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CVD SYNTHESIS OF SPIRAL CARBON NANOTUBES OVER ASYMMETRIC CATALYTIC PARTICLES

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Abstract

The influence of asymmetric catalytic particles prepared by various methods was investigated on the growth of spiral carbon nanotubes using the CVD method. Asymmetric particles were prepared by either milling or crystallization from oversaturated solution onto the surface of catalyst support or catalyst impregnation at pH 8-9. As-prepared catalysts were tested in the decomposition of acetylene. Carbon deposit, thus carbon nanotubes and spirals were observed by transmission electron microscopy the activity was characterized by carbon yield.

Keywords: Coiled carbon nanotubes; CVD; TEM

INTRODUCTION

Due to their unique physical and electronic properties, carbon nanotubes (CNTs) have induced great interests among researchers since their discovery [1]. Since it is a cheap and simple technique, catalytic vapor deposition (CVD) as a possible synthesis method for carbon nanotube production has become popular [2]. CVD synthesis has a further undisputable advantage: this is the only method suitable for the synthesis of coiled carbon nanotubes so far. Occurrence of coil-shaped fibers in the jungle of straight catalytically grown nanotubes has been noticed from the early days of studying their catalytic synthesis [3]. These coiled nanotubes do not appear when an arc-discharge process is used, nor any other process.

It is clear that such nanospirals would on one hand have a toughness resembling the toughness of nanotubes more than of carbon fibers, and that on

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the other hand, if used in composites [4, 5], they would be better anchored in their embedding matrix than straight nanotubes. The resistivity linearly increased with increasing extension length and decreased along the same line when contracting, probably caused by the formation of inner stresses with extension. This property can be applied to pressure or tactile sensors [6], for example. Coiled carbon nanotubes can also be used as nano-velcro which might achieve a major role in nanotechnology. They can be used for anchoring different component parts to each other.

The structure, the morphology and the size of as prepared carbon nanoparticles significantly depend on the preparation and deposition conditions of catalysts. The first experimental observation for the production of coiled carbon nanotubes was in 1994 [7-9], when Zhang et al. in a Belgian research group observed the multi-walled coiled carbon nanotubes with inner and outer diameter of 15-20 nm in the sample grown by catalytic decomposition of acetylene over silica-supported Co catalyst at 700°C. Thereafter, Amelinckx et al. [10] proposed the concept of a spatial-velocity hodograph to describe the extrusion of helix-shaped carbon nanotube from a catalytic particle quantitatively. J.B. Bai [11] reported a method to prepare spiral carbon nanotubes with controlled diameter using alumina supported catalyst. Hou et al. [12] produced helically shaped multiwalled carbon nanotubes by co-pyrolysis of $Fe(CO)_5$ as floating catalyst precursor and pyridine or toluene as carbon source. A growth mechanism at a molecular level was described by Fonseca et al. [13, 14] to explain the formation of knees, tori and coils using the heptagon-pentagon construction proposed by Dunlop. A few years ago, we investigated the correlation between the pH of the catalyst solution, asymmetry of the catalyst particle, and the curvature of the coiled nanotubes [15]. The probability of deposition of larger and asymmetric particles increases with increasing pH. The assumption is that growth of coils is rather similar to that of straight carbon nanotubes except for the fact that some difference in rates for the catalytic reaction at the edges of catalyst particles probably induces different growing rates at various circumference point of a particle. A higher carbon deposition rate at one side of the particle would generate the „outer" part of the spirals.

Improving observations described above, the idea of our experiments was to produce asymmetric catalyst particles by a different method. In this work, asymmetric particles were prepared by either milling or crystallization from oversaturated solution onto the surface of catalyst support or catalyst impregnation at pH 8-9.

EXPERIMENTAL

Catalyst preparation and synthesis

Catalyst samples containing asymmetric particles were prepared by three different methods. In the first method, particles were obtained from

oversaturated cobalt acetate solution. The saturated cobalt acetate solution was prepared at 60°C, the $CaCO_3$ support was suspended in it, then the beaker was placed into a cold bath (0°C) under continuous stirring. The sample was filtered and dried. In the second method, three different catalyst supports were used, thus Co/$CaCO_3$, Co/13X zeolit, Co/silicagel catalysts were prepared by impregnation keeping the pH of the solution continuously 8-9 during preparation. In the third method, catalyst precursors ($Co(CH_3COO)_2$, Fe(III)acetylacetonate, $Co(NO)_3$, $Fe(NO_3)_3$) and support ($CaCO_3$ or 13X zeolit) were mixed mechanically in a ball mill. Both mono and bimetallic catalysts contained 5% metal and the latter one contained Fe and Co in 2:1 scale. Promising samples (13X/Co-acetate, 13X/Fe-Co-acetate, 13X/Fe-Co-nitrate) were treated in ammonia atmosphere for 4 days with the expectation of further improvement becuase of the possible favorable effect of slightly basic conditions on spiral carbon nanotube formation [15]. Catalytic nanotubes were grown by acetylene decomposition at 720°C for 30 min in a fixed-bed flow reactor using gas feed of nitrogen (500 mL/min) and acetylene (10 mL/min). In order to give some quantitative characterization of the catalytic decomposition of acetylene, carbon yield was calculated as follows:

$$\text{Carbon yield} = m_{carbon\ deposit}/m_{corr.\ catalyst}$$

Planetary ball mill

A Pulverisette 6 type planetary ball mill, equipped with a 250 mL grinding bowl and stainless steel balls of 10 mm size were used for homogenization. The rotational speed was 450 rpm. The respective treatment times of planetary ball milling were 75 minutes.

