Control of (n,m) Selectivity in Single Wall Carbon Nanotubes (SWNT) Growth by Varying the Co-Ni Ratio in Bimetallic Co-Ni-MCM 41 Catalysts

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Metals incorporated in the silica framework of MCM-41 mesoporous molecular sieves have been previously used as catalyst precursors for the synthesis of single wall carbon nanotubes (SWNT). Among other metals, cobalt and nickel gave very good selectivity for SWNT with narrow diameter distribution. Here, we report on the synthesis and characterization of bimetallic Co-Ni catalyst precursors incorporated in MCM-41 by isomorphous substitution of silicon ions in the framework. Bimetallic Co-Ni-MCM-41 catalysts were synthesized by the sol-gel method at 3 wt% total metal loading with 1:1, 3:1 and 5:1 Co:Ni molar ratios, using a C16 surfactant template. The resulting structure was characterized by N2 physisorption and X-ray diffraction (XRD) and the stability of the transition metal ions incorporated in the MCM-41 silica framework was assessed by temperature programmed reduction (TPR). The catalysts were employed in the CO disproportionation (Boudouard reaction) to form SWNT. The synthesis conditions consisted of catalyst pre-reduction in hydrogen at 300, 400 and 500 °C for 30 min followed by reaction with pure CO at 6 atm and 750°C for 1 h. The diameter distribution of the nanotubes grown was investigated by Raman spectroscopy and high resolution transmission electron microscopy (TEM). The total carbon yield was determined by thermo-gravimetical analysis (TGA). The Raman results suggest that the synthesized nanotubes have a rather wide diameter distribution and introduction of Ni to monometallic catalyst had shifted the diameters of the tubes in the direction of smaller diameter. However, the large G/D ratio indicates that the resulting SWNT have very good structure and low concentration of amorphous and defective carbon.

Keywords: Single Walled Carbon nanotubes, Cobalt, Nickel, selectivity, diameter

The MCM-41 (Mobile Composition of Matter) is a highly aligned silica structure which offers advantages towards a good accommodation of metal ions. The MCM-41 structure is characterized by high surface area, low diffusion resistance, ion exchangeable, alteration of pore size, flexible framework structure (isomorphous substitution of Si with a broad range of metal ions). The mainly features of using MCM-41 as catalyst rely on its special geometric and chemical properties.

Metal ions directly incorporated in the silica framework of MCM-41 mesoporous molecular sieves have been successfully used as catalyst precursors for the synthesis of single wall carbon nanotubes (SWNT), mainly because this catalyst type provides basic geometric template for SWNT structure or controllable subnanometer scale metallic clusters as seeds for SWNT growth. The main advantage of using metal incorporated MCM-41 is that the reducibility of metallic species incorporated into the walls can be widely varied in a convenient way [1-3].

The interest for SWNT relies on their unusually small size and excellent electronic and mechanical properties that have made them attractive for a large number of applications such gas filtration, sensing, energy storage devices or solid phase extraction.

SWNT posses nonpolar bonds, high length/diameter ratio, good surface area to volume ration, excellent van der Waals physisorption properties, excellent thermal stability in inert atmosphere and the possibility of good stability up to 1200°C, high affinity for aggregation, are insoluble in water but can be solubilized in aqueous medium by surfactant addition, can be immobilized onto solid supports such silica or steel and can be modified covalently [4].

The electronic properties of SWNT depend on their geometry, i.e. diameter and chirality and the great challenge nowadays is to synthesize SWNT with desired structure.

Along the time, there were many attempts focused on controlled particle size SWNT synthesis based on different metals such cobalt, nickel, iron, chromium, vanadium incorporated in the framework of MCM-41 [5-8]. By changing different synthesis parameters, interesting results related to the SWNT diameter distribution were obtained for Co-MCM-41 catalysts and Ni-MCM-41.

In order to optimize the distribution of the diameter of SWNT we propose a study that presents our investigation on the effect of associating Co with Ni as catalyst precursors incorporated in the pore walls of MCM-41 by isomorphous substitution of silicon ions in the framework on the performance of the catalytic synthesis of SWNT. In case of the bimetallic catalysts, the advantage of MCM-41 as templates is that subnanometer particles can be formed in the confined environment and are stabilized by the high radius of curvature of the pore wall [2, 16].

