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Investigation of low and mild temperature for synthesis of high quality carbon nanotubes by chemical vapor deposition

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ABSTRACT

The low reaction temperature for synthesis of carbon nanotubes (CNTs) with high quality was investigated by Ni/MgO catalytic decomposition of CH_4 using a home-designed micro-fluidized bed reactor. It was found that the low and mild temperature at 500 ~ 550 °C would bring the dynamic equilibrium between the rate of CH_4 decomposition and the rate of carbon diffusion over Ni catalyst for continuous precipitation of CNTs in the micro-fluidized bed condition. The CNTs synthesized at the corresponding conditions exhibited high quality with relatively small and mean outer diameter, less defect, and high purity.

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention for potential application, such as electronics, field emission, gas and energy storage, biosensors, functional polymers, due to unique physical, chemical, mechanical, and electrical properties [1–5]. Since the first discovery of CNTs in 1991, many techniques for preparation of CNTs have been explored, including electric arc discharge, laser vaporization, and chemical vapor deposition (CVD) [6–8]. Among them, CVD techniques possess the greatest promise for volume production, controllable process, and easy implementation. Furthermore, fluidized bed CVD (FBCVD) allows continuous operation, and thus is regarded as one of the most promising techniques for large-scale and low cost synthesis of CNTs [9,10]. However, a major issue that remains unresolved for FBCVD is the synthesis of CNTs with high quality (mean outer diameter, less defect, and high purity). A large number of parameters such as temperature, carbon source, pressure, catalyst, and reactor size, may influence the quality of CNTs. Of these, temperature has been widely regarded and studied as a key variable in the synthesis process, because higher or lower temperatures will result in lower yields and an increase in non-CNTs product, amorphous carbon, encapsulated particles, etc., [11].

Compared with the common carbon sources of acetylene, ethylene, ethanol, etc., methane (CH_4) has higher decomposition temperature for synthesis of CNTs due to the strong C—H bond of the CH_4 molecular. Generally, higher temperature, above 600 °C, is studied for CNTs growth by decomposition of CH_4, according to most previous reports [9,12–15]. However, few published reports show that CNTs can be obtained at 550 °C by catalytic decomposition of CH_4, and carbon nanofibers (CNFs) may generate when the temperature further decrease to 500 °C [16–18]. In addition, the preparation of CNTs in these reports is mostly carried out in fixed bed reactors. So it is significant to investigate, systematically, the growth of CNTs by cracking CH_4 below and above 600 °C utilizing a fluidized bed reactor.

In this work, reaction temperature ranging from 450 to 700 °C were employed in an attempt to investigate the mild temperature for synthesis of high quality CNTs by Ni/MgO catalytic decomposition of CH_4 using a home-designed micro-fluidized bed reactor. It is noteworthy that we call the fluidized bed reactor with inner diameter less than 20 mm a micro-fluidized bed reactor to make a difference with industrial fluidized bed reactor. The micro-fluidized bed of this size is helpful to provide a homogenous gas-solid mixing along the catalyst bed and the isothermal reaction conditions due to its better heat and mass transfer coefficients and fluidized state controllable than reactors of bigger size, as a consequence of producing an intrinsic reaction atmosphere for CNTs growth [10,19]. Several reports have shown the application of micro-fluidized bed in investigation the thermal decomposition reaction of biomass

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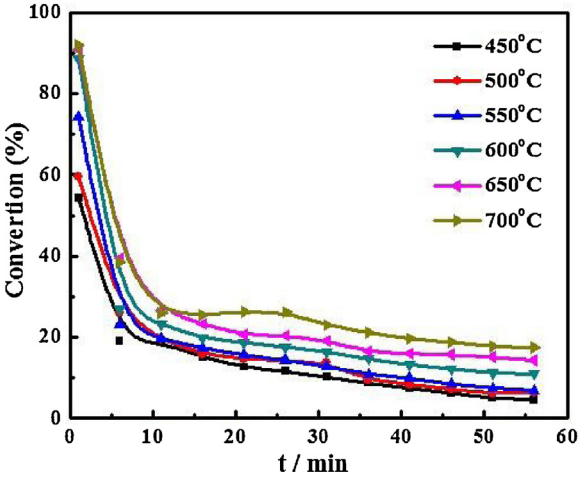

Fig. 1. CH_4 conversion plotted as a function of the reaction time under different growth temperature.

[19,20]. However, there are few articles that reported the investigation of CNTs growth by using a micro-fluidized bed. In this study, the advantages of the micro-fluidized bed was fully adopted to synthesize CNTs. The effect mechanism of temperature was discussed, and the quality of CNTs was evaluated.

