Contents lists available at ScienceDirect

Chemical Engineering Research and Design

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

Methane decomposition for carbon nanotube production: Optimization of the reaction parameters using response surface methodology

Ghazaleh Allaedini[a,*], *Payam Aminayi*[b], *Siti Masrinda Tasirin*[a,**]

[a] *Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia*

[b] *Department of Chemical and Paper Engineering, Western Michigan University, Kalamazoo, MI 49008, USA*

ARTICLE INFO

Article history:
Received 27 September 2015
Received in revised form 29 May 2016
Accepted 10 June 2016
Available online 18 June 2016

Keywords:
Carbon nanotubes
Chemical vapor deposition (CVD)
Yield and diameter optimization
Response surface methodology (RSM)

ABSTRACT

In this study, the chemical vapor deposition (CVD) process in a fluidized bed reactor was employed for the decomposition of methane over a Mo/Ce catalyst. The effects of temperature, flow rate, and catalyst loading parameters on the CNT production have been investigated and optimized using response surface methodology (RSM). The formation of the Mo/Ce catalyst was confirmed using Fourier transform infrared (FT-IR) spectroscopy. Field emission scanning electron microscopy (FESEM) was employed to visualize the surface morphology of the obtained catalyst. The XRD patterns suggested a high crystallinity of the prepared catalyst. Small average particle diameter (253 nm) and high surface area (54.4 m^2/g) were reported using a particle size analyzer and Brunauer–Emmett–Teller and Barrett–Joyner–Halenda (BET & BJH) analysis, respectively. The SEM micrographs of the nanocarbons deposited via methane decomposition indicated that uniform carbon nanotubes were grown on the surface of the catalyst. The transmission electron microscopy (TEM) images showed that the carbon nanotubes were multi-walled with an average diameter of ~18 nm. Raman spectrum was used to evaluate the graphitization degree of the obtained CNTs. The thermal analysis of the nanotubes showed the high oxidation stability of the multi-walled carbon nanotubes.

1. Introduction

Carbon nanotubes have gained much attention because of their excellent mechanical properties and high electrical and thermal conductivities (Baughman et al., 2002). Given these properties, carbon nanotubes have become useful in a number of industrial applications such as electrode material in batteries and hydrogen storage medium for fuel cells (Chen et al., 2012; Reyhani et al., 2011). There are numerous methods to produce carbon nanotubes such as arc discharge, laser ablation, electrolysis, horizontal furnace, fluidized bed reactor, and chemical vapor deposition (Thostenson et al., 2001). However, among these methods, chemical vapor deposition is the most common (Allaedini et al., 2015a; Cantoro et al., 2006). This is because CNTs can grow at a relatively low temperature, and their size, growth rate, diameter, length, and crystallinity can be manipulated by varying the reaction parameters as well as the type and morphology of the catalysts employed (Esconjauregui et al., 2009). In addition to these advantages, the nanotubes can be used directly without further purification unless removal of the catalyst particle is necessary. In addition, the CVD method allows for the growth of well-aligned nanotubes (Ren et al., 1998). Reports are available which explain that modifying the synthesis parameters of the catalytic chemical vapor deposition (CCVD) process leads to controlling the physical

* *Corresponding author*. Tel.: +60 3 89218428.
** *Corresponding author*. Tel.: +60 3 89216425.
E-mail addresses: jiny_ghazaleh@yahoo.com (G. Allaedini), masrinda@eng.ukm.my (S.M. Tasirin).
http://dx.doi.org/10.1016/j.cherd.2016.06.010

characteristics of the resulting CNTs (Bernardo and Abella, 2012).

Numerous reports exist on the application of mono-metallic catalysts. However, there are advantages for using bi-metallic catalysts for the CNT production. The most important advantage is that CNTs could be grown at significantly lower temperatures. This is due to the fact that the melting point of mixture of catalysts is lower than its individual counterparts, which enhances the catalytic activity (Allaedini et al., 2015b). Molybdenum has been reportedly used as promoters for catalyst in numerous studies (Sivakumar et al., 2010). When combined with catalysts, molybdenum has appeared to behave as a dispersive agent and increases the initial methane conversion. It is also reported that the use of molybdenum extends the activity of the catalyst (Sivakumar et al., 2010). The catalytic activity performance of cerium based bi-metallic nano particles with different weight percentage of molybdenum (8–20 wt% MoO_3) was also investigated. It was found that the activity of this bimetallic increases with increase in the Mo wt% loading (Rathod et al., 2010). Therefore, in this study bimetallic Mo/Ce catalyst has been employed as an effective catalyst for the production of CNTs.

