

Influence of synthesis process on preparation and properties of Ni/CNT catalyst

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Received 12 May 2005; accepted 23 June 2005

Available online 6 September 2005

Abstract

The Ni catalyst was deposited on multi-walled carbon nanotubes using electroless-plating method. The experimental results show that not only the concentrations of the compositions such as NaOH, HCHO (formaldehyde solution) (38 wt.%) and $C_4H_4O_6KNa \cdot 4H_2O$ (Rochelle salt crystal) in Ni bath affect the rate of Ni deposition greatly, but also the acid pretreatment of carbon nanotube precursors have a great influence on Ni content and Ni particle size deposited on the surface of the carbon nanotubes and hence the catalytic properties of Ni/CNT in the synthesis of new carbon nanotubes.

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Keywords: Carbon nanotubes; Electroless-plating; Ni/CNT catalyst; Catalytic properties

1. Introduction

Carbon materials can be used as support materials, due to their flexibility as support in tailoring the catalyst properties to specific needs [1,2]. Activated carbon has many advantages if utilized as catalyst support: resistant to acidic or basic media, stable at high temperatures in an inert atmosphere, possible to tailor its pore structure and chemical nature of the surface, etc. [3]. However, activated carbon support also suffers several drawbacks: low mechanical stability which induces the formation of fines during operation and high tortuosity, with the presence of a large amount of micro-pores which could hinder the full accessibility of the reactants to the active sites. Carbon-based materials also severely suffer from their low oxidation resistance which does not allow their use at high temperature under an oxidative atmosphere [4].

Carbon nanotubes outperform activated carbon due to their exceptionally high mechanical strength, high thermal conductivity, medium to high specific surface areas and high

external surface area, which render them interesting candidates for use as catalyst supports for preparing nano-sized metal and metal oxide particle catalysts [3,5–13]. Rh/P [5], Pt-WO₃ [6] and Pt [7,8] catalysts supported on carbon nanotubes have been studied and show exceptional properties. Moreover, carbon nanotube-supported nickel or nickel/aluminum mixed oxide have been used for carbon nanotube/nanofiber production [14,15]. Baker and co-workers [16,17] have reported that Ni decorating carbon nanofibers, exhibits a high catalytic activity when compared to classical supported catalysts, for light hydrocarbon hydrogenation reactions in the gas-phase, at atmospheric pressure. It was suggested by the authors that when nickel is supported on graphite nanofibers, the metal crystallites adopt a different morphology, i.e. hexagonal thin morphology, compared to those observed when the nickel is dispersed on classical support carriers such as alumina or silica. Such a peculiar metal morphology observed on the carbon nanofiber carrier was considered to be due to a strong metal–support interaction between nickel crystallites and exposed graphite planes. In our experiments, carbon nanotube-supported Ni catalyst also shows high catalytic activity in the synthesis of carbon nanotubes at 700 °C.

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In this paper, carbon nanotubes used as supports were refluxed in nitric acid and directly immersed in the Ni electroless-plating bath for the Ni deposition without activating and sensitizing. And the influence of the concentrations of the compositions such as NaOH, HCHO and $C_4H_4O_6KNa \cdot 4H_2O$ (Rochelle salt crystal) in Ni bath and the acid treatment of carbon nanotube precursors on the preparation and the catalytic properties of Ni/CNT catalyst was investigated.

2. Experimental

The carbon nanotubes used as supports were synthesized using floating catalyst method in a horizontal quartz tube furnace. During the experiment, xylene was used as carbon source, hydrogen as carrying gas and ferrocene as catalyst precursor. A sulfur-containing additive (thiophene) was employed to enhance the growth of carbon nanotubes. Then the carbon nanotube precursors were immersed in 4 M of nitric for 6 h to remove the amorphous and Fe catalyst at room temperature.

