shows the TPR profiles of the calcined samples. A main peak occurs at around 870 K for the sample calcined at 700 K, corresponding to the reduc-

Fig. 2 TPR of catalysts calcined at 773, 873 and 973 K respectively

Fig. 3 Influence of the calcination temperature on the rate of decomposition at 873 K (H_2 , 15 mL/min; Ar, 30 mL/min; CH_4 , 60 mL/min)

tion of NiO particles with weak $\text{NiO}-\gamma\text{-Al}_2\text{O}_3$ interaction. However, for the sample calcined at 873 K, this peak shifts to 950 K. The peak occurs at around 1073 K is attributed to the reduction of the NiAl_2O_4 phase.

The rates of methane decomposition on catalysts calcined at different temperatures are presented in **Figure 3** and the unit yields of the CNFs are 5.7, 6.1 and 4.2 g-c/g-cat respectively. Figure 3 shows that the calcination temperature has significant effects on the CNFs growth rate, in terms of the rate of initial carbon growth and the rate of catalyst deactivation. Wang *et al.* (2002) reported that the optimal crystal size of Ni was around 30 nm and smaller crystals gave lower growth rates because of faster deactivation as a result of higher surface coverage of carbon on the metal surface. Our results indicate that a catalyst with a smaller particle size has a higher initial carbon growth rate but also undergoes a faster deactivation, thus leading a low carbon yield. Since catalyst calcined at 873 K has the highest yield in the three sam-

Table 3 The yields of CNFs under different reaction temperature

Calcination temperature [K]	CNFs yields [g-c/g-cat]
773	1.65
823	4.94
873	7.97
898	8.30
923	10.28
948	5.91
973	5.19

Fig. 4 Influence of temperature on the reaction rate (H_2 , 15 mL/min; Ar, 30 mL/min; CH_4 , 60 mL/min)

ples, further kinetic experiments are carried out on this catalyst.

2.2 Influence of reaction temperature

The influences of reaction temperature on the carbon growth rate are shown in **Figure 4**. The reaction becomes prominent above 823 K. The initial CNFs growth is faster at higher temperature and the deactivation is also faster as a result of rapid formation of encapsulating carbon. **Table 3** shows the yields of CNFs produced at different reaction temperatures. The highest yield was obtained at 923 K.

The reaction temperature also influences the graphitic order of the CNFs. **Figure 5** shows the Raman spectrum of the CNFs samples produced at 823, 873 and 973 K, respectively. The graphitic order of CNFs can be deduced from the observation of D- and G-bands. The existing band at 1580 cm^{-1} , G mode, is assigned to the in-plane displacement in the hexagonal graphite layer, whereas the bands at 1345 cm^{-1} , D mode, is assigned to the disorder in the graphitic structure. The integral intensity ratio, I_D/I_G , is inversely proportional to the micro-crystalline planar size L_a . Low I_D/I_G ratio reflects high graphitization order.

The intensities of D mode and G mode are obtained

Table 4 Graphitic order of CNFs produced at 823, 873 and 973 K respectively

Formation conditions	I_D/I_G	Fitting residual error
823 K, $P_{H_2} = 0.14$ atm, $P_{CH_4} = 0.57$ atm	3.62	0.22
873 K, $P_{H_2} = 0.14$ atm, $P_{CH_4} = 0.57$ atm	3.27	0.66
973 K, $P_{H_2} = 0.14$ atm, $P_{CH_4} = 0.57$ atm	2.51	0.48

Fig. 5 Raman spectra of CNFs produced at 823, 873 and 973 K respectively

by fitting the Raman spectrum and results are listed in **Table 4**.

All the samples have high G band intensity which means that they all have graphitic structures. Moreover, the CNFs grown at higher temperatures have more ordered graphite structure, which is in accordance with previous observations (Hernadi *et al.*, 2000; Singh *et al.*, 2003).

2.3 Influence of methane partial pressure

The effect of methane partial pressure (P_{CH_4}) on the rate of CNFs growth at a given P_{H_2} (0.14 atm) was studied at 873 and 923 K and the results are shown in **Figure 6**, from which we can see that the CNFs growth rate is continuously decreasing and holds at a residual constant value. The initial rate of CNFs formation is fast at high P_{CH_4} , and the deactivation of the catalyst is also high. High P_{CH_4} will increase the rate of surface reaction then lead to a boost in the diffusion–precipitation process through the Ni crystallites, which in turn causes the increase in the initial reaction rate. However, the higher the P_{CH_4} , the higher the rate of formation of the polymeric species which can encapsulate and deactivate the surface of the Ni crystallites. Also it is interesting to note that the residual rate of carbon growth, which is relatively small when compared with the initial growth rate, is larger at

Fig. 6 The effect of P_{CH_4} on carbon growth rate at 873 K (up) and 923 K (down) at $P_{H_2} = 0.14$ atm

lower P_{CH_4} . Perhaps this is because the encapsulating carbon formed on the catalyst is not tightly compacted when the initial carbon growth rate is low, which makes it easier for methane to diffuse through the encapsulating carbon layer.

