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# Catalytic growth of carbon nanoballs with and without cobalt encapsulation

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#### Abstract

Carbon nanoballs encapsulated with cobalt were prepared by decomposition of methane. After acid treatment, the encapsulated cobalt can be removed to produce hollow carbon nanoballs. The content of hollow carbon nanoballs as high as 90 vol% in acid-treated carbon product can be obtained by increasing the content of cobalt from 50 to 75 mol% in the catalysts. However, under the same catalytic conditions, the main carbon products are multi walled carbon tubes (MWNTs) over Co/Al<sub>2</sub>O<sub>3</sub>, Co/La<sub>2</sub>O<sub>3</sub>, Co/CeO<sub>2</sub> and Ni/MgO catalysts by decomposition of CH<sub>4</sub>, or by decomposition of CO over Co/MgO catalysts. These carbon nanoballs encapsulated with cobalt are novel magnetic materials. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Since the discovery of buckminsterfullerene molecules in 1985 [1] and carbon nanotubes [2] in 1991, there has been a worldwide research effort on novel carbon products due to their unique physical properties that could potentially impact on broad areas of science and technology. For example, it has been reported that nanotubes have potential applications as superconductors [3], single-molecular transistors [4,5] and carbon nanotubes or particles filled with metal or metal oxides have potential applications in magnetic recording technology [6–8]. The synthesis of these carbon pro-

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ducts can be roughly divided into two types of methods. The first is mainly based on the sublimation of carbon in an inert atmosphere, such as electric arc-discharge process, laser ablation or sublimation by solar energy, and the second includes catalytic decomposition of suitable organic precursors, electrolysis in a molten ionic salt, heat treatment of polymers and low-temperature solid pyrolysis, etc. [9,10]. In most cases, the structures and morphologies of carbon products vary with the different preparation methods and conditions. It has been reported that single- and multi-walled carbon nanotubes (SWNT and MWNT), fullererene molecules, carbon nanopolyhedra, or their mixture, have been prepared by arc-discharge and laser ablation methods [11–14], and by catalytic chemistry methods, SWNTs and MWNTs or their mixture can also be obtained [15–18]. Moreover,

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even the same carbon product can possess various structure and shape. For example, the SWNTs have theoretically three conformations, namely armchair, zig-zag and chiral, and a particular carbon nanotube can further exhibit various shapes in straight, curved, helical and planarspiral [11,18,19]. So we believe the carbon production reaction should be an ideal model catalytic reaction to study the relationship between the nature of the catalysts, reaction kinetics and the structures as well as the morphologies of carbon products. However, we have found that, though several reaction models have been proposed [11,20-22], the catalytic mechanism and reaction kinetics are still not very clear, and in most cases, the control of the composition and structure of carbon product still poses a big challenge. Our strategy is to study systematically the nature of catalyst and the carbon product formation mechanism, and if possible, to develop technologies to control the structure and morphology of carbon products. Here we demonstrate a simple catalytic approach to the growth of carbon nanoballs under controlled conditions.

### 2. Experimental

The preparation of catalysts was carried out according to the method described in literature [23]. For example, 2.91 g of nitrate salt of cobalt was mixed with 2.56 g of magnesium nitrate (50 mol% Co/MgO) and dissolved in distilled water, followed by addition of citric acid with a molar ratio of citric acid: metal ions = 1:1. The aqueous solution was gelled at 60-70°C with stirring and dried at 200°C for 1 h. The dried powder was further heated in air at 400°C for 1 h. and 700°C for 5 h. For comparison, pure MgO and Co powder, which were prepared according to the above procedures using their nitrate as precursors, were also used as catalysts, respectively, and several catalysts were calcined at 900°C for 2 h. All the above chemicals were from Aldrich and in AR grade.

The catalytic conditions were studied very carefully. For a typical catalytic reaction, 0.20 g of catalyst was loaded in a quartz tube with a diam-

eter of 1.5 cm, and prior to the reaction, the catalvst was pre-reduced at 700°C for 40 min in the flow of hydrogen. The reaction was then conducted at 600°C for 1 h in the flow of CH<sub>4</sub> with a flow-rate of 30 ml/min. After reaction, the mixture was cooled in hydrogen and subjected to treatment with concentrated sulfuric acid to dissolve metallic catalyst. The microstructure and the morphology of the carbon product were observed by low and high resolution transmission electron microscope (TEM and HRTEM) on a JEM-100CX and a Philips FEG CM300 electron microscope, respectively, and SEM and EDX measurements were carried out on a XL-FEG scanning electron microscopy. Magnetic measurements were carried out using a superconducting vibration sample magnetometer (Oxford Instruments) at room temperature. The saturation magnetization was measured at the maximum field of 3 T. Prior to the magnetic measurement, the powder was shaped into small pellet.

