

Catalytic growth of carbon nanotubes with large inner diameters

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Abstract: Carbon nanotubes (2.4 g/g catalyst), with large inner diameters were successfully synthesized through pyrolysis of methane on a Ni–Cu–Al catalyst by adding sodium carbonate into the carbon nanotubes growth system. The inner diameter of the carbon nanotubes prepared by this method is about 20–60 nm, while their outer diameter is about 40–80 nm. Transmission electron microscopy and X-ray diffraction were employed to investigate the morphology and microstructures of the carbon nanotubes. The analyses showed that these carbon nanotubes have large inner diameters and good graphitization. The addition of sodium carbonate into the reaction system brings about a slight decrease in the methane conversion and the yield of carbon. The experimental results showed that sodium carbonate is a mildly toxic material which influenced the catalytic activity of the Ni–Cu–Al catalyst and resulted in the formation of carbon nanotubes with large inner diameters. The growth mechanism of the carbon nanotubes with large inner diameters is discussed in this paper.

Keywords: carbon nanotubes, Ni–Cu–Al catalyst, pyrolysis.

INTRODUCTION

Carbon nanotubes discovered by Iijima¹ in 1991 exhibit many interesting properties which promise a wide range of potential applications. Also, due to their nanometer hollow channel, carbon nanotubes can be used as a template for the synthesis of nanowires,^{2–5} and as a microscopic reactor for some reactions which are not easily performed under normal operation conditions.⁶ For such applications, carbon nanotubes with large inner diameters have to be produced. Although there are many methods of synthesizing carbon nanotubes,^{7–11} carbon nanotubes manufactured by these methods have relatively small inner diameters (less than 20 nm). So far, the template method^{12–14} is the only method effective in controlling the inner diameter of carbon nanotubes. However, this method does not meet the requirements for application because of the lower yield of carbon produce and the loss of

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expensive template. In this paper, a convenient way to produce carbon nanotubes with large inner diameters in high yield (2.4 g/g catalyst) is reported.

In the experiment, methane was cracked to carbon nanotubes on a Ni–Cu–Al catalyst at 1023 K under normal pressure. Generally, carbon filaments, nanometric carbon particles and carbon nanotubes with small inner diameters are formed.^{15,16} In a chemical vapor deposition process at a fixed temperature, the properties and morphologies of the as-grown carbon products mainly depend on the nature of the catalyst. The factors influencing the nature of the catalyst could possibly lead to a change in the properties and morphologies of as-grown carbon products. Sodium carbonate, a mildly toxic material, was used to tailor the activities of the Ni–Cu–Al catalyst.

EXPERIMENTS

Catalyst preparation

The catalyst (Ni/Cu/Al = 20/3/2) precursor was prepared by the co-precipitation method. Precipitation was carried out from an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Sodium carbonate was used as a precipitate. The sample was carefully washed with distilled water. Calcinations were carried out in a flow of nitrogen (99.99 %) for 5 h at a final temperature of 623 K which was achieved by heating at a rate of 5 K/min.

Growth of carbon nanotubes

The experiments were carried out in tubular reactor made of a horizontal ceramic tube (inner diameter 20 mm, length 100 mm) and this ceramic tube was placed in a tubular electric furnace. In order to avoid direct contact of sodium carbonate with the catalyst, sodium carbonate powder (0.2 g, less than 350 mesh) was put into a ceramic boat at the inlet of the tube and catalyst particles (0.2 g) were put into another ceramic boat in the middle part of the tube. Thus, only sodium carbonate vapor of very small particles contacts the catalyst. Since the concentration of sodium carbonate is uniform in the entire reactor, the sodium carbonate has a much more uniform effect on the active sites of the nickel catalyst and, hence, on the morphologies of the carbon nanotubes.

The catalyst was heated at a rate of 5 K/min from room temperature to 973 K in a nitrogen flow and then reduced by hydrogen (99.99 %) at 973 K for 1 h. After the reduction of the catalyst, the temperature was increased to 1023 K at a rate of 10 K/min. Hydrogen was flushed out with argon (99.99 %) and methane (99.999 %) was reacted with the catalyst at 1023 K. During the methane decomposition, a part of the gases at the exit of the reactor was analyzed by on-line gas chromatography.

Characterizations

The morphology of the carbon nanotubes was observed using a Hitachi H-600 transmission electron microscope (TEM).

The microstructure of the carbon nanotubes was studied using X-ray diffraction (XRD) with CuK_α radiation (Ray wave length, 0.15418 nm). A small amount of pure silicon powder was used as an internal reference to calibrate the carbon nanotubes (002) peak. The interplane distance (d_{002}) between the graphene layers of the carbon nanotubes was determined from the diffraction peak (002) using the Bragg equation.

