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Production of Carbon Nanotubes over Pre-reduced $LaCoO_3$ Using Fluidized-bed Reactor

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Abstract: Carbon nanotubes were synthesized on a large scale by the catalytic decomposition of hydrocarbons over pre-reduced $LaCoO_3$ using a fluidized-bed reactor. Reaction parameters such as reduction temperature, reduction time and reaction temperature were discussed.

Keywords: Carbon nanotubes, fluidized-bed reactor, production, $LaCoO_3$.

A great amount of research on carbon nanotubes (CNTs) has been carried out since its observation in 1991[1]. It has been predicted that CNTs can be novel materials of semiconductor, electric-field-induced electron emitters, quantum wire, catalysts *etc*[2–5]. Nowadays, CNTs can be synthesized by arc discharge[6] laser ablation[7], and pyrolysis of hydrocarbon gases[8]. In order to make CNTs of practical importance, the criteria for assessing any synthesis technique must include the feasibility and potentiality for scale-up production at low cost. In this letter, we describe a novel method for producing bulk quantities of CNTs through the catalytic decomposition of acetylene using a fluidized-bed reactor over the pre-reduced $LaCoO_3$ catalyst. This method can be operated at atmospheric pressure and moderate temperature. The selectivity of CNTs is very high.

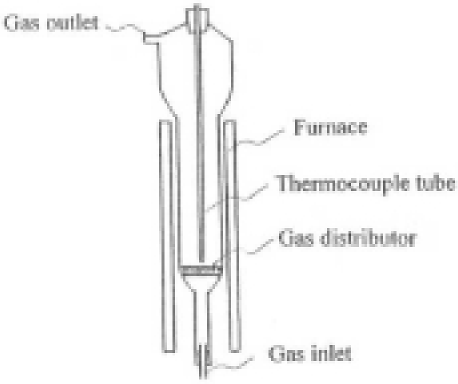
The fluidized-bed quartz reactor is illustrated schematically in **Figure 1**.

The catalyst precursor ($LaCoO_3$) was prepared by dissolving a stoichiometric mixture of cobalt nitrate and lanthanum nitrate in water and then mixing them with citric acid. When the solution was evaporated, it was vigorously stirred at 80℃, when it got dense, the evaporation temperature was increased to 100℃, and then the slurry burned and turned into a black power. The black power obtained was calcined at 600℃ for 1.0 h, subsequently at 800℃ for 3.0 h. Finally, a black sample of catalyst precursor was obtained. The X-ray diffraction (XRD) pattern of the catalyst precursor matched with the standard X-ray diffraction pattern of cubic $LaCoO_3$.

100 mg of the $LaCoO_3$ catalyst precursor were packed into the reactor, followed by heating the sample in a flow of purified N_2 from room temperature to desired reduction temperature. Then we introduce the purified H_2 at the same temperature for 1.0 h to reduce $LaCoO_3$. Feedgas C_2H_2 (C_2H_2 / N_2 =1 / 9, V / V, flow rate = 700 ml / min) was introduced through the reactor at the desired reaction temperature for 30 min. After the

scheduled time, the reactor was cooled to room temperature by the passage of nitrogen gas. The sample of a black powder was then collected.

Figure 1 Schematic diagram of fluidized-bed reactor used for carbon nanotube synthesis



The scanning electron microscopy (SEM) (KYKY-AMRAY-1000B) and a transmission electron microscopy (TEM) (JEOL JEM-100CX) were employed to characterize the morphologies of CNTs. The reduced catalysts were analyzed by X-ray diffraction (XRD) (D/max-rA).

Figure 2 shows the SEM images of as-synthesized CNTs samples. It clearly illustrates the purity and homogeneity of the tubes, where graphitic particles and nano-capsules are completely absent.

Figure 3 is the TEM image of the CNTs. It shows that the tubes are thin, having an inner diameter of 5-10 nm and an external diameter of 10-40 nm.

The influence of reduction temperature on the CNTs formation was evaluated in the range from 200 to 800℃. the yield of CNTs varied with reduction temperatures, being a maximum at 400℃(**Figure 4**). However, the high yield of CNTs does not mean the highly-qualified CNTs. For example, at below 650℃, the diameter of tubes were found not even; and at 800℃, about 5% helical CNTs was found. TEM images shows that with the increasing of reduction temperature, the diameter of CNTs increased. Comparing with the results of XRD patterns of reduced catalysts, we have found that the average diameter of CNTS is approximately equal to the size of cobalt metal particles.

