Effective synthesis of carbon nanotubes *via* catalytic decomposition of methane: Influence of calcination temperature on metal–support interaction of Co–Mo/MgO catalyst

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A R T I C L E I N F O

A B S T R A C T

The present work investigated the influence of calcination temperature for bimetallic Co–Mo/MgO catalyst on the synthesis of carbon nanotubes (CNTs) *via* catalytic chemical vapor deposition (CCVD) of methane. The experimental results showed that variation in the catalyst calcination temperature affected carbon yield, diameter distribution and quality of the CNTs. Increasing the catalyst calcination temperature enabled Co–Mo/MgO catalysts in growing CNTs at higher yield, narrower diameter distribution and better degree of graphitization, credited to the strong metal–support interaction (MSI) formed between CoO species and MgO support. We also discovered that the catalysts of weak MSI were beneficial to the nucleation and growth of CNTs, meanwhile the catalysts with strong MSI provoked the growth of CNTs with narrow diameter distribution. The catalyst calcined at 700 °C, possessing moderate MSI, was found to be the most suitable catalyst for the growth of high quality CNTs with the diameter of 7.70 ± 0.77 nm and the carbon yield of as high as 647.4%.

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1. Introduction

Hollow carbon fibers have been discovered decades ago [1], but it was the ground breaking report by Iijima in 1991 [2] that made this new carbon material well known among researchers. This new carbon material was named "carbon nanotubes" (CNTs) after the nanosized and hollow core of the tubular carbon structure. The explosive interest in this new form of carbon allotrope is credited to their superior electronic, mechanical and chemical properties [3], revealing their various potential applications, which include hydrogen storage [4], catalyst support [5], selective adsorption agents [6], composite materials [7], and field emission devices [8]. Various methods have been developed to synthesize CNTs, and catalytic chemical vapor deposition (CCVD) outstands the others, appearing to be the most promising method and the most versatile one for up scaling to a large production capacity at a relatively low cost. In addition, CCVD offers the opportunity to control and adjust multiple physico-chemical properties of the synthesized CNTs, such as morphology, diameter (and therefore chirality [9]), length, surface structure and alignment. The important parameters of CCVD method which will affect the reaction product include the catalyst components and composition [10], the carbon precursors [11] and the reaction conditions [12].

Among the transition metals from group VIII, cobalt (Co) was chosen as the active metal to grow CNTs considering Co is widely reported to grow hollow and higher graphitized CNTs [13,14]. On the other hand, Mo was selected as the catalyst promoter for the enhancement of the catalyst performance. This is mainly due to Mo is suitable to be paired with Co to form a bimetallic catalyst which is effective for high yield synthesis of high quality CNTs [15–17]. In order to develop an easily-washable catalyst, the main component of the catalyst, *i.e.* catalyst support, must be easily removed from the raw product to obtain the high purity CNTs. With this consideration, the chosen catalyst support in this study was MgO, an alkaline earth metal oxide, which can be easily dissolved in mild acid. Besides, MgO has been reported to be a good support for bimetallic Co–Mo catalyst for the synthesis of high quality CNTs at high yield [15,18,19]. Previously, we reported on the effects of catalyst components and composition of Co–Mo/MgO in producing CNTs of nearly uniform diameter distribution in a large quantity [20,21].

Numerous attempts have been made by researchers for synthesizing CNTs with nearly uniform diameters [22–28] considering the chirality of CNTs is governed by the diameter and it affects directly their physico-chemical properties [29]. It is believed that CNTs with narrower diameter distribution possess better uniformity

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in their properties. Most of the research works focused on controlling the size distribution of transition active metals of the catalyst which are responsible for the growth of CNTs. It has been widely reported in literatures that the diameter of CNTs synthesized *via* CCVD is determined by the diameter of the active metal which is deposited on its support [30]. However, we believe that study on the interaction between the active metal and the catalyst support should be emphasized. The strength of metal–support interaction (MSI) plays an important role in the determination of the degree of mobility of the active metal on the catalyst support, indirectly contributing to the stabilization of the size of the active metal and its distribution during CNT growth. In this work, we varied the calcination temperature for the bimetallic Co–Mo/MgO catalyst with aim at investigating its effect on the size of CoO species (active metal) formed on the MgO support and the interaction strength between CoO species and MgO for the growth of CNTs with nearly uniform diameters.

2. Experimental method

Bimetallic Co–Mo/MgO with weight ratio fixed at Co:Mo: MgO=10:20:70 was prepared by the sol–gel method [21]. Initially, the precursors for preparing 10Co–20Mo/70MgO, *i.e.* $Co(NO_3)_2 \cdot 6H_2O$, $(NH_4)Mo_7O_{24} \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$, were weighted and dissolved in distilled water. Then, 1 mol of citric acid was added to the homogenous mixture as foaming agent to create a porous catalyst. The homogenous mixture was stirred at 90 °C for 1 h, and the resulted high viscous sol was then baked overnight at 120 °C. The foamy catalyst was grounded in a mortar to break the chunks into fine powders and calcined in air ranging from 250 to 850 °C for 2 h. The CCVD process was carried out in a simple experimental setup as reported previously [31]. Typically, 50 mg of freshly prepared catalyst was distributed uniformly over a quartz boat and inserted into the middle of quartz tube. The furnace temperature was slowly ramped from room temperature to 800 °C in the nitrogen flow (150 ml/min). When the furnace temperature reached 800 °C, an equal volumetric flow rate of nitrogen and methane mixture was introduced into the quartz tube for 30 min to grow CNTs. After 30 min, the furnace was cooled down to ambient temperature in nitrogen atmosphere.

