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HIGH-YIELD PRODUCTION OF MULTI-WALLED CARBON NANOTUBES BY CATALYTIC DECOMPOSITION OF BENZENE VAPOR *

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Multi-walled carbon nanotubes (CNTs) have been synthesized on γ-Al_2O_3 supported unitary, binary or trinity metal (Fe, Co, Ni) catalysts with benzene as carbon source in the range of 600 to 810 °C. The growth of CNTs was carried out in a fixed bed flow reactor and the quality of carbon deposits was characterized by transmission electron microscopy. The preparation was optimized and the high-yield production of CNTs has been achieved for three mixture catalysts with the yield of high-quality CNTs higher than 200% within 60 min, reaching a maximum of 278% for 1.51 mmol/g Fe-1.51 mmol/g Co/γ-Al_2O_3 catalyst. This provides a good alternative for future large scale and low cost production of CNTs for applications.

Keywords: carbon nanotube, chemical vapor deposition (CVD), benzene
PACC: 6146, 8115H

I. INTRODUCTION

Since Iijima discovered carbon nanotubes (CNTs) in 1991,[1] a worldwide research upsurge on CNTs is currently taking place due to their unique structure and technically important properties.[1−3] CNTs are now being regarded as one of the most attractive nanomaterials for many potential applications, e.g., as reinforcing elements in composites,[4] cold cathode electron field emitters,[5] data memorizer,[6] hydrogen and electric power storages,[7−8] single molecular transistors in microelectronics,[9] and catalyst supports.[10] Classified according to the synthesis temperature, three kinds of techniques have been developed to prepare CNTs at (1) high-temperature (over 4000 °C), e.g., by graphite arc-discharge and laser ablation methods,[1,11] (2) moderate-temperature (around 1000 °C) by chemical vapor deposition (CVD) through catalytic decomposition of hydrocarbons,[12] and (3) low-temperature (below 666 °C[13] or even down to 100 °C[14]) by plasma-enhanced chemical vapor deposition. Among these, only the CVD method has the possibility for large scale and low cost production of CNTs, which is one of the main challenges for future applications. In this respect, high-productive catalysts and the optimization of experimental conditions are especially important. To date, tremendous effort has been devoted to the high-yield production of CNTs through, e.g., regulating the catalysts, supports, carbon-containing precursors, and optimizing the experimental conditions such as the gas flow rates, synthesis time and temperatures. Taking 60 min as a reference, the best results reported so far give a total yield of CNTs lower than 200%,[12,15,16] defined as the weight gain ratio of the produced CNTs to the starting catalyst.

In this paper, systematic preparation of multi-walled CNTs has been performed by using γ-Al_2O_3 supported unitary, binary or trinity metal (Fe, Co, Ni) catalysts with benzene vapor as carbon source. The synthesis conditions have been optimized in order to obtain a high yield and high quality of CNTs. A new yield record of CNTs as high as 278% has been reached for 1.51 mmol/g Fe-1.51 mmol/g Co/γ-Al_2O_3 catalyst within 60 min.

II. EXPERIMENTAL

The first step of our experiments was to prepare a series of supported catalysts. The preparation procedure is briefly described as follows. As an example, an Fe-Co/γ-Al_2O_3 catalyst containing 1.51 mmol Fe and 1.51 mmol Co per gram of γ-Al_2O_3 was prepared by

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impregnating 5.00 g γ-Al_2O_3 with 7.00 ml water solution containing 7.55 mmol $Fe(NO_3)_3 \cdot 9H_2O$ and 7.55 mmol $Co(NO_3)_2 \cdot 6H_2O$. The impregnation typically lasted for 24 h at ambient temperature until drying. The material was then dried at 110 °C for 3 h followed by grinding into 0.45∼0.90 mm particles in diameter. This resulting catalyst was denoted as 1.51 mmol/g Fe-1.51 mmol/g Co/γ-Al_2O_3. For each round, about 20 mg catalyst was placed in a quartz tube with 10 mm inner diameter inside a larger quartz tube with 35 mm inner diameter and 550 mm length, mounted in a tube furnace with 300 mm length. The catalyst was pre-heated to a certain reaction temperature between 560°C and 810°C under nitrogen atmosphere at a flow rate of 70 ml/min. Subsequently, benzene vapor was led into the system by means of the nitrogen flow passing through a triplet benzene saturator at 25°C. The nitrogen and benzene vapor flow lasted for 60 min for growing CNTs. The furnace was then cooled down to ambient temperature in nitrogen flow. In all experiments, the nitrogen flow rates and the temperature of the benzene saturator were fixed. After the reaction, the yield of carbon deposit in each synthesis was calculated using the equation:

carbon deposit (%) $= (m_{\rm tot} - m_{\rm cat})/\ m_{\rm cat} \times 100\%$,

where $m_{\rm cat}$ is the initial weight of the original catalyst and $m_{\rm tot}$ is the total weight of the resulting product.