The carbon nanotube precursors purified were boiled in 4–14 M of nitric acid solution for 0–6 h before Ni deposition. The mixed solution was filtered with a ceramic filter and washed with distilled water until neutral, and dried. This support (0.50 g) was dispersed into 10 ml ethanol (99.7%) and the suspension stirred in the Ni bath with 300 ml electroless-plating solution of the composition $NiSO_4 \cdot 6H_2O$, 10 g/l; $C_4H_4O_6KNa \cdot 4H_2O$, 0–50 g/l; NaOH, 0–10 g/l; HCHO (38 wt.%), 5–20 ml/l. After 15 min the mixture was filtered through a ceramic filter, washed several times with distilled water and dried in air at 80 °C. Thus, carbon nanotube-supported Ni was obtained. In the experiment, $C_4H_4O_6KNa \cdot 4H_2O$ can keep Ni electroless solution stable. $NiSO_4 \cdot 6H_2O$ reacted with HCHO and NaOH to form metal Ni. Actually, during the reaction HCHO served as reducing agent and NaOH accelerated the formation of Ni atom. The concentrations

of NaOH, HCHO and $C_4H_4O_6KNa \cdot 4H_2O$ (seen in Table 1) in the Ni bath were varied to study their effects on the rate of nickel deposition. And the duration of acid treatment of carbon nanotube precursors and the concentration of nitric acid (seen in Table 1) were changed to study their influence on the preparation of Ni/CNT and its catalytic properties in the synthesis of carbon nanotubes.

A known amount (0.05 g) of catalyst precursor was spread in a ceramic boat, and then placed in the reaction region of a horizontal CVD quartz tube furnace, which was heated to 580 °C under nitrogen. The nitrogen was then substituted by hydrogen at a flow rate of 200 ml/min for 30 min, and subsequently the catalyst was reduced. After this the reaction region was heated to 700 °C in hydrogen and ethyne introduced with a flow rate of 100 ml/min. The catalytic decomposition reaction proceeded for 30 min. The products were then cooled to room temperature under nitrogen and the boat with the reaction products was taken out. The black powder produced was dispersed onto a supporting Cu membrane for transmission electron microscopy.

For the removal of the amorphous carbon and metallic catalyst in the product, the raw soot produced was first suspended in 0.2 l of 4 M diluted nitric acid and refluxed at 117 °C for 2 h. Then the solution was filtered and rinsed with pure water up to neutral and dried. Finally pure carbon nanotubes were obtained.

Transmission electron microscopy (TEM) was used to observe the microstructures and morphologies of Ni/CNTs catalyst and new carbon nanotubes and EDX used to determine the elemental compositions of Ni/CNTs catalyst.

3. Results and discussion

EDX analysis was performed on the carbon nanotube precursors before and after Ni deposition. The experimental results showed only C and no Fe catalyst in the carbon nanotube precursors acid-treated. After they were intro-

Table 1
Synthesis parameters of preparing Ni/CNT catalyst

Ni/CNT Samples	HNO ₃ (mol/l)	Acid-treatment duration (h)	NiSO ₄ ·6H ₂ O (g/l)	C ₄ H ₄ O ₆ KNa·4H ₂ O (g/l)	HCHO (38 wt.%) (ml/l)	NaOH (g/l)	PH value
1	4	6	10	45	16	1	11.40
2	4	6	10	45	16	3	11.87
3	4	6	10	45	16	5	12.09
4	4	6	10	45	16	7	12.43
5	4	6	10	45	16	10	12.86
6	4	6	10	45	5	5	12.09
7	4	6	10	45	10	5	12.09
8	4	6	10	45	20	5	12.09
9	4	6	10	25	16	5	12.09
10	4	6	10	35	16	5	12.09
11	4	6	10	50	16	5	12.09
12	4	0.5	10	45	16	5	12.09
13	14	6	10	45	16	5	12.09

duced into the Ni bath without activating and sensitizing, Ni catalyst successfully deposited on the surface of the carbon nanotube precursors. Furthermore, the rate of Ni deposition varied with increasing concentrations of NaOH, HCHO and $\text{C}_4\text{H}_4\text{O}_6\text{KNa}\cdot 4\text{H}_2\text{O}$ in Ni bath (as shown in Fig. 1). Fig. 1a describes the relation between the concentration of NaOH and the rate of Ni deposition. It is seen that the rate of Ni deposition increases greatly with increasing NaOH concentration. However, for more than 5 g/l, the rate of Ni deposition increases slowly. Therefore, in this experiment the concentration of NaOH should be 5 g/l.

