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# The effect of the cobalt loading on the growth of single wall carbon nanotubes by CO disproportionation on Co-MCM-41 catalysts

Yuan Chen [a,b], Dragos Ciuparu [a,c], Sangyun Lim [a], Gary L. Haller [a], Lisa D. Pfefferle [a,*]

[a] Department of Chemical Engineering, Yale University, New Haven, CT 06520, USA
[b] School of Chemical and Biomedical Engineering, Nanyang Technological University, 637722, Singapore
[c] Department of Petroleum Processing and Petrochemistry, "Petrol-Gaze" University, 2000 Ploiesti, Romania

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**Abstract**

Highly ordered MCM-41 mesoporous molecular sieves in which silicon was isomorphously substituted with 0.5–4 wt.% cobalt were synthesized using an alkyl template with a 16 carbon atoms alkyl chain length. These materials were used as catalysts for the synthesis of uniform diameter single wall carbon nanotubes (SWNT) by CO disproportionation (Boudouard reaction). The SWNT synthesis conditions were identical for all Co-MCM-41 samples, and consisted of pre-reduction of the Co-MCM-41 catalyst in hydrogen at 500 °C for 30 min followed by reaction with pure CO at 800 °C and 6 atm for 1 h (conditions previously optimized for 1 wt.% Co-MCM-41). The SWNT grown in the Co-MCM-41 catalysts were characterized by TGA, multi-excitation energy Raman spectroscopy and TEM. The state of the catalyst and the size of the metallic cobalt clusters formed in Co-MCM-41 during the SWNT synthesis were characterized by X-ray absorption spectroscopy. The mechanism controlling the diameter distribution of the SWNT produced is related to the size uniformity of the cobalt clusters nucleated in the Co-MCM-41 catalytic template: the SWNT growth selectivity and size uniformity is influenced by the cobalt concentration in the framework. If the cobalt is not initially strongly stabilized in the MCM-41 framework during template synthesis, the catalyst produces SWNT with a wider diameter distribution. Co-MCM-41 catalysts with up to 3 wt.% cobalt can be used to grow SWNT with a diameter distribution similar to that obtained with 1 wt.% Co-MCM-41, but at yields greater by a factor of approximately 2.4.


*Keywords:* Carbon nanotubes; Carbon yield; Catalyst

## 1. Introduction

Since their discovery in 1991, carbon nanotubes have stimulated an intense research effort due to their high mechanical strength [1] and thermal conductivity [2], their unique electronic properties [3–6], and the possibility of building nanoscale molecular devices. Among known nanomaterials, carbon nanotubes exhibit perhaps the richest diversity of structures and structure-property relations [7]. Their physical and chemical properties are determined by the chirality, that is, the way in which an equivalent structure would form by a graphite sheet rolling up, in addition to the nanotube length and diameter. The SWNT growth techniques explored so far cannot produce significant amounts of SWNT with predetermined specific properties. The lack of purity and uniformity in length, diameter, and chirality has been a significant hindrance to the development of a successful technology for large scale production of electronic devices using carbon nanotubes. With cleaning and separation, narrow tube diameter distributions are

* Corresponding author. Fax: +1 203 432 4387.
*E-mail address:* lisa.pfefferle@yale.edu (L.D. Pfefferle).

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obtainable, but electronic properties are compromised by contamination and introduction of defects.[1]

It has been suggested that the diameter of SWNT is controlled by the size of metal catalyst particles [8,9]. Therefore, the key to the controlled growth of SWNT is to control the similar metal clusters in catalysts, avoiding aggregation into large particles during the high temperature reaction. Among the three main processes used for carbon nanotubes synthesis—the arc discharge, laser ablation, and chemical vapor deposition (CVD)—the last may offer more control of the tube diameter and chirality because it is relatively easy to control metal cluster size in solid catalysts. Several efforts have been made to control the metallic particles for SWNT growth [8,10–14], but in most studies the sizes of the nanoparticles are relatively large for SWNT growth, ranging from 1 to 14 nm, which leads to the formation of SWNT with a wide diameter distribution with amorphous carbon, multi-wall carbon nanotubes (MWNT), and graphite impurities. We [15,16] and other authors [17] have reported that the increase of the cobalt particle sizes in the catalysts during SWNT synthesis leads to wider SWNT diameter distribution and poor SWNT selectivity. Resasco and coworkers found that molybdenum [18,19] and tungsten [20] can be used to stabilize the cobalt against reduction and investigated the effect of the Co to Mo ratio on the SWNT synthesis performance. Using an optimized catalyst, these authors were able to achieve a narrow diameter distribution for the semiconducting SWNT as determined from fluorescence measurements [21].