Electron microscopy

For qualitative characterization of the carbon deposit on the surface, products were imaged by transmission electron microscopy (TEM, Philips CM10). In order to observe representative portions, the TEM sample preparation involved grinding the synthesized material mechanically and gluing the ground powder on a Cu TEM-grid.

RESULTS AND DISCUSSION

The activity of catalysts prepared by the crystallization method

Since crystallization provides particles different from spherical, the catalyst precursor was precipitated from oversaturated solution onto the surface of

calcium carbonate. Carbon yields obtained after CVD reaction and occurrence of coiled nanotubes are summarized in Table 1. Data revealed that this sample showed no activity in acetylene decomposition. Therefore, the reaction temperature was increased to 750°C and the catalyst was subsequently treated under ammonia atmosphere. At higher temperature, the carbon yield became 0.67 but no carbon nanostructures could be observed on the surface during TEM investigations. Ammonia treatment increased the activity further (1.02). However, neither carbon nanotubes nor spirals were found in the deposit. A possible explanation for this phenomenon is that the size of precipitated particles is too large which results zero selectivity for nanotube formation.

Table 1

Carbon yields and spiral formation data of CVD catalysts prepared by various methods

Catalyst/support	***Preparation method***	***Carbon yield***	***Spiral formation***
$Co^{acetate}/CaCO_3$	crystallize	0.0000	-
$Co^{acetate}/CaCO_3$(750°C)	crystallize	0.6688	-
$Co^{acetate}/CaCO_3$	crystallize+ ammonia atm.	1.0186	-
$Co^{acetate}$/13X	impregnation	0.5126	+
$Co^{acetate}/CaCO_3$	impregnation	0.3258	+
$Co^{acetate}$/silicagel	impregnation	0.2479	+
$Co^{acetate}/CaCO_3$	milling	0.1236	-
Fe-$Co^{acetate}/CaCO_3$	milling	0.4559	-
$Co^{nitrate}/CaCO_3$	milling	0.5882	-
Fe-$Co^{nitrate}/CaCO_3$	milling	1.8124	+
$Co^{acetate}$/13X	milling	1.8064	-
Fe-$Co^{acetate}$/13X	milling	0.6705	+
$Co^{nitrate}$/13X	milling	0.1396	+
Fe-$Co^{nitrate}$/13X	milling	1.0184	+
$Co^{acetate}$/13X	milling+ ammonia atm.	0.5585	+
Fe-$Co^{acetate}$/13X		1.8439	+
Fe-$Co^{nitrate}$/13X		1.2429	+

The activity of catalysts prepared by the impregnation method

Following previous results [15], catalysts were prepared by impregnation from a basic solution of cobalt using different catalyst supports. At this pH, cobalt hydroxide starts to precipitate which results in asymmetric catalytic particles afterwards on the surface. From Table 1, it can be seen that all three catalysts prepared with this method produced moderate activity. TEM observations revealed that the surface was covered by carbon nanotubes, and spiral structures were also found in all cases. As an illustration, a spiral carbon nanotube grown on Co/13X catalyst is shown in Fig. 1.

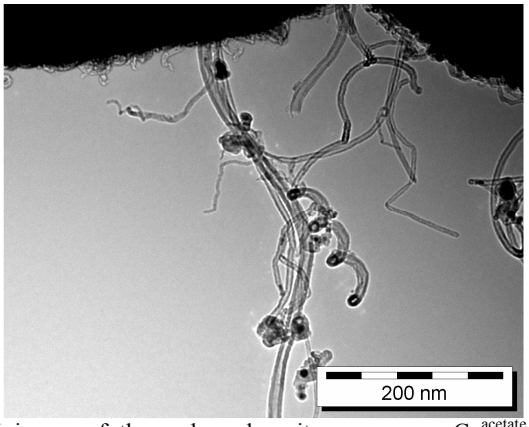

Fig. 1. TEM image of the carbon deposit grown over $Co^{acetate}$/13X catalyst prepared by the impregnation method