The rate of Ni deposition has a similar tendency with increasing HCHO concentration (as shown in Fig. 1b). It increases rapidly with the increment of HCHO concentration for values less than 10 ml/l. For higher concentrations it increases slowly. Fig. 1c showed that the rate of Ni deposition gradually declines with increasing of the $\text{C}_4\text{H}_4\text{O}_6\text{KNa}\cdot 4\text{H}_2\text{O}$ concentration between 25 and 45 g/l. Above this value the rate of Ni deposition decreases greatly.

The result shows that the optimum range of HCHO concentration is from 10 to 20 ml/l. The importance of $\text{C}_4\text{H}_4\text{O}_6\text{KNa}\cdot 4\text{H}_2\text{O}$ in the Ni bath for Ni deposition on carbon nanotubes was because it can keep the Ni solution stable during the reaction. The rate of Ni deposition increased rapidly as the concentration of free Ni^{2+} increased. However, if the concentration of free Ni^{2+} is too high, nickel deposition would stop because a subsidiary reaction between Ni^{2+} ions takes place. The addition of $\text{C}_4\text{H}_4\text{O}_6\text{KNa}\cdot 4\text{H}_2\text{O}$ could chelate Ni^{2+} and keep the concentration of the free Ni^{2+} low thus preventing the subsidiary

reaction of Ni^{2+} ions. When the concentration of $\text{C}_4\text{H}_4\text{O}_6\text{KNa}\cdot 4\text{H}_2\text{O}$ was more than 45 g/l, the rate of Ni deposition decreased greatly. This is because the increasing $\text{C}_4\text{H}_4\text{O}_6\text{KNa}\cdot 4\text{H}_2\text{O}$ chelated more Ni^{2+} so that the concentration of free Ni^{2+} in the solution decreases greatly. Therefore, an appropriate amount of $\text{C}_4\text{H}_4\text{O}_6\text{KNa}\cdot 4\text{H}_2\text{O}$ (25 to 45 g/l) is beneficial to the reduction of Ni^{2+} and hence Ni deposition.

During the experiment, the influence of the acid pretreatment of the carbon tube precursors on Ni deposition under different conditions (parameters seen in Table 1) was studied and the corresponding morphologies of the Ni/CNT catalysts are shown in Fig. 2. Fig. 2a shows that, when carbon nanotubes precursors were refluxed in 4 M of nitric acid for 0.5 h, the Ni particles deposited are spherical with the average diameters about 65 nm and the metal–support contact area is smaller than the diameters of Ni particles. As the duration of acid pretreatment of carbon nanotube precursors increased from 0.5 to 6 h in 4 M of nitric acid, the density of the Ni particles deposited and the metal–support contact area increased while the particle size decreased slightly (as shown in Fig. 2b). Fig. 2c shows the morphologies of the Ni supported on carbon nanotubes refluxed in 14 M of nitric acid for 6 h. One can see that a continuous, not uniform Ni layer can be formed on the outer surface of carbon nanotubes supports. Because the interaction between nickel particles and nanotubes is not a strong bonding, some nickel particles may detach from the nanotubes in TEM sample preparation. Therefore, the density of the Ni particles deposited on the carbon nanotube precursors should be higher.