The subject of our study is how to use the bimetallic Co-Ni-MCM-41 as catalyst for synthesis of controllable particle size SWNT. By introducing the second metal into the system we have expected to detect smaller, more uniformly distributed sizes of the clusters that lead to a more uniform distribution of SWNT and chiralities [9, 10].
Experimental part

Catalyst synthesis

Bimetallic NiCo-MCM-41 with 3 wt% total metal loading with different Ni:Co molar ratios (1:1, 3:1 and 5:1) were synthesized together with monometallic Ni-MCM-41 with 3 wt% Ni loading and Co-MCM-41 with 3 wt% Co loading, for comparison, according to isomorphous substitution of silicon from silica framework with Co and/or Ni, the method being described in detail elsewhere [11, 12]. All catalysts were synthesized using C16 organic template and a surfactant, a silica source (Tetramethylammonium silicate) and a metal source (Co and Ni salts) were used as base materials for catalysts preparation. Studies showed that the structure and properties of MCM-41 are highly sensitive to synthesis parameters such as silica sources, period of aging of the synthesized gel, silica solution concentration, surfactant concentration, anti-foaming agent, pH of solution, synthesis method, and calcinations condition [1]. The prepared catalysts evidence a high degree of structural order and uniformity of mesoporous pores.

Catalyst characterization

Temperature programmed reduction (TPR)

Temperature programmed reduction is a useful characterization technique for investigating and designing of catalysts i.e. CoNi-MCM-41. TPR can provide important surface chemical information such as material species, stability, metal distribution, etc. The reducibility of Ni and Co ions incorporated in MCM-41 has been determined by temperature programmed reduction. About 100 mg of catalyst sample were loaded in a quartz cell. The gas flow used for each TPR run was a mixture of 5% hydrogen and 95% argon and the base line was monitored until stable. After stabilization of base line, the quartz cell was heated into H2 flow under atmospheric pressure and 5°C/min from room temperature to the desired pre-reduction temperature, and kept constant for 30 minutes. Between the two synthesis steps, the catalyst was purged with high purity argon and then heated up to 800°C at 5°C/min in argon flow. SWNT were grown for 60 min at different temperatures under 6 atm pressure [6, 7, 13, 14].

SWNT characterization

Raman spectroscopy

In order to evaluate the SWNT diameter distribution Raman spectra of the SWNT samples were recorded using a Jasco LASER Raman Spectrophotometer NRS-3100 Series. All spectra were recorded using two excitation laser wavelengths 532 nm (2.40 eV) and 785 nm (1.58 eV).

Transmission electron microscopy (TEM)

TEM with atomic scale resolution remains the most powerful tool to image nanoscale materials and to evaluate the diameter of SWNT, the pore structure of MCM-41 and metallic clusters with diameter larger than 10nm. TEM images of the SWNT were recorded using a Tecnai F 12 200 kV microscope. The SWNT samples were sonicated in ethanol and then dispersed previous to investigate the carbon framework.

Thermo-gravimetical analysis (TGA)

The analyses were collected in a NETZSCH model STA 449 F3 Jupiter® instrument for measurement of the temperature-dependent mass changes and energetic effects.

Results and discussions

Catalysts synthesized

By TPR investigation we are expecting to obtain the temperature of the maximum reaction rate as well as the area underneath the profile corresponding to the hydrogen amount needed in the reaction process. The TPR profiles for monometallic Co-MCM-41, Ni-MCM-41 are in agreement to Yang's [3]. The temperature of maximum reduction rate for Ni-MCM-41 (740°C) was approximately 61°C lower than that corresponding to monometallic Co-MCM-41, therefore we are expected that Ni-MCM-41 will require a lower pre-reduction temperature
than Co-MCM-41 (810 °C) in order to achieve controllable
metallic nickel clusters suitable for SWNT synthesis.

In the case of bimetallic catalysts, nickel and cobalt
seem to behave differently under temperature controlled
exposure to hydrogen when compared to the monometallic
Co-MCM-41 and Ni-MCM-41.