RESULTS AND DISCUSSION

TEM analysis

As can be seen from Fig. 1a, the carbon nanotubes, prepared by adding sodium carbonate into the carbon nanotubes growing system, are typically multiwalled

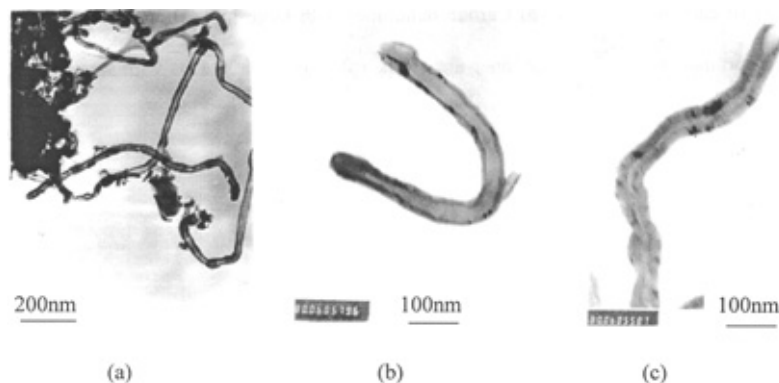


Fig. 1. TEM of carbon nanotubes. (a) Carbon nanotubes with large inner diameters. (b) The largest carbon nanotube with a large inner diameters. (c) Carbon nanotubes with small inner diameters.

nanotubes. Their outer diameter is about 40–80 nm and their inner diameter is about 20–60 nm. The hollow core of the carbon nanotubes is large. The largest nanotube (Fig. 1b) found had an inner diameter of about 60 nm. In contrast, a pristine carbon nanotube (Fig. 1c), prepared in a normal experiment without the addition of sodium carbonate, has thick walls and smaller cavities. The inner diameter of this carbon nanotube is about 10–15 nm. The above results clearly show that when both of the catalyst and reaction conditions are the same, the influence of the morphology change from small-inner-diameter tubes to large-inner-diameter tubes can be attributed to the addition of sodium carbonate into the reaction system.

XRD Analysis

Figure 2 (a and b) show the XRD patterns of the carbon nanotubes with large and small inner diameters, respectively. The patterns of the two samples show a major (002) peak at nearly the same positions (a: $2\theta = 26.1^\circ$; b: $2\theta = 26.3^\circ$) as graphite $2\theta = 26.5^\circ$.

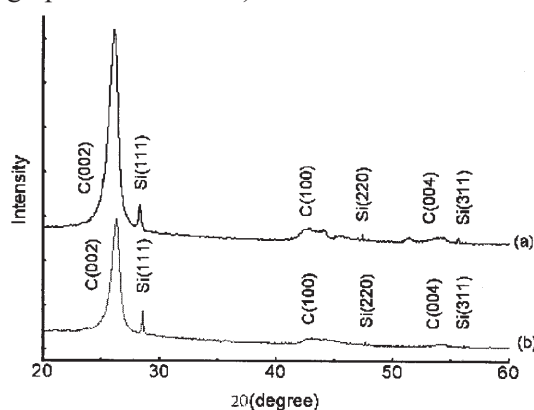


Fig. 2. XRD Patterns of the carbon nanotubes samples. (a) Carbon nanotubes with large inner diameters. (b) Carbon nanotubes with small inner diameters.

For graphite-like carbons, the degree of graphitization is often judged by the interplane distance (d_{002}) determined from the position of the diffraction line 002. The degree of graphitization of the carbon samples is calculated using the Maire and Mering formula¹⁷

$$d = 3.354 + 0.086 (1-g),$$

where d is the interplane distance (d_{002}) in angstroms, g is the percentage graphitization. If $d_{002} = 3.35 \text{ \AA}$, the graphitization degree is taken as unity; the higher is d_{002} , the lower is the degree of graphitization. Pertinent XRD analysis results (Table I) show that large-inner-diameter nanotubes have a smaller interplane distance (d_{002}) and a higher degree of graphitization degree than small-inner diameter ones. This result is in agreement with the observation of Zhang¹⁸ of single wall nanotubes with different diameters, indicating that nanotubes with large-inner-diameters do not have seriously distorted carbon layers and is a more stable structure.

TABLE I. XRD Analysis results

Sample	$2\theta_{\text{Si}(111)}$ degree	$\Delta 2\theta_{\text{Si}(111)} =$ $2\theta_{\text{Si}(111)} - 28.442$ degree	$2\theta_{c(002)}$ degree	$2\theta_{c(002)} =$ $2\theta_{c(002)} - \Delta 2\theta_{\text{Si}(111)}$ degree	$d_{c(002)}$ Å	g %
a	28.30	-0.142	26.10	26.242	3.393	55
b	28.58	0.138	26.30	26.162	3.403	43

These results indicate that the morphology and microstructures of carbon nanotubes can be improved by adding sodium carbonate into a carbon nanotubes growth system.

