

Templated growth of single walled carbon nanotubes by CO disproportionation on cobalt incorporated MCM-41

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ABSTRACT

Cobalt substituted MCM-41 with a high degree of structural order and a narrow pore diameter distribution (± 0.15 nm full width at half maximum) was synthesized and used for the templated growth of single walled carbon nanotubes (SWNT). The nanotubes obtained were characterized by Raman spectroscopy, temperature programmed oxidation (TPO) and high-resolution transmission electron microscopy (HRTEM).

Catalysts exposed to several cycles of carbon deposition and oxidation preserved their structure and showed improved selectivity for SWNT with increasing number of cycles. Neither carbon nanotubes, nor amorphous carbon could be identified in transmission electron micrographs recorded with samples after carbon deposition, suggesting all the carbon is inside the pores of the MCM-41 material. Physisorption measurements performed with carbon containing samples and after carbon removal suggest the synthesized SWNT are open ended and the Raman spectroscopy indicated they are of metallic structure.

Keywords: Co-MCM-41, single walled carbon nanotube, templated synthesis.

1 INTRODUCTION

As widely reported [1-5], carbon nanotubes exhibit technologically important electronic properties that will likely allow new device development. They can be found in both metallic and semiconducting structures. Metallic (m) nanotubes can carry extremely large current densities [6]; semiconducting (s) nanotubes can be electrically switched on and off as field-effect transistors (FETs) (e.g. [6]). The structure of the SWNT is defined by how the graphitic sheet is aligned in the rolled up configuration. Most electronic applications of carbon nanotubes require significant amounts of aligned SWNT that are reasonably homogeneous in diameter, length and helicity. Odom *et al.* [7] used scanning tunneling microscopy (STM) to correlate atomic structure with electronic properties of SWNT. They found that the electronic properties correlate both with the diameter and helicity (twist). This important work

illustrates why control of SWNT structure is of crucial importance for the development of new electronic devices based on SWNT.

In this paper we discuss the synthesis of SWNT inside the pores of MCM-41 mesoporous molecular sieves having a parallel system of pores that are uniform in size and structure. The catalytically active site derives from framework substitution with cobalt. The results presented here suggest that MPMS catalytic templates with metals incorporated in the framework can exhibit good structural stability and can be used for growth of ordered SWNT of uniform size and structure at yields and selectivity promising for large scale applications.

2 EXPERIMENTAL

The mesoporous molecular sieve used as a catalytic template for SWNT growth was produced using a surfactant templated synthesis modified from the original Mobil method to improve structural order. The factors that were key to obtaining high structural order were choice of anti-foaming agent, silica sources and pH control. The silica sources used were HiSil-915 from Pittsburgh Plate Glass (PPG) and tetramethyl-ammonium silicate (10wt% silica, SACHEM Inc.). The metal source used was $\text{CoSO}_4 \cdot x\text{H}_2\text{O}$ (Aldrich Chemical Co.). Quaternary ammonium surfactants of the general form $\text{C}_n\text{H}_{2n+1}(\text{CH}_3)_3\text{NBr}$ were purchased from Sigma Co. with $n = 12, 14, 16$ and from American Tokyo Kasei with $n = 10$. The surfactant solutions were prepared by ion-exchanging the 29wt% of $\text{C}_n\text{H}_{2n+1}(\text{CH}_3)_3\text{NBr}$ aqueous solution with an equal molar exchange capacity of Amberjet-400 (OH) ion-exchange resin (Sigma Co.) by overnight batch mixing. The anti-foaming agent was Antifoam A from Sigma Co., a silane polymer alkyl terminated by methoxy groups. Acetic acid (Fisher Scientific) was used for pH adjustment of the synthesis solution. The experimental method is subsequently described.

Aqueous solutions of HiSil-915, tetramethyl-ammonium silicate and the metal precursor were mixed for 30 min with 50 ml of deionized water (the water to silica molar ratio was varied from 74.4 to 86, based on the surfactant chain length). The surfactant solution was added to the prepared silica and metal mixture and a small amount of anti-

3 RESULTS

foaming agent (0.2 wt% of surfactant) was incorporated to control excess foam produced by the surfactant. Acetic acid was added to maintain pH at 11. After additional mixing for about 30 min, this synthesis solution was poured into a polypropylene bottle and placed in the autoclave at 375K for 6 days. After cooling to room temperature, the resulting solid was recovered by filtration, washed with deionized water and dried under ambient conditions. After drying, the solid was calcined by heating from room temperature to 540°C over 20 hours under flowing He, held for 1 hour at 540°C with flowing He and 5 hours at 540°C with flowing air to remove the residual surfactant. The molar ratio of each component in the synthesis solution was controlled at $\text{SiO}_2 : \text{surfactant} : \text{M} : \text{H}_2\text{O} = 1 : 0.27 : 0.017 : X$ (X varying from 74.4 to 86), where M stands for metal. Pure silica MCM-41 was also prepared with the same procedure as used for M-MCM-41 except without addition of metal precursor to the synthesis solution.