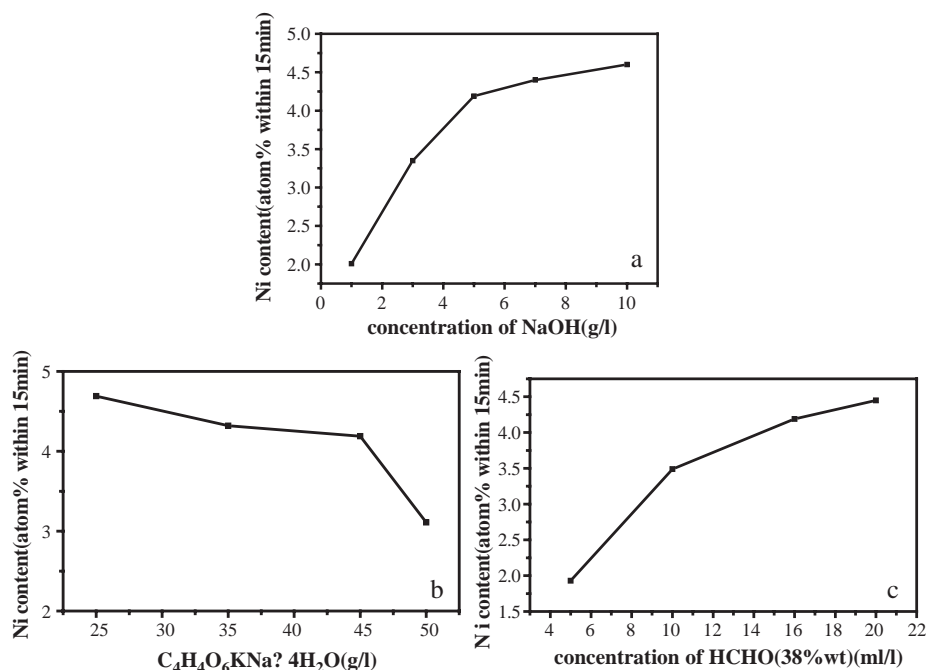


Fig. 1. (a) Influence of NaOH on the rate of the Ni deposition on CNTs; (b) influence of HCHO on the rate of Ni deposition on CNTs; (c) influence of $\text{C}_4\text{H}_4\text{O}_6\text{KNa}\cdot 4\text{H}_2\text{O}$ on the rate of Ni deposition on CNTs [37].

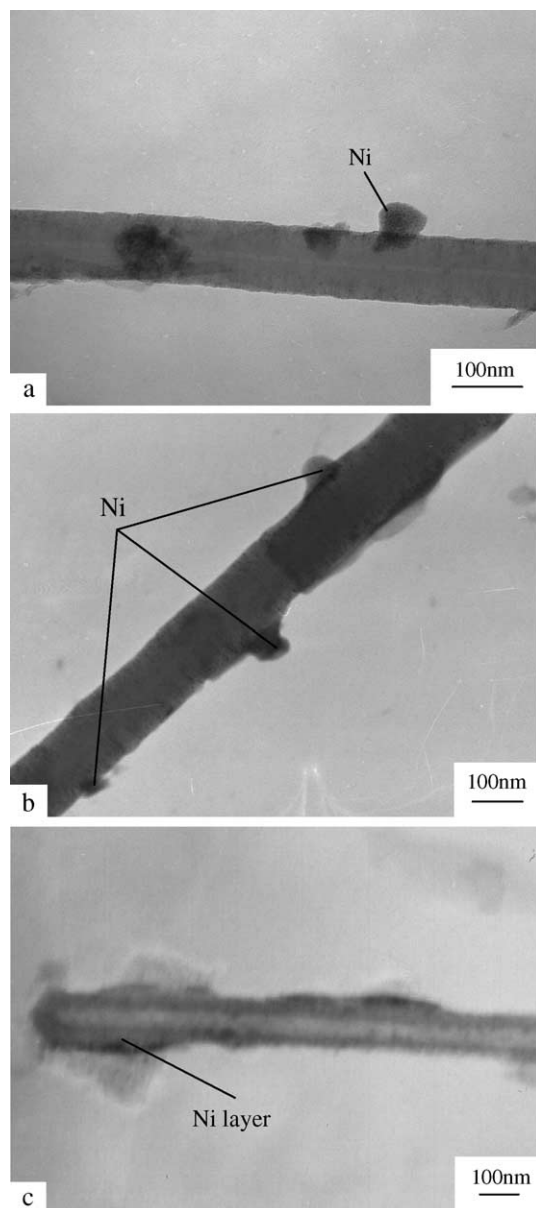


Fig. 2. Micrographs of Ni-deposited carbon tubes (a) carbon nanotubes precursors refluxed in 4 M of nitric acid for 0.5 h; (b) carbon nanotubes precursors refluxed in 4 M of nitric acid for 6 h [37]; (c) carbon nanotubes precursors refluxed in 14 M of nitric acid for 6 h.

The above three Ni/CNT catalysts were used to synthesize new carbon nanotubes. And TEM analysis was performed on the carbon nanotube products to determine the morphologies. The TEM image in Fig. 3 shows the morphologies of new carbon nanotubes synthesized with Ni catalyst supported by carbon nanotubes refluxed in 4 M of nitric acid for 0.5 h. It can be seen that new carbon nanotubes are curvous multi-walled CNTs with various diameters ranging from 40 to 80 nm. An important feature is that the tube consists of many separation layers in hollow, looking like the bamboo. The inside of CNT is hollowed without any catalyst particles and the root is opened. The surface of carbon nanotubes in Fig. 3a is not so smooth. Fig.