To determine how the incorporation of cobalt, nickel
and the mixture cobalt-nickel affect the structure of MCM-
41, the catalyst samples were characterized by nitrogen
physisorption technique. Few papers [3, 15, 17] claim that
up to a certain amount of metal, the incorporation will
improve the structure of the silica polymer by knitting the
defects, which results in a increase in a pore diameter due
to a larger transition element ion size or higher metal oxygen
bond length while the unimodal pore size distribution is
maintained.

Figure 1 shows the nitrogen physisorption isotherms and
pore size distribution of the monometallic Co-MCM-41 and
bimetallic Co:Ni 1:1, 3:1 and 5:1. All isotherms are
reversible with no hysteresis and all samples present sharp
capillary condensation which indicates that all samples
have uniform structure.

A slight decrease in the pore diameter and mesopore
volume was observed as Co:Ni ratio increases. The pore
size distribution pattern of samples synthesized at different
Co:Ni molar ratio, which are calculated by BJH method,
are shown in figure 1 b. All the samples prepared at Co:Ni
1:1, 3:1 and 5:1 molar ratio show narrow pore size
distribution, with the full width at half maximum (FWHM)
about 0.5 nm, shown in table 1.

The XRD patterns of CoNi-MCM-41 samples synthesized
using different Co:Ni molar ratios are illustrated in figure 2.

The XRD pattern, attributed to hexagonal mesoporous
arrangement, shows three or four peaks, in our case only
three. The first one gives a sharp (100) plane diffraction
and the other two peaks correspond to higher Miller index
planes (110) and (200), indicating that the mesostructures
are well developed. The XRD pattern from figure 2 proves
that the catalyst structure is formed for all three samples
and all are suitable for the synthesis of single-wall carbon
nanotubes by catalytic vapour phase deposition method.
The intensity of (100) peak decreases with rising of Co:Ni
molar ratio.

We also calculate the crystallite size for all samples.
The Scherrer equation (1) gives a correspondence between
the crystallite size (LC) and the full width of half maximum
(FWHM):

$$LC = \frac{180}{\pi} \frac{k \lambda}{\cos \Theta \cdot \sqrt{FWHM^2 - s^2}}$$  \hspace{1cm} (1)

where:
- $k$ is the Scherrer constant (0.89),
- $\lambda$ - the wavelength of the radiation (1.54Å);
- $s$ - the instrumental broadening (for our instrument is
0).

In table 1 is presented the indexing of diffraction lines
for CoNi-MCM-41 catalysts with different Co:Ni molar ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$ (°)</th>
<th>d-spacing (nm)</th>
<th>Counts</th>
<th>$FWHM$ (Å)</th>
<th>LC (Å)</th>
<th>BJH pore diameter (Å)</th>
<th>Pore volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co:Ni (1:1)</td>
<td>2.345</td>
<td>3.764</td>
<td>1972</td>
<td>0.418</td>
<td>188</td>
<td>28.62</td>
<td>1.031</td>
</tr>
<tr>
<td>Co:Ni (3:1)</td>
<td>2.231</td>
<td>3.956</td>
<td>1566</td>
<td>0.427</td>
<td>184</td>
<td>27.85</td>
<td>1.028</td>
</tr>
<tr>
<td>Co:Ni (5:1)</td>
<td>2.336</td>
<td>3.779</td>
<td>123</td>
<td>0.579</td>
<td>135.7</td>
<td>27.82</td>
<td>1.018</td>
</tr>
</tbody>
</table>

Fig. 1. Nitrogen physisorption results of the monometallic Co-MCM-41, Ni-MCM-41 and bimetallic
Co:Ni 1:1, 3:1 and 5:1: (a) adsorption isotherms; (b) pore size distribution

Fig. 2. XRD patterns of CoNi-MCM-41 synthesized with different
Co:Ni molar ratio
The crystallite sizes for our samples are between 135.7-188 Å and decrease with rising of Co:Ni molar ratio.

**SWNT synthesized**

Raman spectra of SWNT show three features: The Radial Breathing Mode (RBM) below 300 cm⁻¹, the Disorder-induced band (D band) around 1300 cm⁻¹ and the Graphite-like band (G band) around 1550-1600 cm⁻¹.

