Preparation of CNTs with the Controlled Porosity using Co-Mo/MCM-41 as a template

A.M. Rashidi*[1], M.M. Akbarnejad[1], A.A. Khodadadi[2],
Y.Mortazavi[2], M. Attarnejad[1]

[1]Gas and Catalyst Research Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

[2]Department of Chemical Engineering, University of Tehran, Tehran, Iran

Gas Research Division, Research Institute of petroleum Industry, NIOC.Pajouheshgah Blvd, Qom Old Road. P.O.Box: 18745-4163,Tehran, IRAN, Fax:(+98) 215699385,

E-Mail: Rashidiam@ripi.ir

Abstract

A template synthesis method based on catalytic MCM-41 was applied for the preparation of ordered nanotubes via thermal decomposition of acetylene in the range of 600-700 ^{0}C. A bi-metallic catalyst using cobalt and molybdenum with 5-8 wt% was prepared by incipient wetness impregnation method on MCM-41 support as it has been found that these metals are able to produce good carbon nanotube in terms of yield and selectivity. Nitrogen adsorption isotherm and TEM images of the template and nanotube products clearly shows that the shape and pore size of nanotubes exactly reflect the pore size of the template. The result indicates that manipulating the template and thermal conditions during vapor deposition can control the pore size of CNTs. The present investigation is of great interest for synthesis of nanotubes with the defined pore size distribution.

Introduction

Carbon nanotubes (CNTs) have attracted much attention because of their extraordinary properties and potential applications in various technologies. In order to suitably make use of the nanotubes, it is necessary to prepare them in uniform size, with narrow pore size distribution. This makes the synthesis of carbon nanotube a real challenge [1-4]. Among various CNT synthesis methods, e.g., arc discharge [5], laser vaporization [6] and catalytic method [7], the later is simple, cheap and also the best method for the large-scale production of CNTs. The bamboo-structured carbon nanotubes, a special morphology of CNTs, were synthesized by DC arc-evaporation [8] and catalytic growth methods [9-12]. Understanding the growth mechanism of CNTs would help in controlled growth and development of new synthesis methods. Different preparation procedures and formation mechanisms for bamboo-structured carbon nanotubes were proposed [12-14] and possible growth of CNT within the pores of a template catalyst (ALPO-5) was also reported [13]. In this regard, multi- wall CNTs was synthesized by mesoporous MCM-41 silicalits in the absence of any metal traces [14]. In the present investigation, the MCM-41 incorporated with

* Corresponding Author

cobalt and molybdenum in its silica framework, is chosen as a template for the preparation of nanotubes. The experimental results indicate that the porosity and structure of nanotube products are exactly reflect the MCM-41 framework and by changing the template structure we are able to prepare bamboo-shaped CNTs with the controlled porosity.

Experimental

The MCM-41 samples were synthesized in our laboratory based on the previous works of satio and yoshikawa [16]. The Co-Mo catalysts were prepared by incipient wetness impregnation of MCM-41 supports with aqueous solutions of cobalt nitrate and ammonium hepta- molybdate. The molar ratio of Co: Mo in the catalyst was taken as 1:2. The catalyst was first dried in air at room temperature, then in an oven at 120 ^{0}C, and finally calcined at 550 ^{0}C for 3 hours. A Micromertics ASAP 2000 adsorption apparatus was used to obtain the BET surface area, pore volume, and pore size distribution of the MCM-41 samples as well as catalysts.
The CNTs were synthesized by decomposition of acetylene over catalyst in 700^{0}C temperature and then, purified by extracting the catalyst materials. A horizontal tube furnace is used in the hydrocarbon decomposition stage. Typically, 200 mg of catalyst was placed in the center of a quartz tube located in the tube furnace and acetylene decomposition reaction was conducted at ambient pressure. A gas mixture of acetylene and hydrogen with molar ratio of C_2H_2: H2=1:4 and total flow rate of 200 cm^3/min was introduced into the reactor. The temperature was raised to 973K with a ramp of 5ºC/min and maintained for 5-30 min at final temperature. The acetylene flow was then stopped and sample was cooled down in flow of hydrogen. In order to produce pure carbon nanotube, the catalyst materials were removed by dissolving the sample in 2M NaOH for 24 hours. Afterwards, mixtures of 2.5% of NaOH and EOH/H_2Owith molar ratio of 50/50 were applied for complete removal of catalysts.
TEM, SEM, XRD and BET surface area patterns were employed to characterize the roughly purified samples. TEM was performed on a CM 120 Philips with a tension voltage of 120 kV. PHILIPS X-Ray diffraction model "PW1840" with APO Software package was used for qualitative phase analysis of products. Scanning electron microscopy was taken using a "Cambridge stero scan" SEM model 360.And BET surface area of samples was measured on ASAP2000, using N_2 as the adsorbate at 77K.