3b shows that the separation layers are conical shaped graphite layers directed to the open root of the carbon nanotubes and appear at larger distance. However, the diameter is not uniform: the diameter of the root is larger than that of the tip.

The carbon nanotubes synthesized with nickel catalyst supported by carbon nanotubes acid-treated in 4 M of nitric acid for 6 h are shown in Fig. 4. From Fig. 4 study, the carbon nanotubes products are high purity (about 95wt.%) multi-walled carbon nanotubes without any separation layers in hollow, and with the diameters ranging from 30 to 65 nm, and length up to several tens of micrometers. Moreover, they are curved or straight and the diameter is uniform. Compared with the size distribution of the originally deposited Ni particles, the outer diameters of the carbon nanotubes produced show a wider distribution at the extremes, which demonstrates that the nickel particles govern nanotube diameter [18–25]. Fig. 4a shows that the new carbon nanotubes and the carbon nanotubes supports twister together, indicating that it is difficult to separate the carbon nanotube precursors and new carbon nanotubes. However, when the Ni supported by carbon nanotubes refluxed in 14 M of nitric acid for 6 h was used for the synthesis of carbon nanotubes, a little of carbon fibers were obtained. This is because the continuous Ni layer has lower activity in the synthesis of carbon nanotubes [26,27].

The experimental results show that the acid treatment of carbon nanotube precursors exerts a great influence on the Ni deposition on carbon nanotubes. Acidic oxidation not only broke the nanotubes at the defects, but also introduced a large number of functional groups, such as hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$) and carbonyl ($>\text{C}=\text{O}$) [12,13]. These functional groups decreased the hydrophobicity of the carbon nanotubes and made the surface more accessible to the aqueous solution of the metal precursors or deposits [28]. During the reactions, Ni^{2+} ions were reduced, conglomerated and formed Ni particles and/or layers on the carbon nanotubes. As the duration of acid treatment of carbon nanotube precursors and the concentration of nitric acid increased, more functional groups were introduced and the specific area of carbon nanotubes increased. Therefore, more metal precursors were attached to the nanotubes and metal particles were dispersed more homogeneously on the outer surface of the nanotubes, leading to small diameters on the whole. When the concentrations of nitric acid increased from 4 to 14 M, a large number of functional groups were introduced onto the surface of carbon nanotubes, resulting in high density of Ni nucleation sites and therefore a continuous Ni layer formed on the outer surface of carbon nanotube precursors. However, the Ni layer is not uniform. It is possible that the functional groups didn't distribute homogeneously, giving rise to the different rate of the Ni deposition on the surface. The TEM and EDX analysis confirmed that no nickel particles were found on the surface of CNTs which had not been treated by nitric acid when they were dipped into the Ni bath, indicating that boiling with oxidizing acids

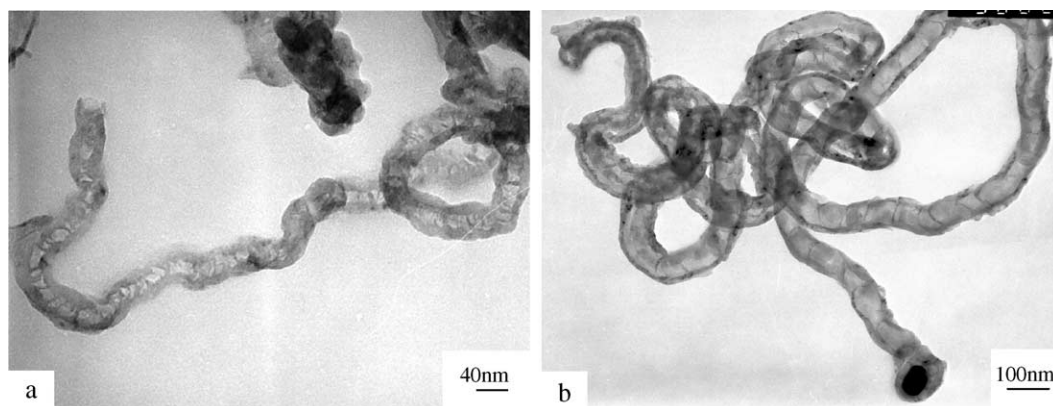


Fig. 3. Morphologies of new carbon nanotubes synthesized with nickel catalyst supported by carbon nanotubes refluxed in 4 M of nitric acid for 0.5 h.

was a critical factor for the deposition of the Ni particles. These results are consistent with those obtained by Li et al. [12].