The MCM-41 catalytic templates were characterized using nitrogen adsorption isotherms. Adsorption-desorption isotherms of N_2 at its normal boiling were measured with a static volumetric instrument Autosorb-1C (Quanta Chrome). The samples were outgassed at 200°C to a residual pressure lower than 1×10^{-4} torr. A Baratron (0.001 ~ 10 torr) pressure transducer was used for low pressure measurements. The structure and pore spacing were also analyzed by X-Ray diffraction (XRD) using a Shimadzu instrument.

The resulting metal-substituted MCM-41 was found to have a parallel pore structure with hexagonal symmetry and the amorphous silica walls are approximately 1 nm thick, as determined by X-ray diffraction at small angle.

Single walled carbon nanotubes were synthesized by CO disproportionation at 750°C in a 7 mm internal diameter quartz reactor. Before reaction the catalyst was heated in flowing oxygen to 850°C and then cooled to 750°C at a constant rate of 10°/min. When the temperature reached 750°C, prior to CO admission the catalyst was flushed with Ar for 15 minutes to remove the oxygen from the reactor. After the Boudard reaction was carried out for 4 hours, the catalyst was again flushed with Ar and naturally cooled to room temperature in flowing Ar. The same catalyst sample was subjected to several similar cycles to observe the catalyst stability and characterize changes in SWNT yield and selectivity.

Temperature programmed oxidation experiments were performed in a Setaram Setsys 1750 instrument under oxygen flow. The change in sample mass was followed over the temperature range from 15 to 900°C at 10°/min rate for two successive ramps, the second being used as baseline correction for the first. A special holey crucible was used to limit mass transfer interference.

Raman spectra were recorded for selected samples in the lab of Professor Daniel Resasco at University of Oklahoma. High resolution transmission electron microscopy was carried out by Professor Abhaya Datye at the University of New Mexico.

Nitrogen physisorption results were used as a standard index of structure because it produces a volume averaged analysis of samples, unlike XRD and TEM. Nitrogen adsorption isotherms and the pore size distribution of the fresh Co-MCM-41 prepared in the optimum synthesis condition are given in Figure 1. The pore size is about 2.8 nm as determined by the BJH method. The pore size distribution for this sample is ± 0.15 nm FWHM. UV-vis results showed in Figure 2 suggest that the main cobalt species is Co^{2+} with tetrahedral coordination in the silica framework and these could be partially oxidized and reduced without aggregation into particles. These molecular approachable and finely dispersed cobalt ions were expected to form catalytic active sites for SWNT production.

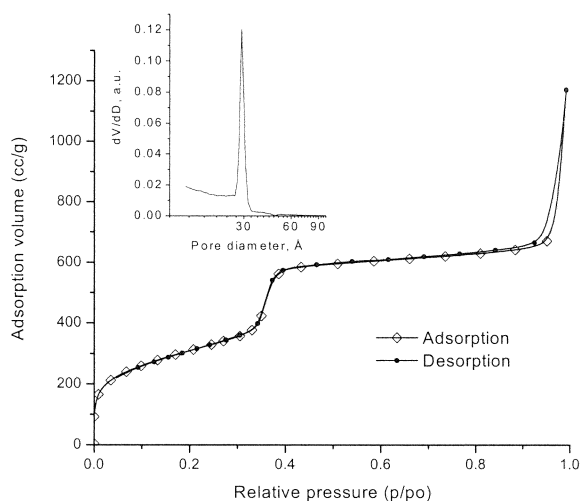


Figure 1. Adsorption isotherms and pore size distribution (the inset) for the fresh Co-MCM-41 template.

A fresh catalyst sample was submitted to three consecutive carbon deposition / oxidation cycles, following the procedure described above in the “Experimental” section. The TPO profiles observed after each of the carbon deposition steps are given in Figure 3. After the first reaction step, the TPO profile indicates a low selectivity to SWNT along with a very low carbon yield. It should be noted here that the physisorption measurement performed with the sample after carbon removal by oxidation indicated only a small loss of the pore volume, the pore size distribution remaining essentially the same. The TPO performed after the second carbon deposition step shows an enhanced selectivity to SWNT accompanied by a significant increase in the carbon yield.