Results and discussion

Figure 1 shows SEM micrograph of sample for CNTs grown on Co-Mo/MCM-41 under the conditions that C_2H_2 gas flow with a rate of 50mL/min for 5-30 min at 700^{0}C. The CNTs are grown with a uniform length of about 10μm The TEM images of the roughly purified bamboo-structured carbon nanotube grown on catalysts are shown in Figure 2. The CNT have a bamboo structure under the mentioned (above) and its diameter in the rang of 150-200 nm. These images reveal the open tip of nanotubes without any encapsulated Co particles. Also, in the compartment layers the curvature is directed to the tip.
Nitrogen adsorption results are used as a standard index of structure as it exhibits a volume averaged results of samples. Figure 4 shows nitrogen adsorption isotherm of sample before and after the decomposition. It shows similar pattern of sharp capillary condensation in the same relative pressure range. Pore size distributions of catalyst and CNT are shown in figure 5. From

the figure, it is clear that pore size distribution is quit narrow, and similar to each other. This is an indication of pore size controlling of the product. It also shows that CNT grown inside the pore and the nanotube diameter are controlled by the pore size of the templates and the amount on catalyst incorporated.

Acknowledgments

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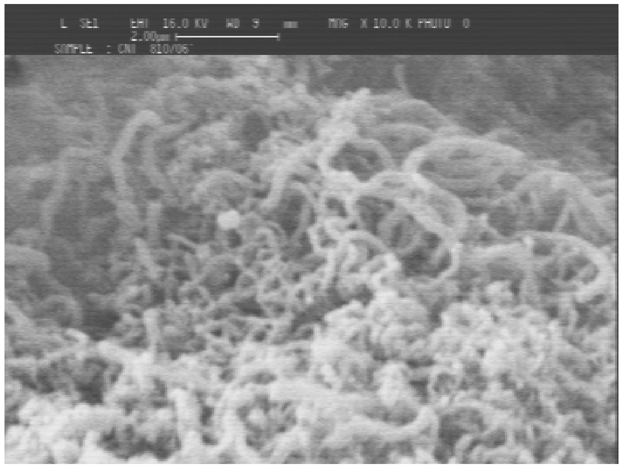