The as-prepared catalysts were characterized by *Siemen D-5000 diffractometer* to examine the changes in the crystallite size and phase for the catalysts loaded with different Co wt%. XRD analysis was performed with CuKα ($\lambda = 1.54056$ Å) at 40 kV and 30 mA. The XRD patterns were measured in the 2θ ranging from 10° to 90° with a step of 0.02° and a measuring time of 2 s per point. Temperature programmed reduction (TPR) was performed to study the reducibility of the catalyst samples. TPR studies were carried out on a *Micromeritics AutoChem 2950 HP*. About 10 mg of catalyst was placed in a U-tube quartz reactor. Prior to the TPR studies, the catalyst samples were pretreated in nitrogen flow (20 ml/min). The temperature was raised to 150 °C from room temperature at a heating rate of 10 °C/min, and held isothermal at 150 °C for 30 min. After pretreatment step, the sample was cooled to room temperature under the carrier gas consisting 10% hydrogen balance argon (20 ml/min). The temperature was increased from ambient to 1000 °C at a heating rate of 10 °C/min. The reduction was measured by monitoring the hydrogen consumption with the TCD detector.

Meanwhile, the as-produced carbon deposits were characterized using transmission electron microscope (TEM), Raman spectroscopy and thermogravimetric analyzer (TGA) to acquire the information on the type and the morphology of carbon nanostructures formed, the degree of graphitization and also their purity. TEM images were taken using *Philips CM 12* transmission

electron microscope in which 80 kV was used to generate electron beam. The samples of catalysts and CNTs were first crushed and mixed with acetone of 99.999% purity in glass vials and shaken vigorously for a few seconds. The suspensions were then left to allow the coarser particles to settle. Later, a drop taken from the upper part of the suspension, containing suspended particles, was dropped onto a carbon-coated copper grid. The sample was dried in air before being transferred to the microscope. The thermal gravimetric analysis of used catalysts was carried out using *TA Instrument SDT Q600* TGA. The weight loss with TGA temperature, corresponding to the oxidation of deposited carbon, determines the thermal stability and the amount of the carbon produced by the catalysts. About half-cup full of the outlet product was heated from ambient temperature 900 °C in air flow (100 ml/min) at 10 °C/min to oxidize the carbon content. The carbon yield of each catalyst was calculated using the following equation.

$$\text{Carbon yield} = \frac{\% \text{ weight loss by carbon oxidation}}{\% \text{ of residue after oxidation}} \times 100\% \qquad (1)$$

3. Results and discussion

Co–Mo/MgO catalysts prepared at different calcination temperatures were tested in the growth of CNTs. Thermogravimetric analysis (TGA) was employed to characterize the activity of each catalyst in terms of carbon yield, through examining the weight loss of the carbon deposits in thermal oxidation. The thermogravimetric (TG) curves of the catalysts after CCVD process are shown in Fig. 1(a). Meanwhile, the carbon yield of each catalyst was calculated using Eq. (1) and the results are presented in Fig. 1
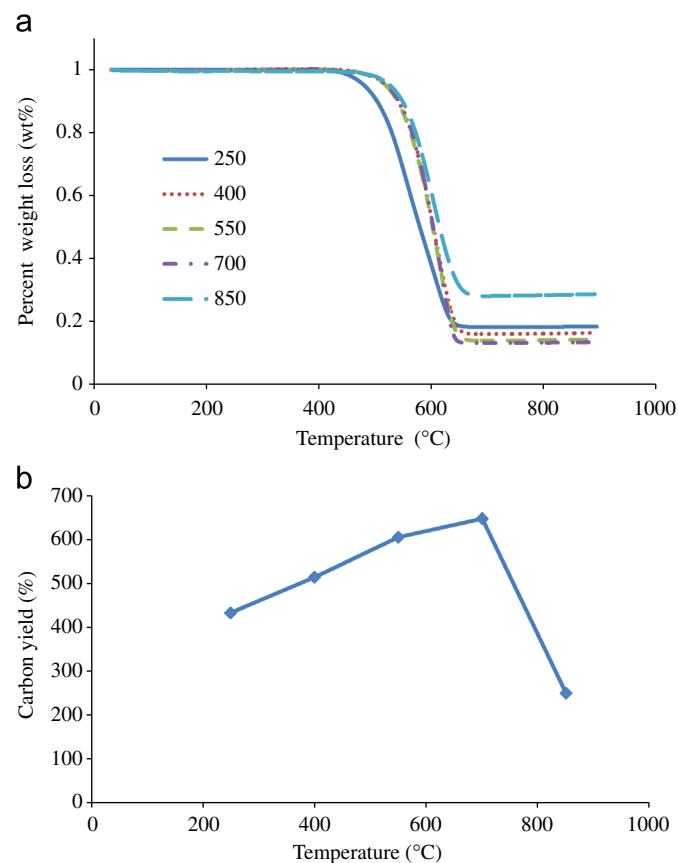

Fig. 1. (a) Thermogravimetric curve of the as-produced CNTs by catalysts prepared at different calcination temperatures. (b) Carbon yield as a function of calcinations temperature of Co–Mo/MgO catalyst.