The formation of bamboo-shaped carbon nanotubes has been reported and the possible growth models, such as the tip growth model or the base growth model, were proposed [29–33]. In our experiments, the hollow tip without any catalyst particles and the open root of the bamboo-shaped CNT, as shown in Fig. 3b, are consistent with the base growth model. According to the base growth model [29,31,33], the carbon radicals formed from the C_2H_2 decomposition are adsorbed on the circle of the contact area between the catalytic particles and CNTs precursors, initiating the aggregation of carbons. Then the carbons

diffused via the surface and/or bulk of the metal particles, forming graphite sheets as a cap on the top of the catalytic particles. The vertical graphite sheets are mainly grown by surface diffusion of carbons, and the compartment graphite sheets are mostly grown by bulk diffusion of carbons [29,31,33]. As the carbon atoms are continuously added to the edge of cap, the cap of graphite sheets lifts off the catalytic particle. Then a closed tip with the inside hollow is formed. As the carbon nanotubes continue to grow, the carbon nanotubes with separation layers are formed. The motive force of lift-off of the cap at the catalytic particle may be the stress accumulated under the graphite cap [31].

In the growth reaction of CNTs, the diffusion of carbon in the catalyst metal has been believed to be the rate-

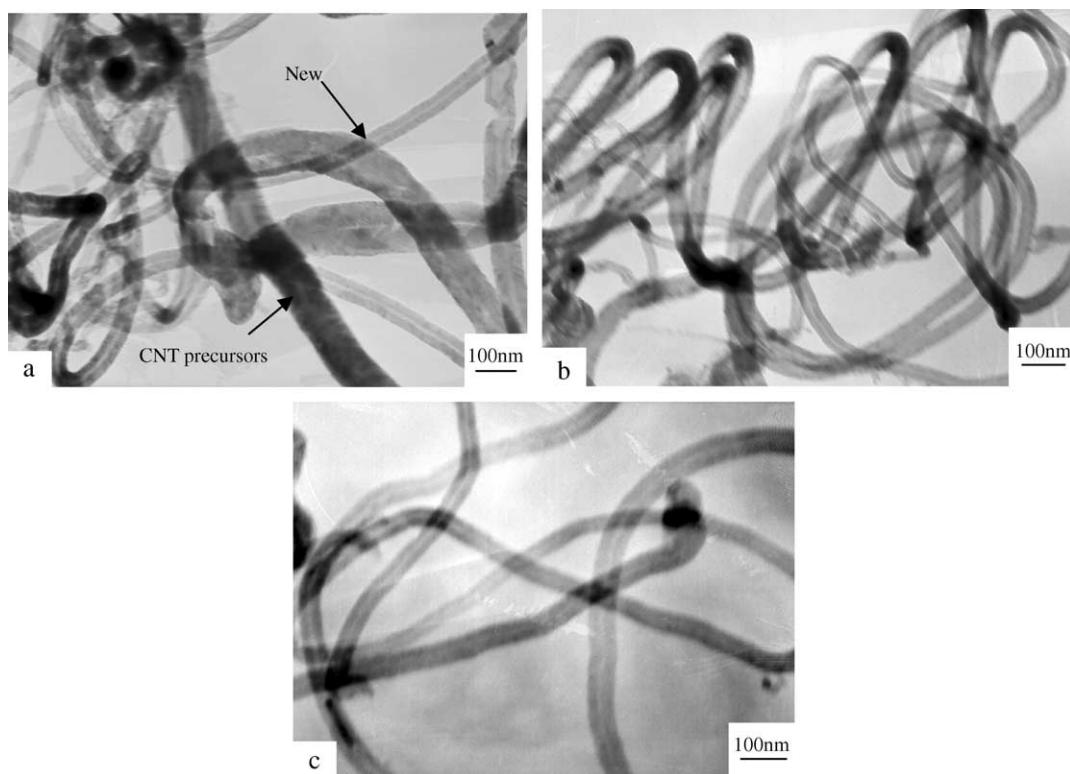


Fig. 4. Morphologies of carbon nanotubes synthesized with nickel catalyst supported by carbon nanotubes acid-treated for 6 h in 4 M of nitric acid.