The RBM position is correlated to the SWNT diameter which can be roughly calculated with an equation developed by Araujo and coworkers

\[ \omega_{RBM} = \frac{A}{d_t} + B, \]

where \( A \) and \( B \) are constants (\( A=219 \), \( B=15 \)), \( \omega_{RBM} \) denotes the Raman shift and \( d_t \) represents the diameter of SWNT [15].

Figure 3 shows the Raman spectra collected at 785 nm laser wavelength for as-reacted catalysts with different molar ratio Co:Ni (1:1, 3:1 and 5:1), prereduced at the same temperature (400°C).

The presence of the characteristic features for the RBM around 140-264 cm⁻¹ and the peak centered at 1590 cm⁻¹ indicate the presence of SWNT.

The Raman spectra of SWNT synthesized with C16-CoNi-MCM41 template at different Co:Ni molar ratio shows three peaks in the RBM region, suggesting a wide distribution of the tube diameters.

In table 2 are depicted the diameters of SWNT calculated for the catalyst samples with different molar ratio Co:Ni (1:1, 3:1 and 5:1), prereduced at the same temperature (400°C). The range of the calculated diameters is between 0.88-1.72 nm. It should be noted that we cannot see a noticeable influence of the molar ratio because, despite of a wide distribution of the tube diameters, the templates with different Co:Ni molar ratio have practically the same diameters. The low intensity of the D band centered at 1292 cm⁻¹, characterized for disorder carbon species coupled with a supra unitary G band/D band ratio suggests a very good selectivity for SWNT synthesized. Related to the high ratio between G band and D band, all three samples show high selectivity but the sample CoNi-MCM41 (Co:Ni 3:1) seems to have smaller defects in the graphene structure of SWNT.

Figure 4 shows the Raman shift recorded after SWNT growth with catalyst sample Co: Ni (3:1) prereduced at different temperatures (300, 400 and 500°C).

As the prereduction temperature increases, the peaks in the RBM region become stronger for 400°C prereduction temperature. By rising the prereduction temperature from 300°C to 400°C the diameter distribution becomes broaden from 0.89 nm to 1.73 nm.

The diameter uniformity of the tubes suggested by Raman was also confirmed by TEM images. The calculated values for the nanotube diameters are given in table 3.

The purity index (G band/D band) for the SWNT synthesized with CoNi-MCM41 (Co:Ni 3:1 molar ratio) at

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter, nm</th>
<th>G band/D band</th>
</tr>
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<tbody>
<tr>
<td>Co:Ni (1:1)</td>
<td>1.69</td>
<td>1.03</td>
</tr>
<tr>
<td>Co:Ni (3:1)</td>
<td>1.70</td>
<td>1.03</td>
</tr>
<tr>
<td>Co:Ni (5:1)</td>
<td>1.72</td>
<td>1.03</td>
</tr>
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</table>

**Table 2**

DIAMETER DISTRIBUTION OF THE CARBON NANOTUBES FOR DIFFERENT MOLAR RATIO CATALYST SAMPLES PREREDUCED AT 400°C AND 750°C REDUCTION IN Co
different prereduction temperatures evidence good selectivity for SWNT synthesized.

Our experimental studies concluded that the diameters of carbon nanotubes can be controlled by changing their prereduction temperature in the presence of CO.

Morphological and structural characterization of carbon nanotubes obtained by vapour phase catalytic deposition was performed using Tecnai F 12 200 kV microscope from Yale University.

In figures 5 and 6 are shown TEM images of CoNi-MCM-41 (Co: Ni 1:1 molar ratio) sample that was obtained by incorporation of 3wt% total metal in MCM-41. In TEM images we can easily evidence the carbon nanotubes grow inside the pores of the catalytic template. Small clusters of cobalt and nickel appear dispersed along carbon nanotubes and attached to the catalyst surfaces as shown in figure 5. The presence of many clusters of cobalt and nickel shows that ions existing in the bimetallic CoNi-MCM-41 catalyst were completely reduced to cobalt and nickel metal which means that these ions incorporated in silica MCM-41 have higher chemical reactivity for CO and could be easily reduced.

