Bimetallic Catalysts for Production of Narrow Diameter Distribution Single Wall Carbon Nanotubes (SWNT)

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Introduction

. Electronic properties of SWNT depend on their diameter and chirality. Progress on applications has been hindered by low quality and knowledge of the diameter distribution in commercial SWNT. Achieving selectivity for nanotube diameters and consequently for the selectivity of their chirality is therefore one of the great challenges of SWNT research.

Highly ordered MCM-41 mesoporous molecular sieves isomorphously substituted with Co make excellent catalysts for the synthesis of uniform diameter SWNT by anchoring of small metallic Co clusters to partially reduced Co species during nanotube synthesis by CO disporportionation[1]. However these anchoring sites will eventually reduce completely under CO atmosphere, leading to an increase in the average Co particle size, which is crucial for the resultant nanotube diameter[2]. This can be overcome by introducing a second metallic component in the monometallic catalyst. The second metal component, inactive for SWNT growth and only partially reducible under the synthesis conditions acts as an anchoring site stabilizing narrow Co particle domains.

We demonstrate selectivity in the growth of single wall carbon nanotubes (SWNT) using a CoCr –MCM- 41 catalyst. The effect of different molecular ratios between the two metals on the SWNT diameter distribution was studied. We have found that by adding Cr to the Co-MCM- 41 monometallic catalyst, the SWNT diameter distribution narrowed in a systematic manner correlated to the development of a bimetallic oxide in the MCM41 framework during catalyst synthesis[3].

Materials and Methods

Catalysts were synthesized by isomorphous substitution of silicon in the MCM-41 framework structure with Co and/or Cr. The SWNT synthesis was carried out in two main steps. The first step is the pre-reduction of the catalyst in hydrogen when the metal ions in the framework are partially reduced followed by reaction with pure CO at the chosen temperature. In this phase metal cobalt clusters are formed that initiate the growth of SWNT.

Various techniques were employed to analyze both the catalysts and the SWNT: Temperature Programmed Reduction (TPR), Extended X-ray Absorption Fine Structure (EXAFS), Raman and Fluorescence Spectroscopy, Transmission Electron Microscopy.

Results and discussion

Both TPR and EXAFS analysis suggest that the initial state of the catalyst is characterized by the formation of a cobalt chromate like specie in the framework in which the oxidation states are +6 for Cr and +2 for Co. During exposure to hydrogen and carbon monoxide, the Cr ions reduce to a +2 oxidation state while the Co ions reduce to zerovalent state. However, when compared to the monometallic Co-MCM41 catalyst the reduction of the Co ions takes place much slower over a broader range of temperature due to the interaction with the Cr. Subsequent EXAFS analysis of the catalysts after exposure to CO shows the average first shell coordination number to be smaller than the size of the same clusters obtained on the monometallic catalyst.

Analysis of SWNT (by multiple excitation wavelength Raman, Fluorescence and TEM) synthesized on both the monometallic and the bimetallic catalysts showed a progressive narrowing of the diameter distribution from the monometallic to the bimetallic more so for the higher Cr:Co molar ratios. This effect was noted at different reaction temperatures. Small narrowly distributed nanotubes (under 0.7 nm diameter) were synthesized at the lower reaction temperature (600 ^{0}C).

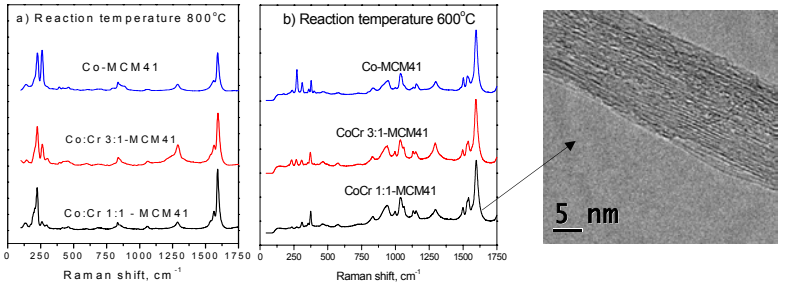

Fig 1: Raman spectra collected for SWNT synthesized on monometallic and bimetallic catalysts at two different reaction temperatures: a) 800^{o}C and b) 600^{o}C at 785 nm excitation wavelength showing the progressive suppression of some of the features present in the RBM region (200-400 cm^{-1}) for the monometallic catalyst. These features are associated with tube diameter. This data shows only a portion of the sample, but is consistent with the other SWNT measurements techniques. TEM imaging (right) shows a narrowly distributed small diameter SWNT bundle synthesized on the bimetallic catalyst with a 1:1 Co:Cr molar ratio.

Significance

The possibility of tuning the SWNT synthesis process towards desired dimeters and chiralities can lead to exciting advancements in SWNT research concerning various applications such as electronic devices.

References

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