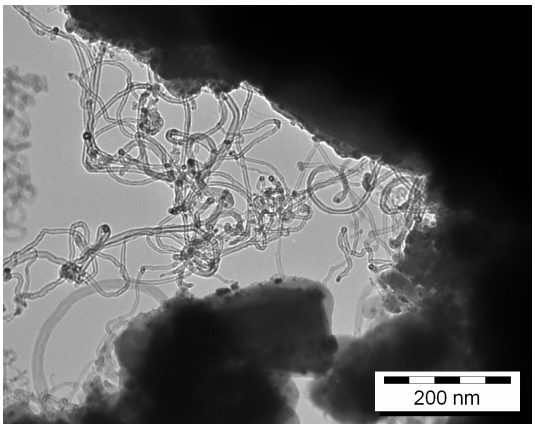

Fig. 2. TEM image of the carbon deposit grown on the surface of $Co^{nitrate}$/13X catalyst prepared by ball milling

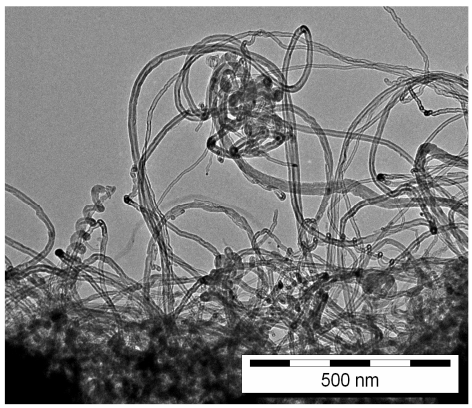

Fig. 3. TEM image of coiled and bent carbon nanotubes over Fe-Co^{acetate}/13X catalyst prepared by ball milling then treated in ammonia atmosphere

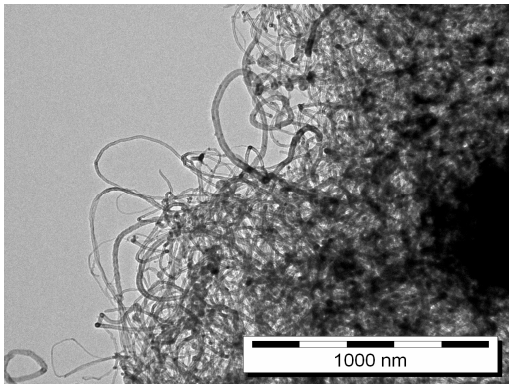

Fig. 4. TEM image of carbon deposit grown on the surface of Fe-Co^{nitrate}/13X catalyst prepared by ball milling then treated in ammonia atmosphere (arrows shows spirals in the forest of carbon nanotubes)

The activity of catalysts prepared by the ball milling method

Due to crystalline structure, mechanical grinding also results in asymmetric particles. Thus, milling catalyst precursor and support together in a powerful planetary ball mill should provide angular asymmetric particles of proper size. Carbon yields obtained after acetylene decomposition over these samples varied widely (Table 1). TEM observations also revealed great variety in the quality of the carbon deposit. Most samples were more or less covered by carbon

nanotubes. Some catalysts, mainly the $CaCO_3$ supported ones produced absolutely no spiral carbon nanotubes. However, in some cases, the deposit contained strongly bent carbon nanotubes as shown in Fig. 2. This feature means undisputable tendency for coiled carbon nanotube formation. 13X supported catalysts provided more spiral carbon nanotubes. In order to increasethe formation of coiled carbon nanotubes, some ball milled samples were treated in ammonia atmosphere, which might help slow recrystallization of catalyst particles on the surface. As can be seen in Figs 3 and 4, the amount of spiral carbon nanotubes increased significantly.

DISCUSSION

Our goal was the production of coiled carbon nanotubes by developing catalysts and by the optimization synthesis conditions. The influence of different anions of iron and cobalt salts, of different catalyst supports ($CaCO_3$, 13X, silicagel) and of synthesis method were investigated on the growth of spiral carbon nanotubes under CVD conditions.

Catalyst samples from an oversaturated solution probably contained particles larger than a few times ten nanometers which is required for carbon nanotube formation. Even if they had asymmetric shape, a carbon deposit differing from regular nanostructure could form after CVD.

Spiral carbon nanotubes could be observed on the surfaces of all three catalyst samples prepared by impregnation ($Co^{acetate}/CaCO_3$, $Co^{acetate}$/13X, $Co^{acetate}$/silicagel). However, the carbon yield and the proportion of spirals among straight nanotubes were rather low.

It was an interesting finding that the average diameter of carbon nanotubes grown over catalysts prepared by ball milling was significantly smaller than those of CNTs generally obtained by CVD. It is well known that the diameter of the catalyst particles on the surface has a strong influence on the diameter of growing carbon nanotubes [13]. Formation of carbon nanotubes of smaller diameter might confirm the efficiency of planetary ball mill and the high dispersity of catalyst prepared by milling.

The 13X zeolit of the three catalyst support provided the best carbon yields among ball milled samples and bimetallic catalysts were more effective than monometallic ones.

Because of its probable advantageous effect, subsequent ammonia atmosphere was applied in order to further improve catalyst performance. In each case, both the quality and the quantity of spiral nanotubes increased. Using Fe-$Co^{acetate}$/13X and Fe-$Co^{nitrate}$/13X catalysts, we hope that further optimization of pH and/or slight modification of catalyst preparation method can provide even better results in spiral carbon nanotube synthesis.

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