2.4 Influence of hydrogen partial pressure

The role of hydrogen has been studied extensively in both the CNF and CNT synthesis researches. The presence of hydrogen has been found to both accelerate (Pineiro *et al.*, 2000; Venegoni *et al.*, 2002; Neumayer and Haubner, 2004) and suppress (Singh *et al.*, 2003) the formation of CNFs.

Figure 7 shows the effect of P_{H_2} on the carbon growth rate at P_{CH_4} of 0.57 atm and 873 or 923 K. Increasing the P_{H_2} will decrease the rate of carbon growth and also the rate of deactivation remarkably, resulting a net increasing in the yield of CNFs. For example, at 873 K, the yield is increased from 4.81 g-c/g-cat to 11.69 g-c/g-cat when P_{H_2} is increased from zero to 0.29 atm. The effect of P_{H_2} on the formation of CNFs is not straightforward. Higher P_{H_2} can enhance hydrogen adsorption, reduce methane adsorption and suppress

Fig. 7 The effect of P_{H_2} on CNFs growth rate at 873 K (up) and 923 K (down) at $P_{CH_4} = 0.57$ atm

methane dissociation, which decreases the rate of carbon growth. On the other hand, higher P_{H_2} will also promote the gasification of the newly formed surface carbon, resulting in a low surface carbon coverage. Furthermore, the increased site coverage by hydrogen will suppress the polymerization of carbon and thus the formation of encapsulating carbon. These two factors account for the decreased rate of deactivation.

Figure 8 shows the Raman spectra of the CNFs samples produced at 873 K with different values of P_{H_2} . The I_D/I_G values obtained by fitting the Raman spectra are listed in **Table 5**. The results indicate that the CNFs produced without additional hydrogen have more ordered structure. Though inducing additional H_2 will decrease the initial rate of CNFs growth, it will increase the averaged rate of carbon growth, yielding a less ordered lattice structure. On the other hand, higher H_2 concentration will help to reconstruct the precipitated carbon by gasification of the unsaturated and highly active carbon atoms.

Table 5 Graphitization degree of CNFs produced at different P_{H_2}

Formation conditions	I_D/I_G	Fitting residual error
873 K, $P_{H_2} = 0.00$ atm, $P_{CH_4} = 0.57$ atm	1.90	0.27
873 K, $P_{H_2} = 0.14$ atm, $P_{CH_4} = 0.57$ atm	3.27	0.66
873 K, $P_{H_2} = 0.29$ atm, $P_{CH_4} = 0.57$ atm	2.62	0.21

Fig. 8 Raman spectra of CNFs produced at $P_{H_2} = 0, 0.14$, and 0.29 atm, respectively

2.5 Relationship between initial reaction rate and microstructure of CNFs

The morphology of CNFs and their diameter distribution were studied by both high and low-resolution TEM. **Figure 9** shows the microstructure of the CNFs produced on Ni/ γ - Al_2O_3 at 823, 873, 923 and 973 K respectively and **Figure 10** shows the microstructure of the CNFs produced on Ni/ γ - Al_2O_3 at 873 K but at different values of P_{H_2} . All the samples have a typical fishbone structure regardless of the growth conditions, but the angle between the graphite planes and axis of the fiber is very different from each other, as seen in **Table 6**.

From the TEM images shown in Figures 9 and 10, it is interesting to find that the angle between graphite planes and axis of the fiber is related to the initial reaction rate, as listed in Table 6. The CNFs produced with a higher initial formation rate has a smaller angle, just as **Figure 11** shows.

