Chemical Engineering Science 134 (2015) 496–503

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Effect of operating variables on synthesis of multi-walled carbon nanotubes in fluidized beds

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HIGHLIGHTS

- MWCNTs were synthesized with high selectivity using MWCNT as the bed material.
- Apparent activation energy is 102 kJ/mol.
- Carbon yield and conversion have a critical point at the space velocity of 136 h^{-1}.
- Carbon yield increased with increased partial pressure.
- Empirical correlation is proposed to predict the carbon yield.

ARTICLE INFO

Article history:
Received 30 November 2014
Received in revised form
7 May 2015
Accepted 10 May 2015
Available online 10 June 2015

Keywords:
Carbon nanotube
Fluidized bed
Operating variables
Carbon yield
Empirical correlation

ABSTRACT

The effect of operating variables (reaction temperature, space velocity, and partial pressure of the carbon source) on carbon yield was determined for synthesizing MWCNTs by catalytic chemical vapor deposition using ethylene as the carbon source in a batch type fluidized bed reactor. Stable fluidization was maintained using the MWCNT agglomerate as the initial bed material and MWCNTs with high selectivity were synthesized. The optimal reaction temperature for the maximum carbon yield was 983 K and the apparent activation energy was 102 kJ/mol. The maximum carbon yield occurred at the space velocity of 136 h^{-1}. The carbon yield increased with increasing partial pressure of ethylene. However, the synthesis reaction of MWCNTs did not proceed at partial pressures above 0.63. A correlation is proposed to predict the yield of MWCNTs.

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1. Introduction

Carbon nanotubes (CNTs) can be synthesized using a variety of techniques including electric arc discharge, laser ablation, and chemical vapor deposition (CVD) (Guo et al., 1995; Journet et al., 1997; Laplaze et al., 1998; Li et al., 2004; Vander Wal et al., 2000). Arc discharge and laser ablation synthesize CNTs at temperatures over 3000 °C, producing materials with great crystallinity. However, a large amount of energy is needed to maintain such a high temperature. Additionally, these techniques are performed under vacuum at very low pressure; therefore, expanding to large scale production is not simple. The CVD method, on the other hand, is considered to be more amenable to mass production (Andrews et al., 1999; Colomer et al., 2000; Dasgupta et al., 2008, 2007; Kumar and Ando, 2003). Advantages of CVD include a relatively low reaction temperature, low production cost, and flexible catalyst yield or CNT structure depending on the reaction conditions. Catalytic chemical vapor deposition (CCVD) with fluidized beds uses powder type catalyst particles with a large reaction specific surface area, which makes the contact area with the reacting gas much larger than that of CCVD using a regular catalytic substrate (Mauro et al., 2003). CCVD using a fluidized bed reactor also exhibits high heat and mass transfer rates. Consequently, it is a useful process for the synthesis of uniform quality MWCNT and makes continuous processing possible, which is desirable for mass production (Corrias et al., 2003).

For CVD methods using a fluidized bed reactor, factors that affect carbon conversion and CNT structure include the specific catalyst, catalyst concentration, type of carbon source, carbon source concentration, reaction temperature, and superficial gas flow rate.

Reaction temperature plays an important role in determining the CNT structure and yield. Under a given set of conditions, carbon yield increases as the reaction temperature is increased but decreases once the temperature exceeds the threshold. In systems using a different carbon source, carbon yield with respect to

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http://dx.doi.org/10.1016/j.ces.2015.05.051
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reaction temperature shows the same trend, but optimal reaction temperatures vary (Morancais et al., 2007; Philippe et al., 2009; Son et al., 2008). In addition, CNT diameter and crystallinity vary depending on the reaction temperature (Muataz et al., 2006; Andrews et al., 2002; Kim et al., 2005; Nourbakhsh et al., 2007; Xiong et al., 2005; Yao et al., 2004). These results suggest that each system requires reaction temperature optimization.

In general, the partial pressure of the reactant gas affects the reaction rate. For the synthesis of CNTs using the CCVD method, research on the effects of partial pressure from the carbon source on the carbon yield has progressed. Many reports demonstrate that carbon yield can be increased by increasing the partial pressure of the carbon source (Gommes et al., 2004; Pirard et al., 2007; Douven et al., 2011; Dasgupta et al., 2014). In addition, there is evidence that at a certain partial pressure from the carbon source, carbon yield reaches a maximum depending on the experimental conditions (Morancais et al., 2007). This result is achieved by increasing the synthesis time for supplying a specific total amount of carbon source. Since the activity of the catalyst is reduced and the effects of the operating variables on the growth of CNTs during synthesis in a batch type fluidized bed reactor are complex, predicting the CNT yield is difficult.

