

Effect of temperature for synthesizing single-walled carbon nanotubes by catalytic chemical vapor deposition over Mo-Co-MgO catalyst

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Abstract

The influence of temperature on synthesizing single-walled carbon nanotubes (SWCNTs) by catalytic chemical vapor deposition of methane over Mo-Co-MgO catalyst was studied by Transmission Electron Microscope (TEM) and Raman scattering. The Mo-Co-MgO bimetallic catalyst was prepared by decomposing the mixture of magnesium nitrate, ammonium molybdate, citric acid, and cobalt nitrate. The results show that Mo-Co-MgO bimetallic catalyst is effective to synthesize SWCNTs. By using Mo-Co-MgO bimetallic catalyst, generation of SWCNTs even at 940 K was demonstrated. The optimum temperature of synthesizing SWCNTs over Mo-Co-MgO bimetallic catalyst may be about 1123 K. At 1123 K, the diameters of SWCNTs are in the range of 0.75–1.65 nm. The content of SWCNTs is increased with the increase of temperature below 1123 K and the carbon yield rate is also increased with the increase of synthesis temperature. Therefore, the amount of SWCNTs increases with the increase of temperature below 1123 K. However, above 1123 K, the content of SWCNTs is decreased with the increase of temperature; therefore, it is not effective to increase the amount of SWCNTs through increasing synthesis temperature above 1123 K.

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1. Introduction

Single-walled carbon nanotubes (SWCNTs) have been an area of intense research since their discovery in 1993 [1,2], because of their extraordinary mechanical [3] and unique electronic properties [4]. Based on their excellent properties, many potential applications, such as high-strength material [5], field-emission [6], supercapacitors [7], SPM tips [8], sensor [9] have been proposed. Therefore, the scale-up synthesis of SWCNTs with high yield and quality is of great significance for both theoretical research and practical use.

Until now, SWCNTs can be synthesized with arc-discharge [10], laser ablation [11], catalytic chemical vapor decomposition (CCVD) [12–19], etc. Compared with other methods such as arc-discharge, the CCVD method appears to be a promising technique since it has the potential for the large-scale synthesis of high-quality SWCNTs at relatively low cost. In the CCVD method, the growth of SWCNTs is affected by catalysts (composition, type of support material and the nature of metal), carbon sources, growth time, synthesis temperature and gas flow rate and so on. Among these

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growth conditions, it is considered that two kinds of experimental parameters play important roles to prepare SWCNTs with high yield and scale up the synthesis of SWCNTs: one is the temperature for synthesizing SWCNTs and the other is to select the catalyst [20]. Recently, pure SWCNTs were prepared by controlled preparations of metal fine particles of Fe, Ni, Co, Mo or mixtures supported by Al_2O_3 , SiO_2 or MgO [15,21–25] and the carbon yield rates of SWCNTs samples synthesized over different catalysts using methane as carbon source were in the range of about 8–150% [20]. Mo-Co bimetallic catalysts prepared by many different methods have been reported [26–30]. However, there were no reports about the preparation of SWCNTs by CCVD over the Mo-Co-MgO catalyst prepared by “citric acid” method, according to our investigation. Our study indicates that the SWCNTs with more than 150% carbon yield rate can be obtained by CCVD over the Mo-Co-MgO bimetallic catalyst. In addition, to uniform gas–solid mixture and avoid catalyst particle sintering, SWCNTs were synthesized by fluidized bed. It is generally known that the temperature of synthesizing SWCNTs by the floating catalyst method is in the range of 1073–1473 K [31–33] and the growth of SWCNTs, especially parameters of interest such as yield and purity, had a close relationship with synthesis temperature. In our present study, generation of SWCNTs even at 940 K was demonstrated by using Mo-Co-MgO bimetallic catalyst. This would propose the large-scale production at lower cost and the direct growth of SWCNTs on conventional semiconductor devices. Mo-Co-MgO bimetallic catalyst is effective to synthesize SWCNTs and the optimum temperature of synthesizing SWCNTs over Mo-Co-MgO bimetallic catalyst may be about 1123 K.

