Journal of Catalysis 309 (2014) 419–427

Contents lists available at ScienceDirect

Journal of Catalysis

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

Increase in the yield of (and selective synthesis of large-diameter) single-walled carbon nanotubes through water-assisted ethanol pyrolysis

Fang Ren [a], Stacy A. Kanaan [a], Magdalena M. Majewska [a], Gayatri D. Keskar [a], Seyla Azoz [a], Hong Wang [b], Xiaoming Wang [a,1], Gary L. Haller [a], Yuan Chen [b], 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, Singapore

ARTICLE INFO

Article history:
Received 25 June 2013
Revised 4 September 2013
Accepted 9 October 2013
Available online 23 November 2013

Keywords:
Increase in yield
Large-diameter carbon nanotubes
Co-MCM-41
Ethanol pyrolysis
Cobalt oxide
Amorphous carbon

ABSTRACT

Single-walled carbon nanotubes (SWCNT) were synthesized using Co-MCM-41 catalysts through water-assisted ethanol pyrolysis. The effect of varying the water to ethanol ratio in the reactant mixture was studied. The data from X-ray absorption spectroscopy indicate that with the addition of water, the cobalt metal particles were oxidized. X-ray diffraction analysis of CoC_x suggests that the formation of amorphous carbon on the surface of the Co particles was suppressed. Cobalt magnetization measurements were performed to study the size and anisotropy of cobalt particles. Thermogravimetric analysis data demonstrate that with a water concentration of 7%, the yield increases by about 100% relative to pure ethanol synthesis. Raman and photoluminescence excitation spectroscopic data demonstrate that the SWCNT diameter increases (within the diameter range detected) with the water/ethanol ratio. From the statistical SWCNT diameter distribution obtained from transmission electron microscopy, 65% of the SWCNT synthesized with 20% water in ethanol have diameters larger than 1.5 nm, but there is a severe decrease in yield and a modest decrease in selectivity of SWCNT. The mechanism of how the water influences the yield and diameter of SWCNT is discussed.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Following the discovery by Iijima in the early 1990s [1,2], single-walled carbon nanotubes (SWCNT) have attracted research interest in many different fields [3–7] based on their extraordinary electrical, chemical, and mechanical properties [7–13]. The electronic properties of SWCNT are determined by their unique quasi-one-dimension structure [10,13–15]. SWCNT can be visualized by rolling up a graphene sheet. Defining two unit vectors a_1 and a_2 in the real graphene plane, the chiral vector C_h, along which the SWCNT is rolled up and the tube diameter d can be represented by two indices, n and m, where $C_h = na_1 + ma_2$ and $d = 0.246(n^2 + m^2 + nm)^{1/2}/\pi nm$. Different types of SWCNT corresponding to different values (n,m) have various band gaps and will display either metallic or semiconducting behavior. The band gap of SWCNT is defined by the van Hove transition energy E_{11} in the density of states (DOS) of SWCNT. Theoretical calculations by Kataura et al. [16] show how the band gap changes with tube diameter, and thus, it is possible to tune the band gap of SWCNT by controlling the diameter through synthesis. Also, the Kataura plot indicates that the change in band gap with diameter is not as significant in the large-diameter range (>1.5 nm) as in small-diameter range (<1 nm), which makes large-diameter tubes more suitable for practical electronic devices due to reproducible behavior.

In addition to the electronic applications, large-diameter SWCNT appear to be more stable with decreased strain energy due to lower surface wall curvature. This implies that the tube structure of large SWCNT will be more stable after incorporation of foreign elements, for example, boron or nitrogen.

Based on the theoretical study of Pederson and Broughton [17], SWCNT that have diameters of a few nanometers should be able to draw up liquids by capillary forces. This characteristic makes large-diameter SWCNT a potential material for hydrogen storage [5].

Our research group has been working on diameter-selective synthesis of SWCNT on Co-incorporated MCM-41 (Co-MCM-41) catalysts using a chemical vapor deposition (CVD) method [18–22]. During SWCNT synthesis on cobalt catalysts, there is a competition between the cobalt particle growth and SWCNT growth. Usually, large cobalt clusters with diameters larger than 5 nm will not catalyze SWCNT growth, but rather MWCNT or graphene growth. The MCM-41 template solves this problem by

---

* Corresponding author.
E-mail address: lisa.pfefferle@yale.edu (L.D. Pfefferle).

[1] Present address: BASF Corporation, 25 Middlesex/Essex Turnpike, Iselin, NJ 08830, USA.

0021-9517/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcat.2013.10.007

anchoring and partially occluding the cobalt particles, thus making it difficult for cobalt to form very large particles [23]. Much research has been performed on Co-MCM-41-catalyzed synthesis of SWCNT, but ethanol has not been used as a carbon source on this catalyst.

Maruyama et al. [24] have reported a technique called alcohol catalytic CVD (AC-CVD) for the synthesis of SWNCT. It was demonstrated that tall, aligned carbon nanotube forests can be grown by the addition of small and controlled amounts of water to the synthesis reactant mixture [25–27], which is also called “super-growth” [28]. An increase in the yield results from water etching the amorphous carbon formed on the catalyst surface during growth of SWCNT, thus reviving the catalyst activity [29,30]. The same mechanism has been observed for CO_{2-} and O_2-assisted SWCNT synthesis [31,32], where it was observed that with an optimum of CO_2 or O_2, the yield of SWCNT increases due to the removal of amorphous carbon from the catalyst surface.