#### 3. Results and discussion

Table 1 lists the composition of catalysts, catalytic reaction conditions and reaction results. Figs. 1-3 show some of TEM and SEM images of carbon products. We found that typical MWNTs were obtained from the decomposition of methane on Ni/MgO catalyst (Fig. 1a). These carbon tubes are slightly curved in shape and have a hollow structure inside. The diameters of tubes range from 10 to 40 nm. In the carbon product produced from NiCo/MgO catalyst, we observed few ringlike carbon balls besides the curved MWNTs. We guessed that the growth of carbon nanoballs should be related to the existence of Co sites in the catalyst, because we did not observe similar structure in the carbon product from Ni/MgO catalyst. The guess was soon confirmed from our experiments. Fig. 1b shows a TEM image of carbon product from Co/MgO catalyst. It is clearly seen that most of the carbon products are carbon ring-like nanoballs. The diameters of these carbon nanoballs range from 50 to 200 nm. We have also found that by simply increasing the content of supported cobalt from 50 to 75 mol% in Co/MgO

Cat.	Transiton metal (mol%)	Reaction temp. (°C)	Reaction gas	Flow rate (cm <sup>3</sup> /min)	Reaction time (min)	Carbon product composition
NiCo/MgO	25 + 25	600	$CH_4$	30	60	MWNTs + few
						nanoballs
Ni/MgO	50	600	$CH_4$	30	60	MWNTs
Co/La <sub>2</sub> O <sub>3</sub>	50	600	$CH_4$	30	60	MWNTs
Co/MgO	50	600	CO	30	60	MWNTs + few
						nanoballs
Co/MgO	50	600	$CH_4$	30	60	MWNTs + ca. 50%
						nanoballs
Co/MgO	75	600	$CH_4$	30	60	MWNTs + ca. 90%
						nanoballs
MgO	0	600	$CH_4$	30	60	No carbon product
Co	100	600	$CH_4$	30	60	Carbon sheets
Co/MgO	50	500	$CH_4$	30	60	MWNTs + nanoballs
Co/MgO	50	700	$CH_4$	30	60	MWNTs + nanoballs
Co/MgO	50	600	$CH_4$	30	3	MWNTs + nanoballs
Co/MgO	50	700	$CH_4$	30	20	MWNTs + nanoballs
Co/MgO	50	600	$CH_4$	15	60	MWNTs + nanoballs
CoMgO	50	700	$CH_4$	60	60	MWNTs + nanoballs

Table 1 Summary of the catalyst composition, reaction conditions and results

catalysts, the content of carbon nanoballs as high as 90 vol% can be obtained in acid-treated carbon product. When the content of Co in the catalysts is lower than 30 mol%, the carbon product is predominantly composed of slightly curved MWNTs. However, in the case of using pure MgO as catalysts, we found there is almost no change in color for the white MgO catalyst after reaction, indicating that MgO is not catalytically active to the decomposition of methane at 600°C (Table 1). When pure Co was used as catalyst, which was prepared by heating and reducing the mixture of cobalt nitrate and citric acid, only sheet-like carbon was observed (Fig. 1f and Table 1).

The effects of various supports and catalytically active metal elements and reaction gases on products were also studied under the same reaction conditions (Table 1). MWNTs and minor component of amorphous carbon were observed in product from Co/La<sub>2</sub>O<sub>3</sub>, and only amorphous carbon was seen in product from Fe/MgO. In the case of using CO as reaction gas and Co/MgO as catalyst, the carbon product mainly consisted of MWNTs with smaller diameter compared to the product of methane decomposition, but few carbon nanoballs could still be observed (Fig. 1c). So the reaction products are determined by the composition of catalysts and reaction gases. Obviously using of Co/MgO catalyst and methane gas favors the formation of carbon nanoballs.

Influence of reaction conditions on carbon products was also studied for decomposition reaction of methane on the Co/MgO catalyst. It is found that there is no obvious difference for the carbon product in morphology as the reaction temperature was changed from 500°C to 700°C, or/and the flow-rate of methane gas from 15 to 60 cm<sup>3</sup>/min, or/and the reaction time from 3 to 120 min. Our TEM and HRTEM results indicated that more amorphous carbon was covered on the carbon nanoballs at higher reaction temperature or higher methane flow rate and longer reaction time. Fig. 1d shows a TEM image with reaction time only 3 min. It clearly shows the ring-like structure of carbon nanoballs. The formation of nanoballs proceeds very quickly. An extension of reaction time only increases the quantity of product.

Fig. 2 shows a SEM image of carbon product from decomposition of methane on Co/MgO catalyst. The carbon product is composed of nanospheres with diameters ranging from 50 to 200 nm.



Fig. 1. TEM images of acid-treated carbon product produced by decomposition of methane on: (a) 50 mol% Ni/MgO; (b) 75 mol% Co/MgO at 600°C for 1 h; (c) decomposition of CO on 50 mol% Co/MgO at 500°C for 1 h; (d) decomposition of methane on 75 mol% Co/MgO at 600°C for 3 min; (e) raw carbon product from decomposition of methane on 50 mol% Co/MgO at 600°C for 3 min and treated by ultrasound for 4 h. The wall of carbon nanoballs encapsulated with catalysts is discernable; (f) sheet-like carbon product from decomposition of methane on pure Co catalyst at 600°C for 1 h. The pure Co catalyst was prepared using the mixture of cobalt nitrate and citric acid as precursors.