determining step. The growth rate of CNTs can be described by an Arrhenius equation that the activation energy is the diffusion energy of carbon in the metal [29]. Lee et al. [29] argued that the smaller catalyst was proposed to favor the growth of hollowed CNTs. Because, as the size of catalyst particles decreases, the ratio of surface area to volume would increase rapidly, leading to the increasing surface activation energy of the catalyst. Thus the surface diffusion of carbon would dominate, instead of bulk diffusion. However, from Fig. 3, as the diameter of the carbon nanotubes increases, the separation layers appear at larger distance, which is inconsistent with the results of the research group of Lee [29]. Here, it is advisable that the structures of the carbon nanotubes in Fig. 2b were prepared by the higher surface activity Ni particles formed on the sites (such as defects) with more functional groups [34]. Due to more functional groups, more Ni atoms melt together to become bigger catalyst particles and therefore the diameter of CNTs increased. Furthermore, as functional groups increased, the stability of the Ni catalyst increased [35] and the outer crystal planes of nickel particles might be changed to benefit the surface diffusion of carbons [30,36], resulting in the increasing of surface diffusion rates of carbons. Therefore, the surface diffusion of carbons becomes dominant to the bulk diffusion of carbons. Since the separation layers are grown by bulk diffusion, the distance between the separation layers increases.

The better quality of the carbon nanotubes products in Fig. 3 than that in Fig. 4 confirms that acid-treatment duration of carbon nanotubes precursors exerts a great influence on the catalytic properties of Ni/CNT catalyst in the synthesis of carbon nanotubes and hence the structures of new carbon nanotubes. Two important reasons, as mentioned in the previous paragraph, may contribute to the growth of hollowed CNTs without any separation layers. As more functional groups are introduced to the surface of carbon nanotubes, the metal–support interaction was enhanced and the outer panel of Ni particles might be changed to favor the surface diffusion of carbons more greatly [16,17,30,35,36]. More important is that, as the size of Ni-particle-deposited decreases on the whole with increasing duration of acid treatment of carbon nanotube precursors from 0.5 to 6 h, it is expected that the surface diffusion becomes predominant in the growth of carbon nanotubes [28,29], which favors the formation of hollowed carbon nanotubes more greatly.

Additionally after purification, carbon nanotube yields of the two products are calculated as follows: carbon nanotube yield = $100 \times (\text{mass of CNT} - \text{mass of catalyst}) / \text{mass of catalyst}$. The results indicate that the carbon nanotube yield of the product (1100%) synthesized with Ni supported on carbon nanotubes acid-treated for 6 h is about 29% larger than that (850%) synthesized with Ni supported on carbon nanotubes for 0.5 h. Therefore, as the duration of acid treatment of carbon nanotube precursors in 4 M of nitric acid increases, the Ni/CNT catalyst produced shows higher

catalytic properties in the synthesis of the carbon nanotubes. Furthermore, our previous study [37] shows that the Ni/CNT has higher activity, compared to conventional catalyst such as pure Ni powder, Co powder and Ni/SiO₂.

4. Conclusions

The synthesis process, including the concentrations of the compositions in Ni bath and acid pretreatment of the carbon nanotube precursors, play key roles for the Ni deposition. With the varied concentrations of the compositions in Ni bath, the deposition rate of Ni on the carbon nanotube was changed, so that the Ni particle size varied during the same deposition time. As the duration of acid treatment and the concentration of nitric acid increased, the specific area of carbon nanotubes and the number of Ni nucleation sites increased due to the introduction of more functional groups, which lead to the decreasing of particle size and increasing of the interaction between metal and support. All these factors influenced the properties of Ni catalyst in the synthesis of carbon nanotubes. When the carbon nanotubes supports were refluxed in 4 M of nitric acid for 6 h and the composition NiSO₄·6H₂O in Ni bath 10 g/l, NaOH 5 g/l, HCHO (38 wt.%) 16 ml/l and C₄H₄O₆KNa·4H₂O 45 g/l, Ni particles distributed homogeneously on the carbon nanotubes and the Ni/CNTs catalyst displayed higher activity.

Acknowledgements

This work is supported by the National Natural Science foundation of China (NSFC, Grant No.10275005).

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