2. Experimental

2.1. Preparation of the catalyst

A mixture of magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ammonium molybdate ($(\text{NH}_4)_5\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) and cobalt nitrate ($\text{Co}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was dissolved in deionized water. In our experiment, the weight ratio of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} : (\text{NH}_4)_5\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O} : \text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O} : \text{Co}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} : \text{deionized water} = 10:0.07:4:1.6:1$ was used to fabricate the Mo-Co-MgO catalyst. After mixing round at 363 K for 4 h, the catalyst was baked at 423 K for 12 h, and then grounded in mortar to break the chunks into powder. The powder was placed into quartz tube, and then heated up to 823 K and air was introduced into quartz tube for 30 min.

2.2. Preparation and purification of SWCNTs

The schematic diagram of the apparatus is given in Fig. 1.

The catalyst was placed into the quartz tube. The furnace was first heated to the desired synthesis temperature at the speed of 10 K/min in Ar atmosphere, and then a mixture of CH_4 (45 ml/min) and Ar (150 ml/min) was introduced into

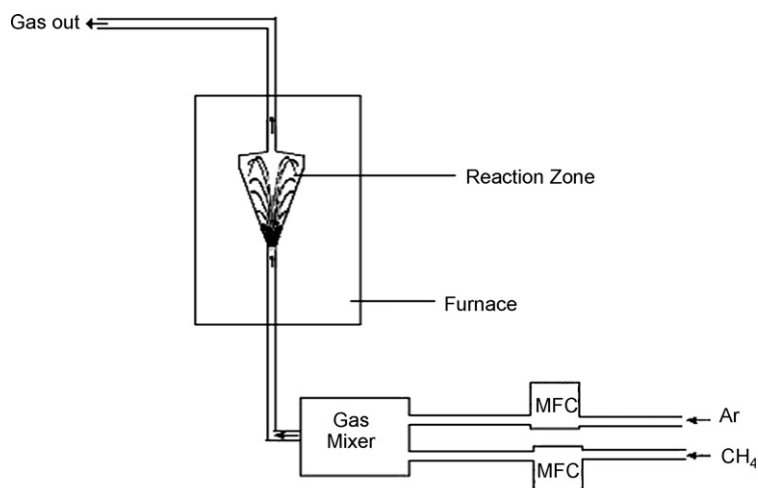


Fig. 1. Schematic diagram of experimental apparatus.

the reactor maintained at the same temperature for the production of SWCNTs. After 30 min reaction, the reactor was cooled to room temperature in Ar atmosphere.

The products were dipped into hydrochloric acid, which can remove the MgO and the most of catalyst. And then products were rinsed with deionized water until the pH of the filtrate became neutral. The samples were then dried at 473 K for 3 h. Purified SWCNTs were obtained.

2.3. Sample characterization

The Raman spectra of the SWCNTs samples were recorded by a microprobe Raman system (RENISHAW H13325 spectrophotometer) with the excitation line at 514.5 nm from an Ar ion laser and an RFS100/S FT-IR spectrophotometer with Nd:YAG laser excited at 1064 nm, respectively. TEM characterization was carried out using H-600 (TEM made by the HITACHI corporation).

3. Results and discussion

Fig. 2 shows the TEM images of SWCNTs samples synthesized at different synthesis temperatures. Fig. 2a is the TEM image of SWCNTs sample synthesized at low temperature 940 K. As shown in Fig. 2a, SWCNTs are observed in the sample, but the SWCNTs are coated by a large amount of amorphous graphite and nano-clusters. Our experimental results show that not only SWCNTs but also multi-walled carbon nanotubes (MWCNTs) were not obtained in the samples synthesized below 940 K. It is difficult to synthesize SWCNTs directly on conventional semiconductor devices, because the high temperature may be destructive to the conventional semiconductor devices. Therefore, the synthesis of SWCNTs at relatively low temperature 940 K proposes the direct growth of SWCNTs on conventional semiconductor devices. Fig. 2b shows the TEM image of SWCNTs sample synthesized at low temperature 973 K. In Fig. 2b, the bundles of SWCNTs are coated by an amount of amorphous graphite and nano-clusters. Fig. 2c–e are the TEM images of SWCNTs samples synthesized at 1073, 1123 and 1173 K, respectively. As can be seen from Fig. 2c–e, the bundles of SWCNTs are attached by less amorphous carbon in comparison with Fig. 2a and b, and the amount of amorphous carbon is smallest in the samples synthesized at 1123 K. Fig. 2f is the TEM image of SWCNTs sample synthesized at 1223 K. The bundles of SWCNTs are coated by a large amount of amorphous graphite and nano-clusters in Fig. 2f. From Fig. 2, we can see that the optimum temperature of synthesizing SWCNTs over Mo-Co-MgO bimetallic catalyst may be at 1123 K.