Strong reactivity between Ni and CO is the main factor in controlling catalyst diameters on CoNi-MCM 41. Experimental studies showed that diameters of carbon nanotubes depend on the reduction temperature in the presence of CO that lead to the idea that diameters of carbon nanotubes could be controlled by modifying the reduction temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter, nm</th>
<th>G band/D band</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co: Ni (300°C, H₂ prereduction)</td>
<td>1.73</td>
<td>1.05</td>
</tr>
<tr>
<td>Co: Ni (400°C, H₂ prereduction)</td>
<td>1.70</td>
<td>1.03</td>
</tr>
<tr>
<td>Co: Ni (500°C, H₂ prereduction)</td>
<td>1.67</td>
<td>1.16</td>
</tr>
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</table>

The TEM images from figure 5 are in agreement to TGA results which prove that the content of ordered species is about 12%.

The TGA of carbon materials is based on the different oxidation temperature of different carbon structures. The amorphous carbon is completely oxidized at temperature below 350°C, the graphite burn at temperature above 750°C, while the SWNT’s have a variable oxidation temperature depending on the synthesis conditions (i.e. differences in the catalytic activity of metallic particles existing into SWNT as impurities) [3]. We are expected to have oxidation of carbon nanotubes (single and multiwall) at temperatures between 400-650°C.

The resulting mass changes (TG) and heat flow rates (DSC) can be seen from figures 7, 8 and 9. The mass loss below ~200°C is due to the evaporation of moisture which is accompanied by an endothermic DSC peak (enthalpy 60-70 J/g). At higher temperatures the SWCNs burn-up in two steps which are exothermic processes. The residual mass of ~88% reflects the molecular sieve matrix. Between ~250°C and ~300°C a slight increase of the sample weight of ~0.1% occurred which is most probably due to oxidation of, e.g., a metallic component like Co or Ni. This can be concluded from the exothermic DSC peak in the same temperature range.

Figure 10 displays again the measured data (at temperatures above the slight increase of the weight) together with non-linear regression curves obtained from the NETZSCH Thermokinetics software. A two-step model and n-th order reactions were used. The kinetic parameters...
Fig. 8. Temperature-dependent mass change (TG) and heat flow rate (DSC) of the SWCN sample measured at 5 K/min.

Fig. 9. Temperature-dependent mass change (TG) and heat flow rate (DSC) of the SWCN sample measured at 10 K/min.

Fig. 10. Temperature-dependent mass changes of the SWCN sample measured at 2, 5 and 10 K/min (symbols) together with the non-linear regression data of the NETZSCH Thermokinetics software using a two-step model.

Table 4

<table>
<thead>
<tr>
<th>Correlation</th>
<th>1st order</th>
<th>2nd order</th>
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</thead>
<tbody>
<tr>
<td>coefficient</td>
<td>Pre-exponential</td>
<td>Activation Energy</td>
</tr>
<tr>
<td></td>
<td>factor</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>0.999427</td>
<td>5.47507</td>
<td>105.16600</td>
</tr>
</tbody>
</table>

KINETIC PARAMETERS OF A 2 STEP MODEL OF nTH REACTION ORDER
like activation energies and pre-exponential-factors can be seen in table 4.

Conclusions

Our studies demonstrate selectivity towards diameter and identity of single wall carbon nanotubes by use of a bimetallic CoNi catalyst supported on a MCM-41 silica template.

Incorporation of a second metal (Ni) into the Co-MCM-41 framework seems to be beneficial for the structural stability and can be successfully used for growth of ordered SWNT of uniform size.

Bimetallic Co:Ni-MCM-41 catalysts with different Co:Ni molar ratio have been synthesized and characterized by N2 physisorption and X-Ray diffraction.

Our results show that by co-incorporating Ni with Co in MCM-41 catalysts the distribution of SWNT types is narrowed, the average diameter is shifted to lower values and the resultant carbon yield is increased as compared with a monometallic MCM-41 catalyst.

The influence of the pre-reduction temperature over the SWNT synthesis on CoNi-MCM-41 catalysts was investigated. We conclude that the diameters of carbon nanotubes can be controlled by changing their pre-reduction temperature in the presence of CO and the diameter and the chirality of SWNT can be modified by adding a second metal phase during the synthesis of molecular sieve.

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