While the effect of water on the yield of SWCNT has been studied in many papers, the effect of water on the SWCNT diameter is not fully understood. We propose that water can affect SWCNT diameter in two ways: changing the cobalt particle size and selectively etching (oxidizing) SWCNT products. First, metal particle size influences the SWCNT diameter [33], i.e. a larger cobalt particle will seed the growth of a larger-diameter SWCNT. How water affects the cobalt particle size was a part of this investigation. Second, water selectively etches small-diameter SWCNT, which are more reactive than large-diameter SWCNT because of sp^2 orbital distortion [34,35]. Both of these effects will change the diameter distribution of SWCNT. To systematically study the effect of water, including the effect on yield and diameter of SWCNT, different percentages of water (0–20%) were added to the reaction mixture used for synthesis.

2. Materials and method

2.1. Catalyst synthesis procedure

We have used Co-MCM-41 catalysts with 3% metal loading, synthesized by isomorphous substitution of cobalt in the silica framework of the MCM-41 structure. A surfactant with a 16 carbon atom alkyl chain length $(C_{16}H_{33}(CH_3)_3NBr$, after ion exchange with a Amberjet-400 (OH) resin (Sigma–Aldrich), was used to template the Co-MCM-41 synthesis. Cobalt (II) sulfate heptahydrate (ReagentPlus®, ⩾99%, Sigma–Aldrich) was used as the cobalt precursor. Details of the experimental procedure are given elsewhere [36].

2.2. SWCNT synthesis procedure

Typically, 100 mg Co-MCM-41 was loaded in a packed-bed quartz reactor with an inner diameter of 18 mm. The packing density of the catalysts is 0.131 g cm^{-3}, making a 3-mm-thick bed. The cobalt in the catalyst was pre-reduced by flowing hydrogen (UHP, Airgas) at 700 °C, 1000 sccm, for 30 min. The reduction temperature was chosen to be 700 °C based on our previous H_2 – temperature-programmed reduction results [37]. SWCNT were produced through water-assisted ethanol pyrolysis (0.5%, 1%, 3%, 7%, 10%, 15%, and 20% H_2O in C_2H_5OH). Pure ethanol pyrolysis was also performed for comparison purposes. During the synthesis, the mixture of ethanol and water was injected by a syringe pump (NE-311, New Era Pump Systems Inc.) at 3 mL/h and carried by 300 sccm Ar (UHP, Airgas). The reaction conditions were constant at 700 °C during the 1-h synthesis. Because of the low packing density, thin-bed thickness, and fast gas flow, the SWCNT growth along the bed depth is nearly uniform.

2.3. Catalyst characterization

2.3.1. Nitrogen physisorption

Nitrogen physisorption measurement was carried out on a Quanta Chrome Autosorb-3B static volumetric instrument. Fifteen milligram of Co-MCM-41 was first outgassed at 300 °C for 3 h, and then, the adsorption–desorption isotherms were measured at −196 °C.

2.3.2. X-ray absorption spectroscopy (XAS)

XAS data were collected at beamlines X19A and X23A2 at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Typically, 100 mg catalysts were pressed into a round, free-standing pellet with the approximate thickness of 0.5 mm. Extended X-ray absorption fine structure (EXAFS) spectra were collected in the transmission mode from 200 eV below to 800 eV above the Co K-edge (7709 eV). A Co metal foil (4 μm thick) was used as a reference to calibrate the edge energy for each EXAFS scan.

2.3.3. X-ray diffraction (XRD)

The XRD patterns were collected using a Bruker D8 Focus Powder. X-ray diffractometer operating in the low-angle X-ray diffraction pattern using Cu Kα radiation at $\lambda = 0.154$ nm.

2.3.4. Superconducting quantum interface device (SQUID)

AC SQUID measurements were performed using Quantum Design MPMS at 10 K using a SQUID magnetometer. The applied field was varied between −20 and +20 kOe. The samples were in powder form and loaded in a plastic capsule.

2.4. SWCNT characterization

2.4.1. Thermogravimetric analysis (TGA)

TGA data on each as-synthesized SWCNT sample were collected using a Setaram Setsys 1750 instrument. Around 10 mg of each sample was loaded in an alumina crucible for each run. The samples were pretreated in air (ultra zero, Airgas) at 200 °C for 30 min to remove moisture; two successive temperature ramps were then run on each sample. During each of the ramps, the sample was heated from 200 to 1000 °C at 10 °C/min and soaked at 1000 °C for 1 h. The change in sample weight versus temperature was recorded during the two ramps, and the second set of data was used for baseline correction.

2.4.2. Raman spectroscopy

Raman spectra of as-synthesized SWCNT samples were collected on a Jasco NRS-3100 laser Raman spectrometer (excitation wavelength = 532 nm, 785 nm) and a Horiba Jobin-Yvon T6400 Raman spectrometer (excitation wavelength = 633 nm).

2.4.3. Transmission electron microscopy (TEM)

TEM images of as-synthesized SWCNT samples were recorded on a Philips Tecnai 12 electron microscope operated at 120 kV. One milligram of SWCNT sample was dispersed in ethanol (200 proof, Decon Labs Inc.) by a bath sonicator (1510R-DTH, Branson) for 1 h, and then, one drop of the suspension was applied to a TEM grid with holey carbon film and dried in air for about 30 min.

2.4.4. Photoluminescence excitation (PLE)

One milligram of silica-removed SWCNT sample (silica template was removed by 1.5 mol/L sodium hydroxide solutions) [38] was dispersed in 20 mL of 2 wt% sodium dodecylbenzenesulfonate (SDBS, 99%, Aldrich) D_2O (99.9 atom% D, Sigma–Aldrich) solution by sonication in a cup-horn ultrasonicator (SONICS,

Download English Version:

https://daneshyari.com/en/article/61132

Download Persian Version:

https://daneshyari.com/article/61132

Daneshyari.com