Raman spectroscopy is a simple and powerful technique to identify and study SWCNTs products. The positions and relative intensities of the Raman peaks can give much information about the structure and diameter or size of SWCNTs. There are several Raman peaks in the low-frequency region, which is attributed to the A_{1g} radial breathing mode (RBM), in which all of the atoms in the SWCNTs are displaced inward or outward by an equal amount. The RBM is strongly dependent on the diameter of SWCNTs. Mode frequency ω_{RBM} has been shown theoretically to exhibit a simple inverse diameter relationship [34]:

$$\omega_{\text{RBM}} = \frac{248}{d_t} \quad (1)$$

where d_t is the diameter of SWCNTs in nm; ω_{RBM} is the RBM frequency in cm^{-1} .

The RBM peaks of the SWCNTs samples synthesized at different synthesis temperatures excited at 514.5 and 1064 nm are displayed in Fig. 3a and b, respectively. It is well known that the Raman spectrum of SWCNTs excited at 514.5 nm may be from most semiconducting SWCNTs in the samples [35]. In Fig. 3a, the RBM peaks are observed at 150, 166, 180, 201, 243, 261 cm^{-1} ; and according to the formula (1), the diameters of SWCNTs corresponding to the RBM peaks at 150, 166, 180, 201, 243, 261 cm^{-1} are 1.65, 1.49, 1.37, 1.23, 1.02, 0.95 nm, respectively. As shown in Fig. 3a, the positions of RBM peaks are almost unchanged; it indicates that the dependence of diameters of most semiconducting SWCNTs on the synthesis temperature is small.

Generally, the Raman spectrum of SWCNTs excited at 1064 nm may be from most metallic SWCNTs in the samples [35]. From Fig. 3b, we can see that the RBM peaks of SWCNTs sample synthesized at 940 and 973 K appear at about 235, 261, 276 and 285 cm^{-1} , corresponding to the metallic SWCNTs with $d_t = 1.05, 0.95, 0.89$ and 0.87 nm, respectively. With the increase of synthesis temperature, it is obvious in Fig. 3b that two new RBM peaks of SWCNTs samples synthesized in the temperature range of 1073–1223 K appear at about 166 and 327 cm^{-1} , indicating metallic