Methane conversions and carbon yield

Figure 3 shows the methane conversion as a function of time for methane flowing over a Ni-Cu-Al catalyst, both with and without the addition of sodium

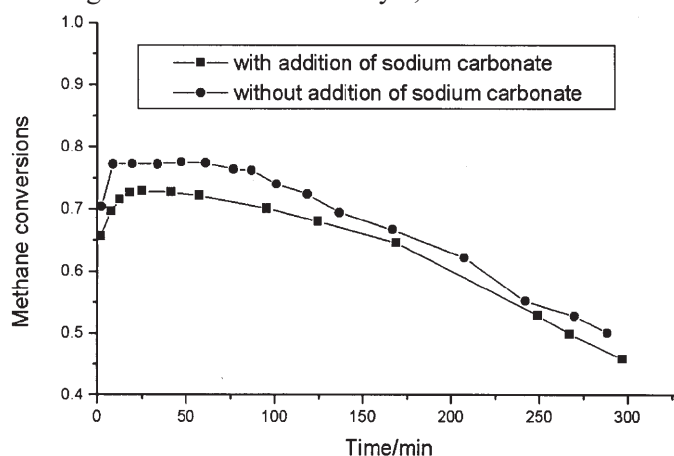


Fig. 3. Methane conversions as a function of time for the decomposition of flowing methane on a Ni-Cu-Al catalyst with and without the addition of 0.2 g sodium carbonate. Reaction temperature 1023 K; catalyst - 0.2 g; CH₄ - 50 ml/min.

carbonate. The addition of sodium carbonate into the reaction system results in a slight decrease in the methane conversions. For the reaction system containing sodium carbonate, the methane conversion initially increases with time, and then decreases gradually after 25 min. The features of kinetic curves of methane conversion are similar to the system without the addition of sodium carbonate. This indicates that the addition of sodium carbonate only decreases the activity of the catalyst but does not shorten the catalytic life of the catalyst. The yield of carbon per gram catalyst at 100 min is 2.4 g, which is slightly lower than that of the system without the addition of sodium carbonate (3.1 g/g cat). This shows that sodium carbonate is a mildly toxic material for a Ni–Cu–Al catalyst.

Formation of carbon nanotubes with large inner diameters

It can be seen from Fig. 1a that one tip of a carbon nanotube is located by the catalyst particles, while the other end of the carbon nanotube is closed. This indicates the end growth mode of the carbon nanotubes in this work. The catalyst particle is not spherical but looks like a plug. It has a relatively large gas–metal interface at the large end of the metal particle, which is not covered by a carbon layer. The small end of the catalyst particle embeds the tube. This suggests that carbon from the decomposition of methane at the large end of the metal particle diffuses through the bulk phase and precipitates at the small end of the metal particle. When the outer surface of the metal particle contacts the poisonous material, the metal particle will lose part of its activities to decompose methane, and, therefore, the carbon concentration inside the metal particle will be relatively low. Hence, insufficient carbon may be to diffuse through the bulk phase and precipitate at the small end of the metal particle, but prefers to diffusion to and deposit at the interface near the large end of the metal particle. Therefore, the inner diameters of the carbon nanotubes become large. It can be concluded that if a large amount of sodium carbonate or stronger toxic material would be added into the carbon nanotube growth system, distorted or fully collapsed carbon nanotubes may be formed.

CONCLUSIONS

Carbon nanotubes with large-inner-diameters were successfully prepared by the catalytic pyrolysis of methane on a Ni–Cu–Al catalyst by adding sodium carbonate. The outer diameters ranged from 40 to 80 nm, and the inner diameters were about 20–60 nm. The sodium carbonate added to the carbon nanotubes growing system plays an important role in controlling the inner diameters of the carbon nanotubes. All of these are important to synthesize carbon nanotubes with a large inner diameters on a large scale and at low cost.

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ИЗВОД

КАТАЛИЗОВАН РАСТ КАРБОНСКИХ НАНОТУБА ВЕЛИКИХ
УНУТРАШЊИХ ПРЕЧНИКА

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Успешно су синтетизоване карбонске нанотубе (2,4 g/g катализатора) великих унутрашњих пречника пиролизом метана на Ni–Cu–Al катализатору додатком натријум-карбоната у реакциони систем. Унутрашњи пречник нанотуба добијених овом методом био је 20 – 60 nm, док је спољашњи био 40 – 80 nm. За испитивање морфологије и микроструктуре карбонских нанотуба коришћена је трансмисиона електронска микроскопија и рендгенска дифракција. Анализе су показале велике унутрашње пречнике карбонских нанотуба и добру графитизацију. Додатак натријум-карбоната у реакциони систем смањује у малој мери конверзију метана, а и принос карбона. Експериментални резултати показују да је натријум-карбонат благи тровач Ni–Cu–Al катализатора и да смањење његове активности доводи до стварања карбонских нанотуба већих унутрашњих пречника. У раду је дискутован механизам раста карбонских нанотуба већих унутрашњих пречника.

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