The quality of the product was evaluated by transmission electron microscopy (TEM). The samples for TEM experiments were dispersed in ethanol solution (50% v/v) with ultrasonic treatment for about 10 minutes and then transferred to a copper grid with polymer membrane. All TEM observations were carried out in a JEOL–JEM–1005 TEM operated at 100 kV.

Ⅲ. RESULTS AND DISCUSSION

Figure 1 shows the typical dependence of carbon deposit on the decomposition temperature for several high-productive catalysts for 60 min growth of CNTs. Below 560°C, the growth of CNTs has not been observed. The yield of carbon deposit increases with decomposition temperature, reaches the maximum around 660°C, and then decreases. Therefore, 660°C is taken as the optimal synthesis temperature for growing CNTs through the catalytic decomposition of benzene vapor. Encouragingly, the yields for two binary and one trinity catalysts could exceed 200%, reaching the maximum of 278% for 1.51 mmol/g Fe-1.51 mmol/g Co/γ-Al_2O_3 catalyst, which is much higher than the literature data to date.[15,16] In addition, the purification of CNTs in our cases is easy because the alumina support could be eliminated by acid or base, e.g. hydrochloric acid or sodium hydroxide. This means a new promising combination of catalyst, carbon precursor and optimal experimental conditions have been established, which provides a good alternative for future large scale and low cost production of CNTs for applications.

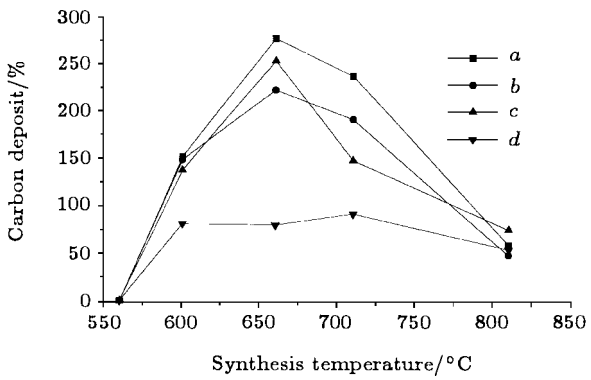


Fig.1. The dependence of carbon deposit on the decomposition temperature for 60 min growth of CNTs. Curve *a*: 1.51 mmol/g Fe-1.51 mmol/g Co/γ-Al_2O_3; Curve *b*: 1.47 mmol/g Fe-1.40 mmol/g Ni/γ-Al_2O_3; Curve *c*: 1.44 mmol/g Fe-0.82 mmol/g Co-0.69 mmol/g Ni/γ-Al_2O_3; Curve *d*: 2.88 mmol/g Co/γ-Al_2O_3.

As a comparison, the yields for unitary metal catalysts of 2.90 mmol/g Co/γ-Al_2O_3, 2.88 mmol/g Ni/γ-Al_2O_3 and 2.88 mmol/g Fe/γ-Al_2O_3 are only 91%, 20% and less than 10% respectively.

The typical TEM images of CNTs prepared with the three high-productive catalysts are shown in Fig.2. From Fig.2(b), 2(e) and 2(f), it is learned that, for the CNTs prepared at 660°C, the quality of CNTs is rather good. Good quality here means clear tubular structure with little carbon deposit in other forms, e.g., the amorphous carbon on the outer surface of CNTs, the carbon nanoparticles and so on. By comparing Fig.2(a) to 2(d), the influence of the decomposition temperature on the quality of CNTs could be inferred, and the quality of CNTs prepared at 660°C is the best.

From the above description, it could be concluded that the decomposition temperature of 660°C corresponds to the highest yields and best quality of CNTs in our synthesis recipes. It should be noted that, in earlier studies, different synthesis parameters have already been greatly investigated to get a high-yield pro-

duction of CNTs.[15,16] It was also indicated that mixture catalysts of different transition metals exhibited relatively high yields. Even so, the yields in the literature were lower than 200% for 60 min. From our present results, it seems that great potential to get much higher yields through the synergism of different parameters still exists. It is interesting to speculate that, if the C_6 unit in benzene could be incorporated directly into the nanotube structure, great increase in the yield of CNTs could be expected.