The Raman spectrum recorded for the sample exposed to the second step of carbon deposition is given in Figure 4. The Raman bands present in the breathing mode ($150\text{-}350\text{ cm}^{-1}$ region) indicate the nanotubes are relatively

uniform in size. The well known correlation between the diameter of the nanotubes and their characteristic signals in the breathing mode region of the Raman spectra [8] is most likely biased for the pore confined nanotubes because of their intimate contact and strong interaction with the pore walls of the MCM-41 material. Therefore, this correlation cannot be used to predict the exact size of the synthesized nanotubes, but still provides information with respect to the homogeneity of SWNT diameter. Also, the band centered near 1600 cm^{-1} suggests the nanotubes produced are mainly of metallic structure. The wide band centered near 1350 cm^{-1} is indicative of the presence of important amounts of amorphous carbon.

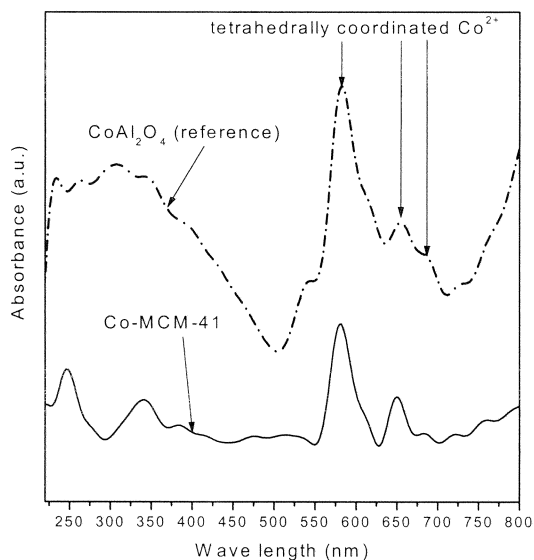


Figure 2. UV-vis spectra recorded for a fresh Co-MCM-41 sample compared with a reference spectrum of CoAl_2O_4 in which Co^{+2} ions are in tetrahedral coordination.

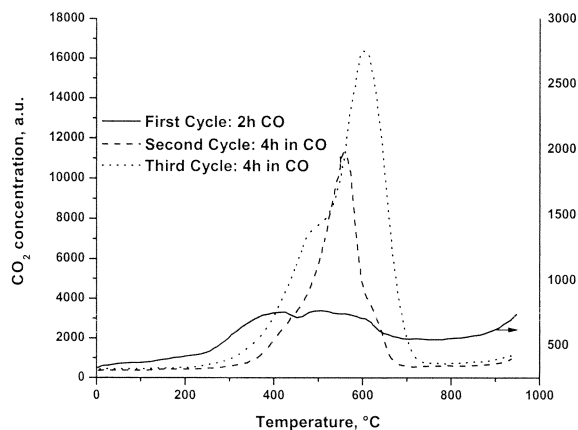


Figure 3. TPO profiles for samples after different carbon deposition step.

The SWNT selectivity was even higher after the third carbon deposition step along with the total carbon yield deposited on the template. However, it should be noted that the peak maximum for the SWNT oxidation shifted towards higher temperatures as the number of cycles increased.

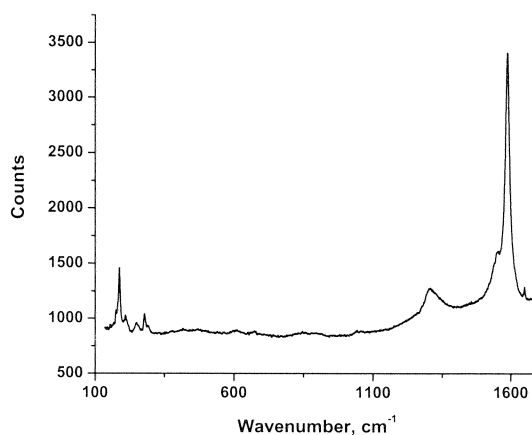


Figure 4. Raman spectrum recorded with the sample resulting from the second carbon deposition step.

Figure 5 shows the dark field TEM micrograph the Co-MCM-41 sample after the third carbon deposition step. The small white dots in the matrix may show the presence of metallic Co particles of the order of less than 1 nm in size located inside the pore system of the MCM-41 template. Interestingly, although both the Raman spectrum and the TPO are indicative of the presence of single wall carbon nanotubes, no SWNT were observed in TEM. This is not surprising as single walled nanotubes inside of the silica pore would not be expected to exhibit enough contrast with the silicon to be distinguishable. From thermo-gravimetric and differential thermal analysis (TG-DTA) the carbon loading on this sample was 4.7 wt%. The apparent pore size from TEM is approximately 2nm. TEM analysis of the empty template resulted in an apparent pore size of 2.8 nm. This difference is likely due to the presence of the SWNT.