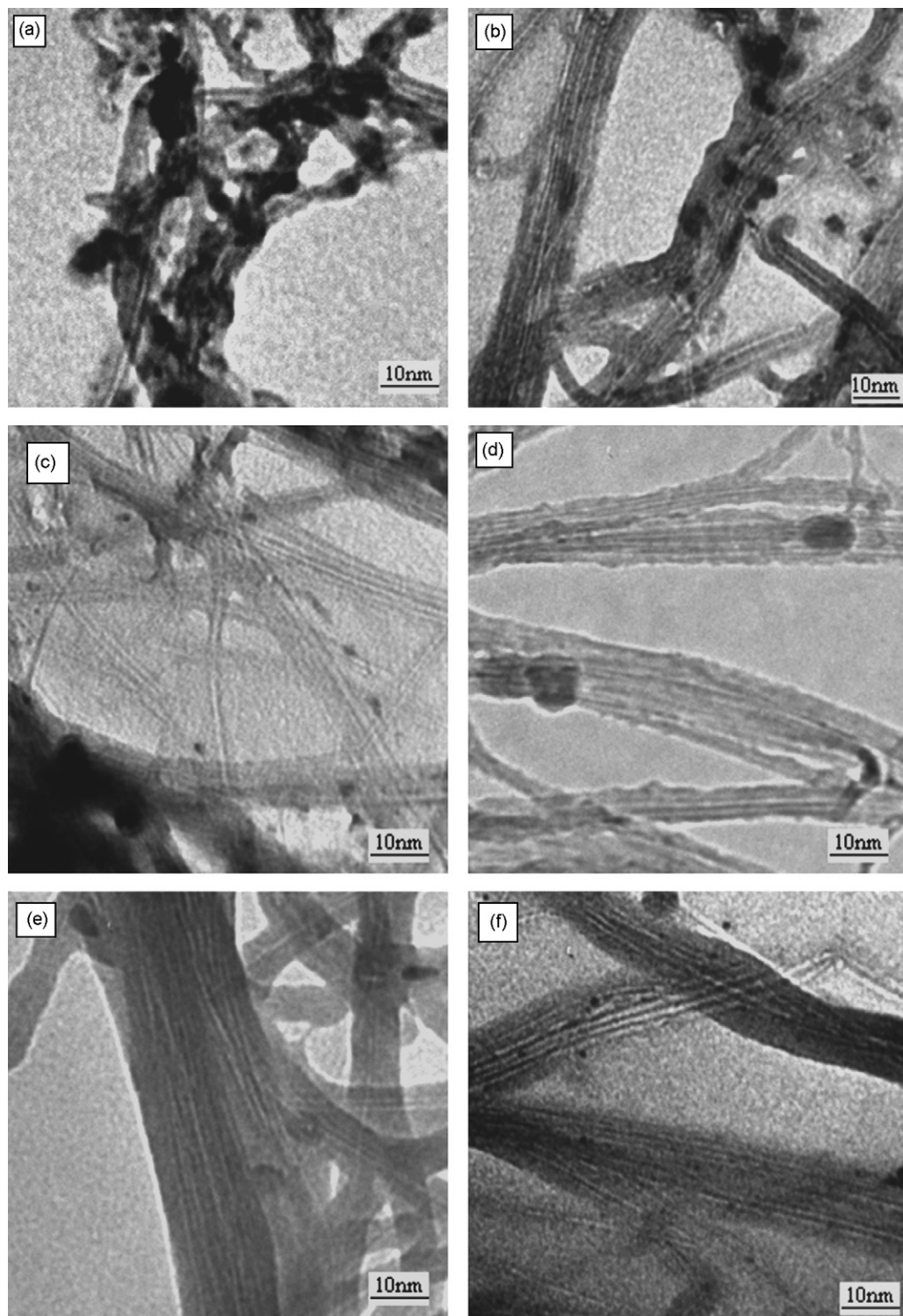


Fig. 2. TEM images of SWCNTs samples synthesized at different synthesis temperatures: (a) 940 K, (b) 973 K, (c) 1073 K, (d) 1123 K, (e) 1173 K and (f) 1223 K.

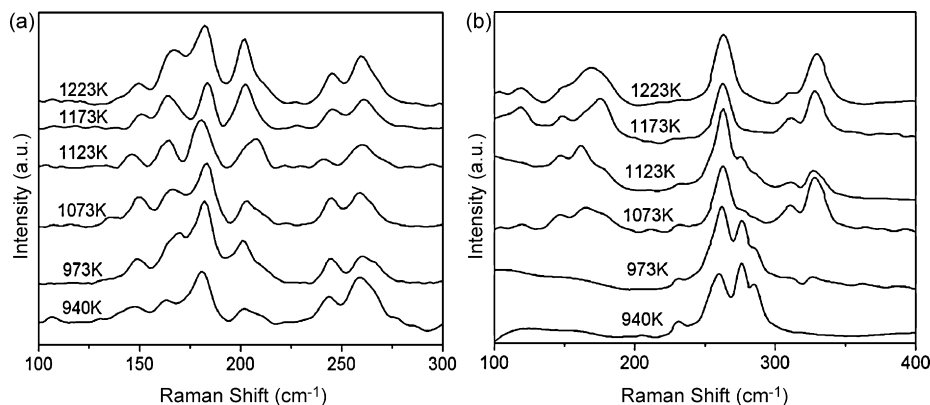


Fig. 3. The RBM peaks of the SWCNTs samples synthesized at different synthesis temperatures excited at 514.5 nm (a) and 1064 nm (b).

SWCNTs with $d_t = 1.5$ and 0.76 nm were obtained in the SWCNTs sample synthesized in the temperature range of 1073–1223 K.