We have recently developed a catalytic system consisting of cobalt as the catalytic component incorporated into the pore wall of MCM-41 mesoporous molecular sieves by isomorphous substitution for silicon, resulting in an initially nearly atomic dispersion [22]. In our SWNT synthesis process using Co-MCM-41 catalyst, the cobalt is reduced and nucleates into sub-nm metallic clusters that initiate the growth of carbon nanotubes. The MCM-41 matrix stabilizes the cobalt against reduction, allowing formation of very small cobalt clusters, uniform in size, that enable growth of SWNT with diameters within ±0.05 nm [23]. The size of the cobalt clusters produced can be engineered by manipulating the pore radius of curvature, that is incorporating cobalt in MCM-41 of different pore diameters, thus allowing the growth of carbon nanotubes of uniform, pre-selected diameter [23,24]. Other template synthesis parameters, notably the initial pH of the synthesis solution, affect the size and state of the cobalt clusters formed during the SWNT synthesis process [25].

All of our previous studies on the effects of the synthesis parameters on SWNT synthesis performance, as assessed by SWNT yield, purity, and diameter uniformity, were performed using catalysts with 1 wt.% Co loading [15,16]. The optimized pre-treatment and reaction conditions allowed synthesis of uniform diameter SWNT, but at a limited yield. The tubes were noted to be significantly more defect free than those from other processes1 most likely due to the milder chemical treatments required for purification. A possible strategy to be considered for the synthesis of larger yields of SWNT is to increase the metal loading in our catalyst. Since the performance of the SWNT synthesis process was observed to depend mainly on the size and uniformity of the sub-nm metallic Co clusters formed on the catalyst surface, changing the cobalt loading may require different SWNT synthesis conditions in order to obtain SWNT with good purity and narrow diameter distribution. Production of larger SWNT yields would provide incentives for the development of large scale production of SWNT with a narrow diameter distribution. Therefore, the present contribution is focused on the investigation of the influence of the cobalt loading on the selectivity and the diameter distribution of the SWNT produced as a critical step to increase the efficiency of the SWNT synthesis process based on the Co-MCM-41 catalyst.

## 2. Experimental

Co-MCM-41 samples with different cobalt loadings of 0.5, 1.0, 2.0, 3.0 and 4.0 wt.% (as determined by inductively coupled plasma, ICP measurement at Galbraith Laboratories, Inc.) were synthesized following the method described elsewhere [22]. Both the purity of the silica source, and the pH during Co-MCM-41 synthesis were observed to influence the reducibility of the cobalt ions in the framework [25]. The catalysts employed in these studies were synthesized using a Cab-O-Sil silica source and the initial pH of the synthesis solution was controlled at 11.5. The physicochemical properties of the Co-MCM-41 samples used in this study are given and discussed in detail elsewhere [22].

SWNT were synthesized by CO disproportionation. For a typical batch, 200 mg of fresh Co-MCM-41 were loaded into a 10 mm internal diameter quartz reactor placed in an Omega ceramic fiber radiant heater, which allowed precise temperature control throughout the entire catalyst bed. Prior to exposure to CO the catalyst was heated in flowing hydrogen at one atmosphere from room temperature to 500 °C at 20 °C/min, and reduced isothermally for 30 min. After this pre-reduction treatment, the catalyst was purged with ultra high purity argon at the reduction temperature, and then heated to 800 °C at 20 °C/min in flowing argon. SWNT were grown for 60 min under 6 atm CO (99.5% from Airgas). Before entering the reactor, the CO stream was passed

[1] Dr. Phaedon Avouris from IBM, private communication.