2. Experimental

The Ni/MgO catalyst (Ni/Mg = 1/9, mole ratio) with a size of 50 ~ 125 μm was fabricated by a sol–gel method [21]. A vertical quartz tube with the inner diameter of 18 mm, the height of 300 mm and with a gas distributor at the middle of the tube was used as the home-designed micro-fluidized bed. The catalyst of 1.0 g was loaded to the quartz tube. Before reaction, the reactor was firstly heat to 500 °C in N_2 atmosphere. A total gas flow rate of 120 sccm was applied to achieve fluidization in the micro-fluidized bed [22]. Then, the catalyst was reduced in a mixture gas of N_2/H_2 at a flow rate 80/40 sccm for 30 min. When the reactor was heated up to the reaction temperature in a range of 450 ~ 700 °C, CH_4 and N_2 were then introduced into the reactor at a total flow rate of 120 sccm with

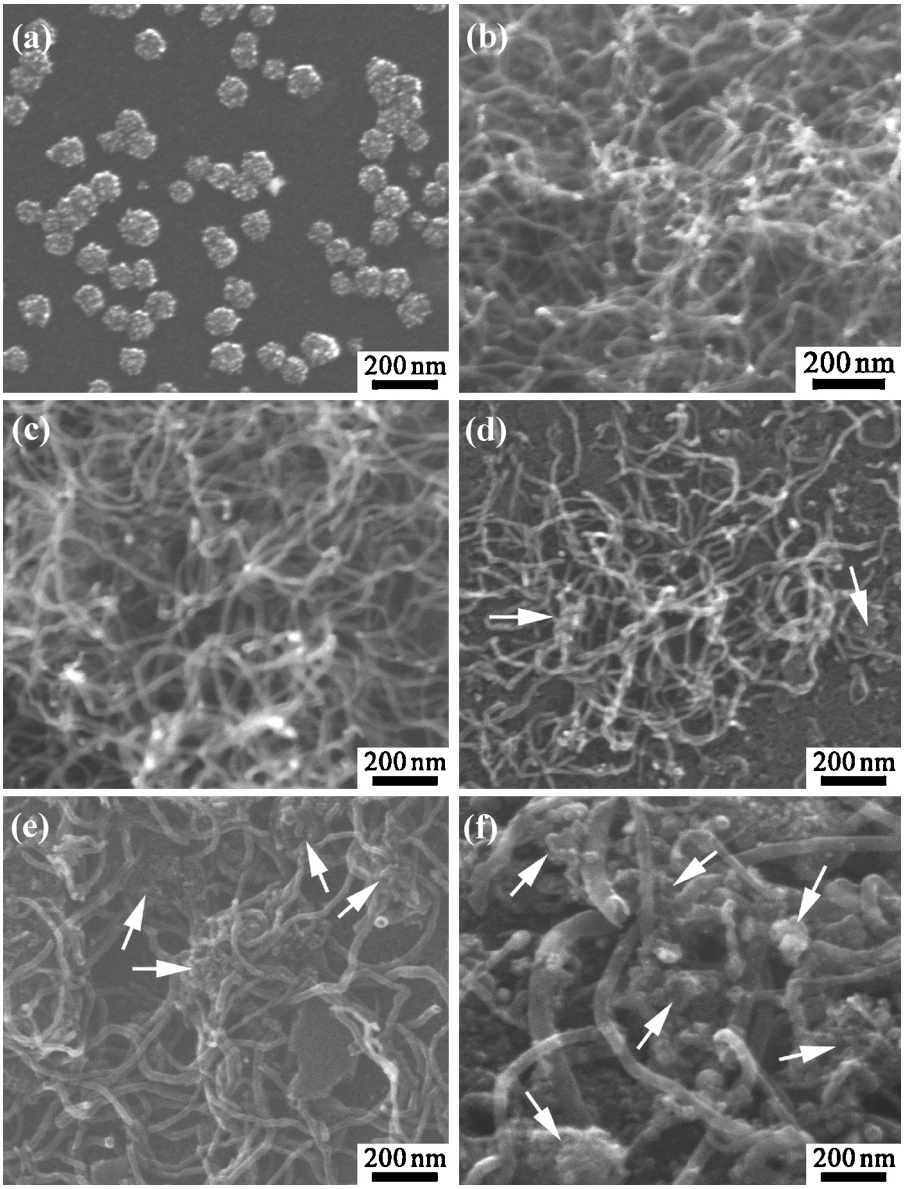

Fig. 2. SEM images of the CNTs synthesized at different temperature: (a) 450 °C, (b) 500 °C, (c) 550 °C, (d) 600 °C, (e) 650 °C, and (f) 700 °C.