In our synthetic process, the reduction time was maintained at 60 min. Any change of this reduction time resulted in lower yields of the nanotubes, For example, either shorten or lengthen the reduction time to 30 min or 120 min, the yield was decreased. Hence, we propose that the optimum reduction time for the maximum production of the tubes is 60 min in the current experimental arrangements. This may be explained that with increasing of the reduction time, cobalt metal particles accumulated into larger size which is not in favor of the formation of CNTs. The XRD patterns of reduced catalyst at 675℃ have revealed that $LaCoO_3$ was reduced into La_2O_3 and Co. On the other hand, if the reduction time is too short, the content of cobalt metal particles on the surface was low, resulting in a lower yield of CNTs.

Figure 2 SEM image of carbon nanotubes

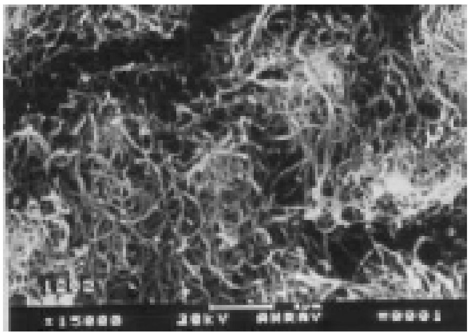


Figure 3 TEM image of carbon nanotubes

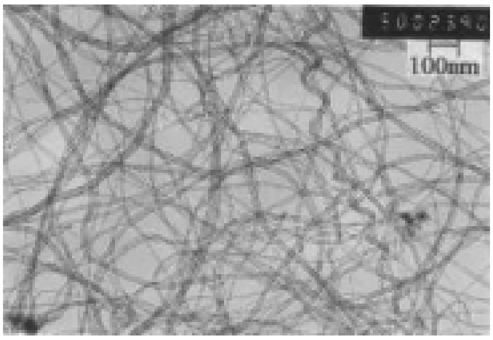
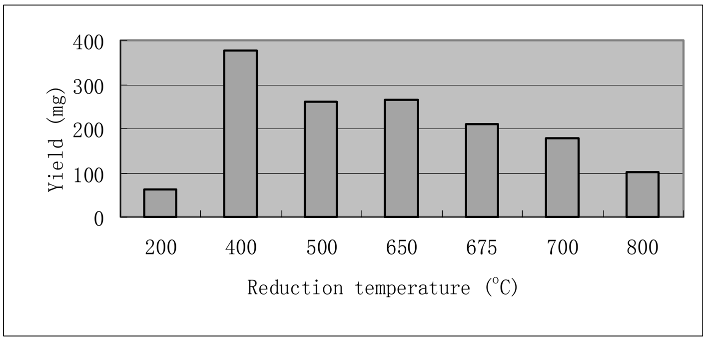
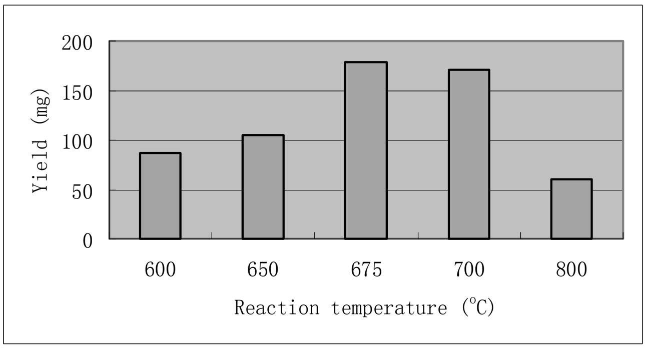


Figure 4 Effect of reduction temperature on the yield of carbon nanotubes



The influence of reaction temperature on the CNTs formation was evaluated in the range from 600 to 800℃, the yield of CNTs varied with reaction temperature, showing a maximum at 675℃ (**Figure 5**).The TEM studies have revealed that at 500℃ no nanotubes were formed at all. So the reaction temperature is a key factor for the formation of

Figure 5 Effect of reaction temperature on the yield of carbon nanotubes



CNTs.

In conclusion, fluidized-bed reactor can be used to synthesize multi-walled carbon nanotubes on a large scale, which could be scaled up easily.

Acknowledgments

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