Another microstructural feature should also be noticed. The CNFs produced with a low initial reaction rate tend to have a solid core, as shown in Figure 9(a) and Figure 10(c), whereas the CNFs produced with high initial reaction rate have “hollow” cores, as can be seen from Figures 9(c), (d) and 10(a). This type of “hollow” CNFs was called “cup-stacked-type” CNFs by Endo *et*

Table 6 The angles between the graphite planes and axis of the fiber of samples produced at different conditions

Reaction condition	$R_{c,max}$ [(g-c/g-cat)/min]	Angle [°]
823 K \ $P_{H_2} = 0.14$ atm	0.08	42.10
873 K \ $P_{H_2} = 0.29$ atm	0.13	34.46
873 K \ $P_{H_2} = 0.14$ atm	0.18	25.66
873 K \ $P_{H_2} = 0.00$ atm	0.28	19.69
923 K \ $P_{H_2} = 0.14$ atm	0.39	7.50
973 K \ $P_{H_2} = 0.14$ atm	0.66	6.64

Fig. 9 HRTEM pictures of CNFs produced at (a) 823 K, (b) 873 K, (c) 923 K and (d) 973 K; $P_{CH_4} = 0.57$ atm, $P_{H_2} = 0.14$ atm

al. (2002).

Figure 12 shows the morphology of CNFs produced at different P_{H_2} . The diameter distribution, which was determined by counting more than 100 CNFs on the TEM images, is also presented as insets. It is also interesting to note that the size of the CNFs increases with the P_{H_2} increasing.

It has been accepted that the microstructure of the CNFs was largely determined by the morphology and structure of Ni. Zaikovskii *et al.* (2001) reported that the state (morphology and structure) of Ni for CNFs growth determined the microstructure of CNFs. Ducati *et al.* (2004) also found that Ni particle could be altered by increasing reaction temperature from 723 to 923 K and thus the wall and bamboo like intersects be changed. Further, the Ni particle could transform its shape during the reaction. Helveg and coworkers (Helveg *et al.*, 2004) found the periodic elongation/contraction of Ni when carbon deposits and grows on Ni surface. The initial shape of Ni transforms into a highly elongated shape, and the elongation of the Ni particle appears to be correlated with the

Fig. 10 HRTEM pictures of CNFs produced at (a) $P_{H_2} = 0.00$ atm, (b) $P_{H_2} = 0.14$ atm and (c) $P_{H_2} = 0.29$ atm

Fig. 11 The relationship between the microstructure and initial growth rate of CNFs

formation of more graphite sheets at the graphite–Ni interface with their basal (002) planes oriented parallel to the Ni surface. The elongation of the Ni nano-crystal continues until it achieves an aspect ratio (length/width) of up to 4, before it abruptly contracts to a spherical shape within less than 0.5 s. The contraction is attributed to the fact that the increase in the Ni surface energy can no longer be compensated for by the energy gained when binding the graphitic fiber to the Ni surface.

The above findings can be used to illustrate the relationship between the microstructures of the CNFs and the initial reaction rate. When the initial reaction rate is high, more carbon atoms will dissolve into the Ni particles, the elongation effect of the particle is remarkable and the

Fig. 12 TEM pictures of CNFs produced at (a) $P_{H_2} = 0.00$ atm, (b) $P_{H_2} = 0.14$ atm and (c) $P_{H_2} = 0.29$ atm

Fig. 13 The effect of initial reaction rate on structure of Ni

particle will have a high aspect ratio. Thus, the Ni particles which have different initial reaction rates of methane decomposition have different shapes, as depicted in **Figure 13**. In a Ni particle with high aspect ratio, carbon atoms tend to precipitate at the side walls where the diffusion path is shorter than that at the bottom of the particle and the produced CNFs will have small diameters and angles between the graphite layers and the growth axis.

These results imply that the initial reaction rate could be used to predict the microstructures of the produced CNFs, whatever the changing of the initial reaction rate is caused by reaction temperature, feed compositions or other reaction conditions. This conclusion is of practical significance for monitoring and controlling the CNFs growth process.

Conclusions

In this work, the rate of CNFs growth by methane decomposition on supported Ni catalysts and the microstructure of CNFs were determined. The following conclusions can be drawn from the experiments:

1. Under the reaction conditions used in this work, increasing reaction temperature, methane partial pressure and decreasing hydrogen partial pressure can increase the initial reaction rate.
2. A high initial reaction rate often leads to a fast catalyst deactivation rate and thus high carbon yield per unit catalyst can only be obtained as a compromise between initial reaction rate and catalyst deactivation rate. The highest carbon yield obtained in this work is 11.69 g/g-cat under the condition: reaction temperature, 873 K, $P_{H_2} = 0.29$ atm, $P_{CH_4} = 0.57$ atm.

3. The microstructures of the produced CNFs, e.g. the angles between the graphene layers and growth axis, diameters, etc., vary with the reaction conditions.
4. The microstructures of the produced CNFs have a close relationship with the initial reaction rate. The CNFs produced with high initial rate tend to have small angles and diameters and a hollow core. This phenomenon can be related to the shape of Ni particles developed in the reaction.

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