During catalytic reactions, space velocity is a factor that represents the activity of the catalyst. It is also an important factor when scaling up the system. In order to design and scale up the fluidized bed system for mass production of CNTs using the CCVD method, it is essential to investigate the influence of space velocity on carbon yield. Wei and coworkers recently reported on the effects of space velocity on the synthesis of MWCNTs in the fluidized bed reactor (Wei et al., 2008; Zhang et al., 2010). However, it is important to obtain more experimental data since there are few results available.

Studies on the impact of various variables have been undertaken in this manner; however, CNTs were synthesized in most of the studies by configuring the initial bed using only the catalyst. In general, the flow characteristics of CNTs and the catalyst at a constant gas velocity differ based on the density difference between the CNTs and catalyst. In a fluidized bed system, if the initial bed is composed of only the catalyst, the flow characteristics change according to the growth of CNTs.

In this study, MWCNTs were synthesized using a mixture of MWCNTs and catalyst as the initial bed material in a batch type fluidized bed reactor with near-continuous process conditions. In the present study, the effects of the operating variables such as reaction temperature, space velocity, and partial pressure of the carbon source on the synthesis of MWCNTs were determined. Based on the experimental results, an empirical correlation for predicting the carbon yield is proposed.

2. Experimental

Fig. 1a shows a schematic diagram of the batch type fluidized bed reactor used for MWCNT synthesis. The reactor was made of stainless steel (SUS 304), with a height of 1.1 m and a diameter of 0.05 m. Heat was supplied to the reactor by using upper (furnace 1), middle (furnace 2), and lower (furnace 3) heat sources to preheat the injection gases. A K-type thermocouple was installed to measure the temperatures 0.05 m (T4), 0.10 m (T3), 0.15 m (T2), and 0.25 m (T1) from the gas distributor and 0.02 m (T5) before the distributor. Furnace controller 1 was connected to T1 to control the heaters, furnace controller 2 was connected to T3, and furnace controller 3 was attached to T5 to maintain the inside temperature of the reactor at the set temperature. The amount of gas injected into the reactor was controlled with a mass flow controller (MFC). A filter was installed at the reactor exit to collect entrained particles, and a gas sampler was installed to analyze gas composition. An accumulated flow meter was installed to measure the effluent gas flow rate at the reactor exit, as shown in Fig. 1a. As shown in Fig. 1b, the cooling distributor was used to prevent the reacting gas from undergoing thermal decomposition until its injection into the reactor after passing through the gas distributor.

A catalyst based on Co–Fe was used to synthesize MWCNTs in the batch type fluidized bed reactor. The metal loading and metal atomic ratios (Co/Fe) were 70 wt% and unity. The mean active metal size in the catalyst analyzed by X-ray diffraction (XRD) was

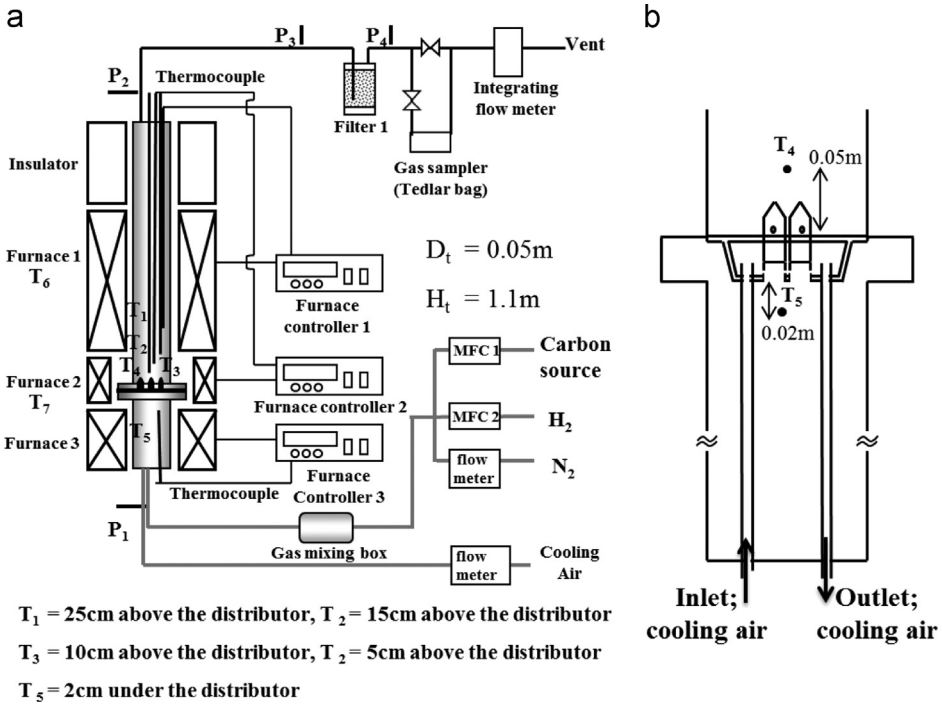

Fig. 1. Schematic diagram of experimental set-up; (a) fluidized bed system, (b) distributor.

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