Fig. 2. SEM image of carbon nanoballs from decomposition of methane at 600°C for 1 h on 75 mol% Co/MgO.



Fig. 3. Image of HRTEM (a) of carbon nanoballs produced from decomposition of methane on 75 mol% Co/MgO catalyst at  $600^{\circ}$ C for 1 h.

These particles are rather regular in shape and most of them have an open window on the surface.

HRTEM image (Fig. 3) shows that it is void in the center of carbon nanoballs but, in the wall of nanoballs, there is no hollow structure or channel as in the case of MWNTs. At the same time a multiwalled structure is discerned. The interlayer distance in the wall is 0.33 nm indicating the multiwall is composed of graphite sheets. The formation of carbon nanoballs without typical hollow channel in the wall suggests the formation mechanism may be as follows: the deposition of carbon from dissociation of methane was initiated on the surface of the catalyst particles that was exposed to the reaction gas. The carbon further diffused through the bulk and other surfaces (these surfaces were connected the bulk of the catalyst) of the catalyst particles to form layered graphite structure. The repulsion among the carbon nanoballs due to their continuous growth would let them be lifted from the bulk of the catalysts with their encapsulated catalyst particles. In this way, the new catalytically active sites were created. So after a short reaction time, we still can obtain carbon nanoballs but in smaller quantity. However, the catalyst particles would be deactivated due to encapsulation of amorphous carbon as observed in our HRTEM measurement, which indicated the existence of amorphous carbon layer on the inner and outside surfaces of carbon nanoballs after longer reaction time or higher reaction temperature. In all TEM observations, for samples, before acid treatment, we did not find any carbon nanoballs without encapsulation of catalyst particle. This suggests that there is no carbon nucleation taking place in the reaction gas. As observed in the Fig. 2, the carbon nanoballs have small 'windows' on the surface. We believe these small windows on the carbon nanoballs originated from the unclosed surfaces that exposed to the reaction gas and were used to deposit the carbon.

The encapsulation of catalyst particles in carbon nanoballs was confirmed directly by TEM measurements. Originally it was very difficult to discern the edge of the carbon nanoballs from the encapsulated metal catalyst particles in the raw reaction mixture, because the particles were covered with amorphous carbon. We tried to remove part of amorphous carbon from the particle surface by heat treatment of the mixture at 300°C for 2 h in air or by ultrasound treatment for 4–5 h before TEM measurement. Similar results were observed for the samples treated with the two methods. Fig. 1e shows a TEM image of the reaction mixture (no acid treatment but with ultrasound treatment) from Co/MgO catalyst. Clearly, the contour of the carbon shell (marked with an

Table 2 Mean composition of several carbon nanoballs determined by EDX for raw carbon product from decomposition of methane on 50 mol% Co/MgO at 600°C for 3 min

Element	Со	Mg (wt%)	С	0	
	88.30	0.42	10.98	0.30	

arrow) is seen along the outer edge of the particles, and the metal particles are indeed trapped in the middle of the nanoballs. The EDX analysis (Table 2) showed that in this sample the mean cobalt content is ca. 88.3 wt% in several carbon nanoballs encapsulated with cobalt, indicating only cobalt was filled in the cage of the carbon balls.

Magnetic results show that the carbon nanoballs encapsulated with cobalt particles are magnetic materials (Fig. 4). It is found that the saturation magnetization for Co/MgO decreases with the deposition of carbon. Adversely, the coercive force increases with the deposition of carbon. So their magnetic properties are tunable by simply controlling deposition of carbon.

In summary, the carbon nanoballs are prepared by decomposition of methane on Co/MgO catalysts. The content of nanoballs in carbon product as high as 90 vol% can be obtained by simply controlling the cobalt content at ca. 75 mol% in catalysts. It is also found that the



Fig. 4. Magnetic curves for catalyst 75 mol% Co/MgO reduced at 700°C in  $H_2$  and reacted with methane at 600°C for 0, 10 and 60 min, respectively. Inset in the figure shows the M–H behavior in the lower magnetic field range.

catalyst particles were trapped in the center of nanoballs, but they could be easily removed by acid treatment. The observation of the catalyst particles encapsulated in the cage of carbon nanoballs before acid treatment suggests that the carbon nanoballs were grown out from the nucleation of carbon on the surfaces of catalyst particles. Also of interest is the influence of supports and reaction gas on carbon products. We found the use of  $Al_2O_3$ ,  $CeO_2$  and  $La_2O_3$  as the support of Co catalysts or using CO as reaction gas resulted in the formation of MWNTs with a slight curvature. A further study is being conducted to clarify this circumstance.

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