A CVD reaction that takes place in a fluidized bed reactor provides numerous advantages in the production of CNTs. Fluidization process utilizes high space velocity, leading to an efficient solid-gas interaction. Consequently, a higher amount of mass and heat can be transferred using this approach. Therefore, high process yield, purity, homogeneity, and selectivity in the final product could be attained (See and Harris, 2008). Moreover, the fluidized bed process is advantageous in its remarkable flexibility in terms of the operating conditions and parameters (gas mixture and temperature), as they can be finely adjusted based on the requirement of the desired product. In addition, residence time as well as accessible space for CNT growth can also be controlled, which favors the selective mass production of CNTs with uniform properties (Hsieh et al., 2009).

A carbon precursor also plays an important role in the production of carbon nanotubes. By selection of an appropriate precursor with the required vapor pressure, both the catalyst's lifetime and the CNTs' growth rate can be increased. Subsequently, the quality and the yield of the obtained carbon nanotubes can be enhanced (Kumar and Ando, 2010). One of the most important factors for selecting a precursor is its molecular structure. It has been reported that linear hydrocarbons(Boulfelfel et al., 2015) such as ethylene, methane, and acetylene decompose and convert into linear dimers/trimers of carbon by heat, and, therefore, result in straight hollow CNTs. In contrast, cyclic hydrocarbons such as xylene, benzene, cyclohexane, and fullerene yield semi-curved CNTs (Morjan et al., 2004).

The availability, high H to C ratio (H/C = 4), and low cost has made methane an ideal raw material for the production of hydrogen from a hydrocarbon. Decomposition of methane is a simple reaction which yields hydrogen and carbon black:

$$CH_4 + 75.3\,kJ/mol \rightarrow C + H_2$$

In this reaction, the produced carbon can be utilized for the production of nanotubes (Allaedini et al., 2015b; Cho et al., 2004). Since the discovery of CNTs by Iijima (1991), many reports have been presented on the production of CNTs using CVD technology, the first study being reported by Kong et al. (1998). Consequently, more attempt were made for the production of CNT via methane decomposition even until recently (Ping et al., 2016). Moreover, numerous reports exist emphasizing the production of hydrogen from methane (Weizhong et al., 2004). However, studies which investigate the parameters that would contribute to the production of CNTs with high yield while preserving their suitable morphology, shape, and diameter are lacking from the literature. There are only a few reports available for the optimization of CNT production parameters using different catalyst systems. For example Chai et al. have employed a 3^k factorial design to optimized the CNT production parameters in the presence of Co–Mo/Al_2O_3 catalyst and the optimum conditions for the CNT production within the experimental ranges were identified in which the carbon yield is predicted to be 607% (Chai et al., 2011). In another study by Liu et al., the effects of reaction temperature, reaction time, and gas (methane/nitrogen) flow rate on the ratio of the intensity of the Raman D band to the intensity of the G band (I_D/I_G) as well as the obtained yield were investigated using a central composite design (Liu et al., 2012). In a similar study, Lee et al. optimized the CNTs production using alumina-based catalyst and the optimum parameters were identified (Lee et al., 2010).

In this paper, nanocarbons have been prepared using the CVD method through the methane decomposition in a fluidized bed reactor in the presence of a Mo/Ce catalyst. The effects of temperature, methane flow rate, and the amount of catalyst present in the reaction (catalyst loading) on the morphology of the obtained nanocarbons have also been investigated using response surface methodology (RSM). Although efforts have been made in the area of single-walled carbon nanotube process optimization (Liu et al., 2012), to our knowledge, this study is the first to investigate the effect of synthesis factors on the yield and diameter of multi-walled carbon nanotubes prepared via the direct decomposition of methane in order to develop a validated model of CNT growth.

2. Methodology

2.1. *Catalyst preparation*

The selection of catalyst was based on a thorough study reported in Allaedini (2016) in which a series of bimetallic and trimetallic catalyst were selected and employed for the CNT production using the same method which will be described later in this study. The conversion yield of the carbonous gas to CNTs was measured for each catalysts and presented in Table 1. As can be noted from Table 1, Mo/Ce catalyst resulted in the maximum CNT yield (94%). Therefore, in this study, Mo/Ce catalyst was selected for optimization in the CVD process.

Table 1 – The yield of methane conversion to CNT using bimetallic and trimetallic catalysts.

Catalyst	Yield of the prepared CNT
Ni/MgO	86%
Ge/MgO	82%
Co/Pd/MgO	88%
Mo/Ce	94%
Ni/Ce/Fe	80%
Ni/Co/Fe	82%
Cu/Si	78%