The peaks at 1250–1350 cm^{-1} (D-band) are activated by the disordered graphite, fibers and nano-clusters in graphite and related to the level of disorder carbon and defect concentration in the SWCNTs. The weak D-band demonstrates that the synthesized samples contain very small amount of amorphous carbon materials [36]. Therefore, the intensity ratio of D-band to G-band is sensitive to the amorphous carbon and can reflect percentage composition of SWCNTs [37]. And the low intensity ratio of the D-band relative to the G-band indicates a small amount of amorphous carbon in the sample and a lower defect concentration in the SWCNTs.

The D-bands and G-bands of the SWCNTs samples synthesized at different synthesis temperatures excited at 514.5 and 1064 nm are presented in Fig. 4a and b, respectively. It is obvious in Fig. 4 that Fig. 4a is similar to Fig. 4b, differences being observed only for the position of D-bands. Both Fig. 4a and Fig. 4b show that, the intensity ratio I_D/I_G is larger at the low temperature 940 K. It indicates that an amount of amorphous graphite was generated and the SWCNTs with higher defect concentration were obtained in the SWCNTs sample produced at 940 K, which agrees well with the TEM image (Fig. 2a). The intensity ratio I_D/I_G is strongly decreased as the synthesis temperature is increased below 1123 K, revealing that the content of amorphous carbon is strongly decreased as the synthesis temperature is increased below 1123 K. The intensity ratio I_D/I_G is small in the temperature range of 1073–1173 K, indicating that a small amount of amorphous carbon was obtained and the defect level in SWCNTs was low in the samples synthesized in the temperature range of 1073–1173 K. The intensity ratio I_D/I_G is smallest at 1123 K, indicating the optimum temperature of synthesizing SWCNTs over Mo-Co-MgO bimetallic catalyst may be at about 1123 K. It is in agreement with the TEM images (Fig. 2). However, when the synthesis temperature is at 1223 K, The

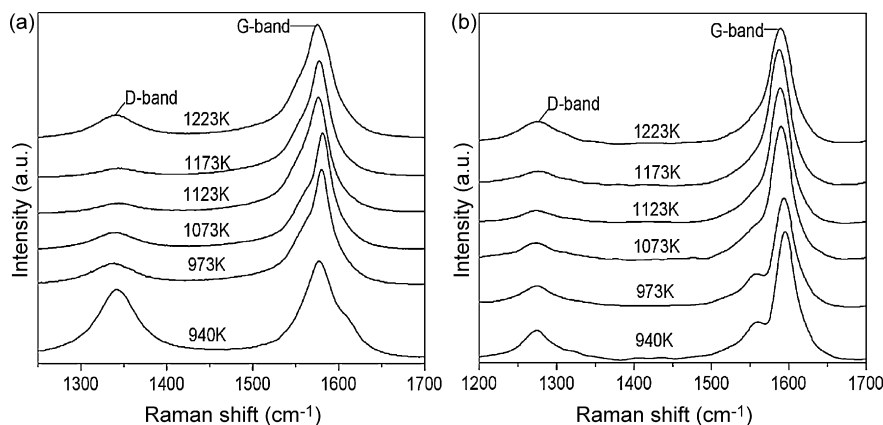


Fig. 4. The D-bands and G-bands of the SWCNTs samples synthesized at different synthesis temperatures excited at 514.5 nm (a) and 1064 nm (b).

intensity ratio I_D/I_G is very large; it indicates that very large amount of amorphous carbon were obtained in the SWCNTs samples produced at 1223 K. It agrees well with the TEM image (Fig. 2f).