Fig 1. SEM micrograph of CNTs grown on Co-Mo/MCM-41at700^{0}C

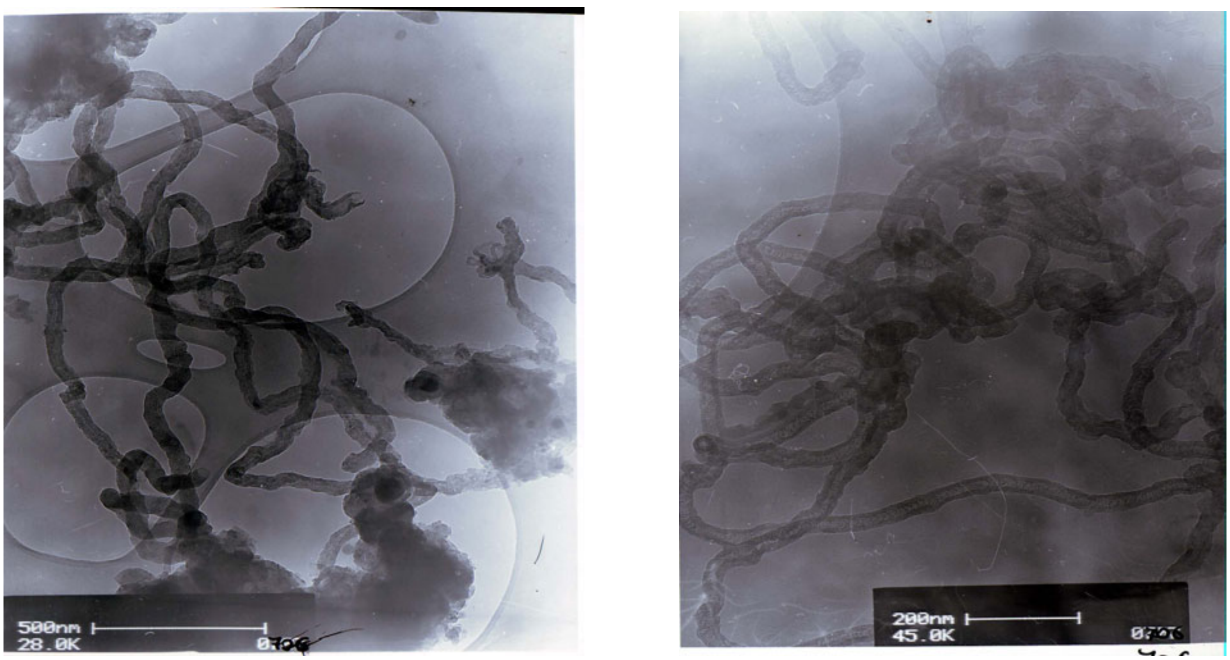

Fig 2. TEM images of CNTs grown at 700^{0}C,

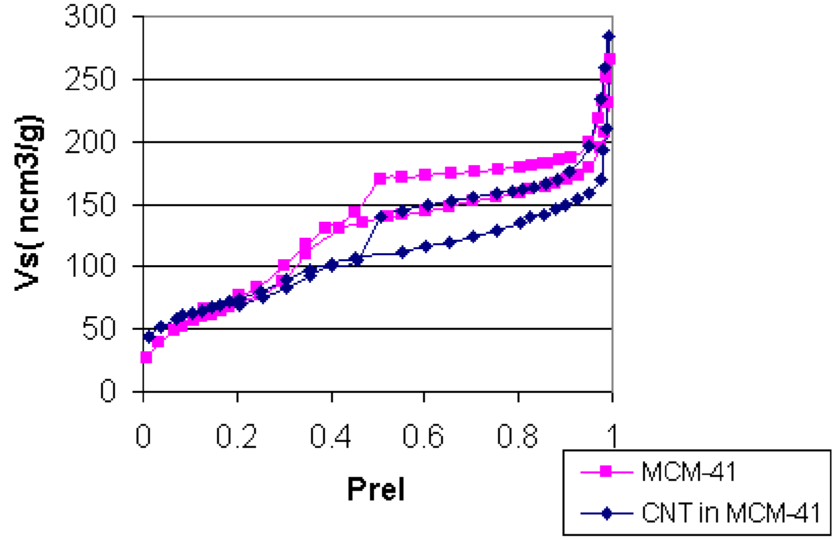

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Fig 4. Nitrogen adsorption isotherm at 77K for (a) MCM-41 and (b) CNT in MCM-41

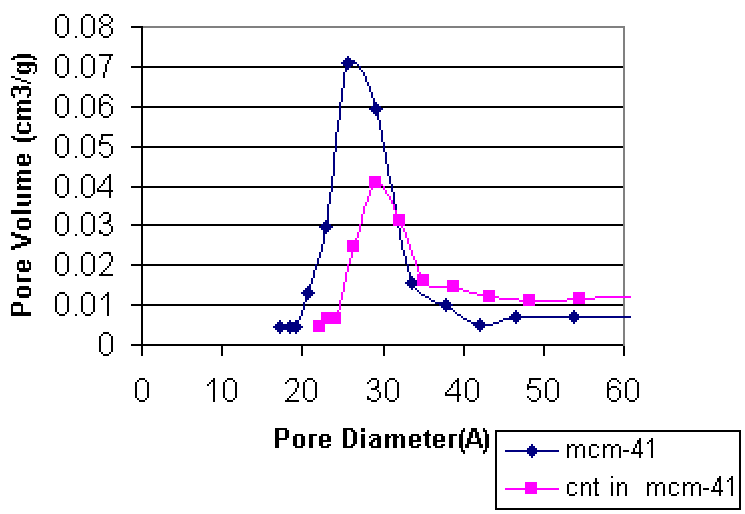

Fig 5. Pore size distribution curves for (a) MCM-41 (b) CNT in MCM-41