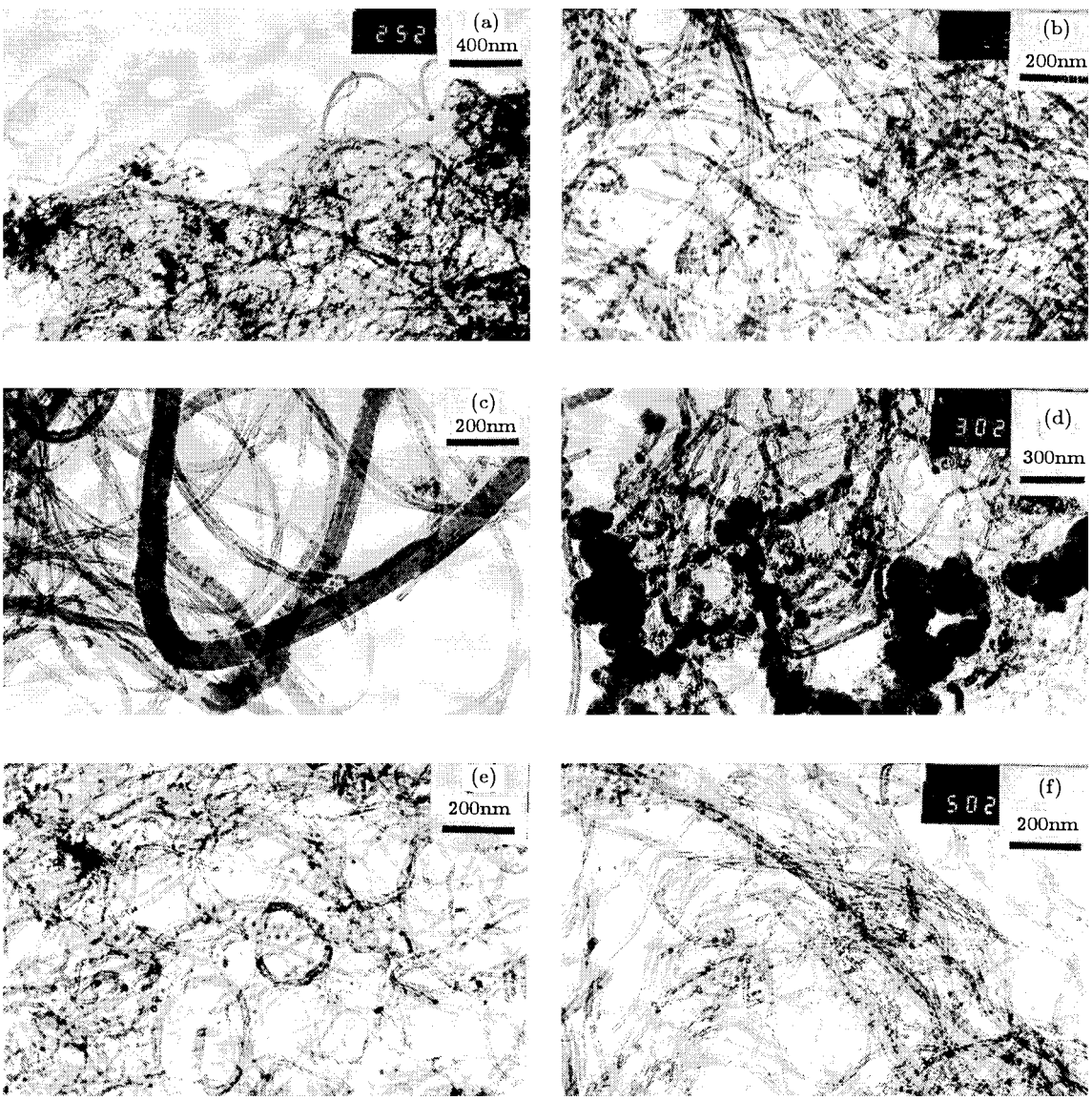


Fig.2. The typical TEM patterns of CNTs prepared with three high-productive catalysts at different conditions. (a) to (d) correspond to the 1.51 mmol/g Fe-1.51 mmol/g Co/γ-Al_2O_3 catalyst with the synthesis temperature of 600, 660, 710, 810°C respectively; (e) and (f) correspond to the 1.47 mmol/g Fe-1.40 mmol/g Ni/γ-Al_2O_3 and 1.44 mmol/g Fe-0.82 mmol/g Co-0.69 mmol/g Ni/γ-Al_2O_3 catalysts respectively, with the synthesis temperature at 660°C.

IV. CONCLUSION

Multi-walled carbon nanotubes (CNTs) could be simply synthesized on γ- Al_2O_3 supported unitary, binary or trinity metal (Fe, Co, Ni) catalysts with benzene as carbon source at low temperatures. High yield production of good-quality CNTs has been achieved on three mixture catalysts at 660°C with yields higher than 200%, reaching a maximum of 278%, for 60 min growth of CNTs. This provides a good alternative for future large scale and low cost production of CNTs for applications.

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