It has been known that the optimum synthesis temperature is determined by two competing factors. On the one hand, the higher the temperature the more catalytic nanoparticles are molten and able to nucleate SWCNTs and to maintain their growth. On the other hand, the driving force for the amorphous carbon-SWCNTs transformation increases with reduction of temperature [38]. A concentration of carbon atoms adsorbed on metal particles during decomposition of carbon source is one of the important factors in CNTs growth [39]. Moreover, the diffusion rate of carbon atoms through the surface of the metal particles is significantly related to the quality of synthesized SWCNTs and this controls the structure and type of SWCNTs grown over the catalysts [39–42]. At low temperature, the ability of catalyst particles is smaller than that at high temperature, and only those catalyst particles that were smaller than a critical size can nucleate CNTs [43,44]. Therefore, at low temperature, only a part of catalytic nanoparticles are molten and less active catalytic sites were exposed; formation rate of SWCNTs was small due to insufficient active catalytic sites and the decomposition rate of methane was faster than the formation rate of SWCNTs. A relatively high decomposition rate of methane was found to generate additional carbon deposition such as amorphous carbon [45]. Hence an amount of amorphous graphite is observed in the SWCNTs sample produced at 940 K. With the increase of synthesis temperature, more active catalytic sites were exposed and the rate of cobalt reduction increases and more cobalt clusters nucleate to reach the optimal size for SWNT growth [46]; hence, with the increase of temperature, the formation rate of SWCNTs approaches gradually the decomposition rate of methane. The decomposition rate of methane nearly equalizes the formation rate of SWCNTs at 1123 K. Therefore, the optimum temperature of synthesizing SWCNTs over Mo-Co-MgO bimetallic catalyst may be about 1123 K. At about 1173 K, most catalytic nanoparticles were molten and active catalytic sites were nearly all exposed. Therefore, when the synthesis temperature is above 1173 K, the amount of the active catalytic sites were nearly unchanged with the increase of the synthesis temperature; But the decomposition rate of methane was strongly increased and the driving force for the amorphous carbon-SWCNTs transformation decreases with increase of synthesis temperature [38]. Therefore, a large amount of amorphous graphite was obtained when the synthesis temperature was above 1173 K.

The carbon yield rate of SWCNTs samples has a close relationship with the synthesis temperature [45]. To quantify the yield, we conducted the weight gain measurement. The carbon yield rate is defined as the weight gain ratio of the carbon deposition to the starting catalyst materials. Fig. 5 shows the carbon yield rates at different synthesis temperatures. Fig. 5 shows that the carbon yield rate at low temperature is low and the carbon yield rate is strongly increased with the increase of synthesis temperature below 1073 K; the increase of carbon yield rate was slowed and the carbon yield rate is high above 1073 K. It is most likely that, at the low temperature, the low decomposition rate of methane and the insufficient of active catalytic sites led to the low carbon yield rate. When the synthesis temperature was above 1073 K, the decomposition rate of methane was high and most active catalytic sites were exposed, leading to the high carbon yield rate. According to above analysis of Raman spectra and TEM images, the content of SWCNTs is also increased with the increase of temperature below 1123 K. Therefore the amount of SWCNTs increases with the

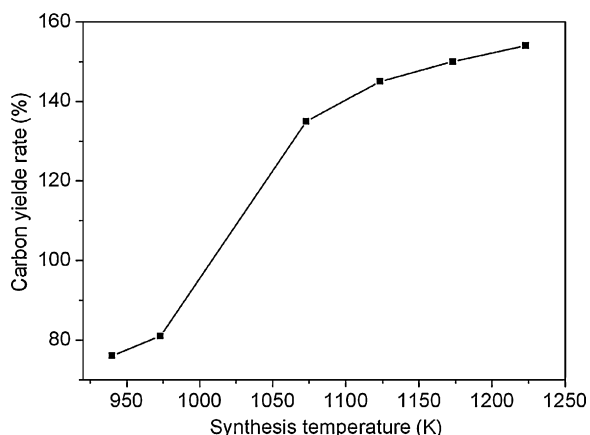


Fig. 5. Carbon yield rates at different synthesis temperatures.

increase of temperature below 1123 K. Although the carbon yield rate is slowly increase above 1123 K, the content of SWCNTs is decreased with the increase of temperature; therefore, it is not effective to increase the amount of SWCNTs through increasing synthesis temperature above 1123 K.

4. Conclusion

It has been confirmed that Mo-Co-MgO bimetallic catalyst is effective to synthesize SWCNTs. By using Mo-Co-MgO bimetallic catalyst, generation of SWCNTs even at 940 K was demonstrated. The optimum temperature of synthesizing SWCNTs over Mo-Co-MgO bimetallic catalyst may be about 1123 K. At 1123 K, the diameters of SWCNTs are in the range of 0.75–1.65 nm. The content of SWCNTs is increased with the increase of temperature below 1123 K and the carbon yield rate is also increased with the increase of synthesis temperature. Therefore, the amount of SWCNTs increases with the increase of temperature below 1123 K. However, above 1123 K, the content of SWCNTs is decreased with the increase of temperature; therefore, it is not effective to increase the amount of SWCNTs through increasing synthesis temperature above 1123 K.

Acknowledgments

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