Our preliminary studies suggest that we are able to fill the pores with open-ended nanotubes. Samples with good SWNT selectivity and carbon loading larger than 2-3.5% show an apparent increase in pore diameter when the capillary condensation data is analyzed with a fixed contact angle (for N_2 and silica) between the nitrogen and the wall. We believe that this is an artifact caused by the change in contact angle between nitrogen and a silica surface, and nitrogen and a carbon surface, respectively. The contact angle of nitrogen with a silica wall is larger than for a carbon wall, thus producing a pore size change consistent with carbon in the pores and open ended SWNT. Another observation consistent with SWNT inside the pores is that up to about 2% - 3.5% loading the samples are whitish gray and show a single SWNT peak in TPO. It should be noted that, assuming circular pores of 30 \AA diameter, pore walls 10 \AA thick and 2.2 g.cm^{-3} for both carbon and the Co-

MCM-41 catalytic template, filling the pores would result in a maximum increase in the weight of the catalyst of 15%. These observations suggest that the SWNT is open ended and inside of the pores.

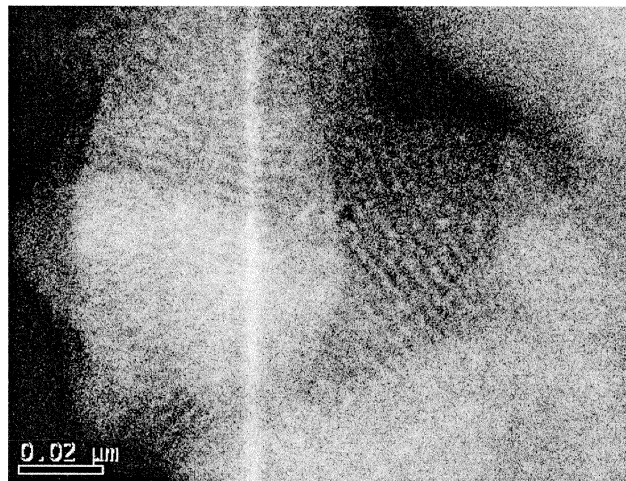


Figure 5. TEM micrograph recorded with the sample after the second carbon deposition step.

4 DISCUSSION

Both Raman spectroscopy and TPO experiments indicated the presence of SWNT on Co-MCM-41 molecular sieve after one or more exposures to CO at 750°C for 4 hours. Interestingly, the selectivity to SWNT increased with the number of carbon deposition – reoxidation cycles, suggesting the catalytic site responsible for SWNT growth is not initially present on the MCM-41 surface, but it is formed during exposure to CO. Because of the reducing character of the CO atmosphere, the active site is most likely a reduced state of cobalt. The TEM micrographs suggest the presence of ultra-small Co particles inside the pores of the MCM-41 catalytic template. This is consistent with the reduced cobalt species active for SWNT synthesis are metallic clusters of less than 1 nm in size, in a mechanism similar to the one proposed by Resasco [9]. Our SWNT diameter, however, may not be controlled by the metal particle size, as they are likely larger than any metal “particles” formed. Tube diameter from correlation with the Raman breathing mode data is 1.4 nm (fig.4). It should be noted that this correlation was shown to predict smaller diameter for SWNT in zeolites due to interactions between the SWNT and the pore wall.

Another interesting feature shown in the TEM data is the lack of sintering to large metal particles. Thus, incorporation of Co into the silica matrix of the MCM-41 material stabilizes Co against rapid reduction in the presence of CO leading to the formation of small Co clusters selective for SWNT formation, similarly to the cobalt – molybdenum catalysts used by Resasco and co-workers. This is consistent with the observation that

multiple cycling of Co-MCM-41 under reaction conditions does not lead to the formation of large metal particles.

The TEM data combined with physisorption measurements showing small differences between the pore volume of samples containing carbon, and after carbon removal suggest that the carbon nanotubes are located inside the pore system of the Co-MCM-41 template and are open-ended.

SWNT growing outside the pores may be responsible for the TPO maximum temperature shift towards higher values with increasing number of cycles, as observed in Figure 3 in that they may initiate formation of multi walled nanotubes (MWNT) or may simply aggregate into bundles that are more difficult to oxidize than isolated SWNT.

5 CONCLUSION

The results presented here suggest that MPMS templates with metals incorporated in the framework can exhibit good structural stability and can be used for growth of ordered SWNT of uniform size and structure at yields and selectivity promising for large scale applications. We are able to fill the pores with high selectivity. The templates become more reactive after being cycled under reaction conditions and a form of Co- silicate may be responsible for maintaining a high dispersion of the active site. The SWNT produced were predominantly metallic possibly suggesting that SWNT of uniform properties can be grown.

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