Synthesis of Single Walled Carbon Nanotubes (SWNT) by Chemical Vapour Deposition on MCM-41 Supported Ni Catalysts Obtained by Incorporation and Impregnation

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Two different methods, incorporation and impregnation, were used for the synthesis of Ni-MCM-41 catalysts used as catalytic templates for producing single walled carbon nanotubes (SWNT). The synthesized Ni catalysts were characterized by X-Ray diffraction (XRD). The SWNT produced by chemical vapour deposition using carbon monoxide as carbon source were characterized by RAMAN spectroscopy at two excitation wavelengths (785 nm and 532 nm) and by transmission electron microscopy (TEM).

Keywords: Ni-MCM-41 catalysts, incorporation, impregnation, SWNT

Single walled carbon nanotubes (SWNT) have attracted a great deal of attention since their discovery in 1991 [1], owing to their unique electrical and mechanical properties [2, 3]. Single walled carbon nanotubes are remarkable nanostructures with promising perspectives for application as batteries [4], actuators [5] and various electronic devices [6]. However, their large scale application in industrial processes has been hindered by the difficulty in selectively synthesizing batches of SWNT with uniform properties and high purity at large yields.

The study of silica-based mesoporous materials started about two decades ago [7] with the discovery of a new type of mesoporous materials based on silica by a group of researchers from Mobil Company at the beginning of the 90's. Several types of these materials are well known such as MCM-41, MCM-48, MCM-50 (Mobil Composition of Matter No. 41, 48, 50). From this series the most investigated material is MCM-41 characterized by a highly uniform structure with parallel pores packed in a hexagonal arrangement, whose diameters can be controlled independently of the chemical composition of their amorphous walls. Due to their high surface area, MCM-41 are attractive for heterogeneous catalysis applications because they provide very good metal dispersion properties and are suitable as catalytic supports.

For several years now, transition metal substituted MCM-41 have been investigated as catalysts for the growth of uniform diameter single wall carbon nanotubes on size-controllable, sub-nanometer metallic clusters obtained by different reduction strategies of the metallic ions isomorphously substituted for silicon ions in the MCM-41 matrix [8]. Since incorporation of catalyst precursor ions in the silica matrix of MCM-41 materials is not necessarily a trivial task, here we report on our attempt to grow SWNT on Ni clusters impregnated on MCM-41 by comparison with nanotubes grown on Ni clusters resulting from the reduction of Ni ions incorporated into the silica framework of MCM-41. The results obtained show the advantage of controlling the Ni reduction process, respectively the size of the metallic clusters formed on the catalyst. Different techniques such as transmission electron microscopy (TEM) and Raman spectroscopy at two excitation wavelengths (785 nm and 532 nm) were used to characterize the SWNT produced. The experimental results showed the Ni catalyst prepared by incorporation is more versatile and its operation can be tuned to obtain tubes of rather uniform diameter with good selectivity, while the impregnated catalyst produces larger amounts of graphite and tubes of wider diameter distribution.

Experimental part

Ni-MCM-41 catalysts were prepared following two different routes. The incorporated Ni-MCM-41 catalyst was obtained following a method described in the literature [9]. The first step was to prepare the surfactant solution. The silica source Cab-O-Sil was mixed with tetramethylamonium silicate aqueous solution under vigorous stirring. Nickel acetate aqueous solution (7.5 g) was added to the solution and mixed for 1h, for the good incorporation of Ni. The *p*H of the final solution was adjusted to 11.5 by adding acetic acid. The final solution was autoclaved into a polypropylene bottle for 6 days at approximately 100°C. The solution was then cooled to room temperature, double filtered and dried at 75°C for 12h. The solid powder obtained was heated to 550°C in flowing He in 18 h and soaked at that temperature for 6 h in flowing air. The resulting powder is further referred to as Ni-MCM-41 incorporated.

The catalyst synthesized by impregnation was obtained by the dispersion of a Ni precursor on the surface of the mesoporous molecular sieve. Preparation of impregnated catalyst was performed in two steps:

- synthesis of the catalytic support (silica MCM-41);
- impregnation of the support obtained with a solution of the active metal salt that is nickel acetate.

Approximately 2 g of the synthesized silica MCM-41 were used for impregnation with nickel acetate solution containing approximately 0.06g Ni to give 3wt% total metal loading in the resulting MCM-41 catalyst. After the incipient wetness impregnation procedure, the catalyst was dried and calcined at 500°C in flowing air for 1 hour, to give the final catalyst, which will be further referred to as Ni-MCM-41 impregnated.

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Both Ni-MCM-41 catalysts, incorporated and impregnated (Ni particles impregnated on the silica MCM-41 support) were characterized by X-ray diffraction. Diffractograms were recorded on a D8 ADVANCE Nova diffractometer using the characteristic radiation K_α of copper, at a voltage of 40 kV and 5mA intensity.

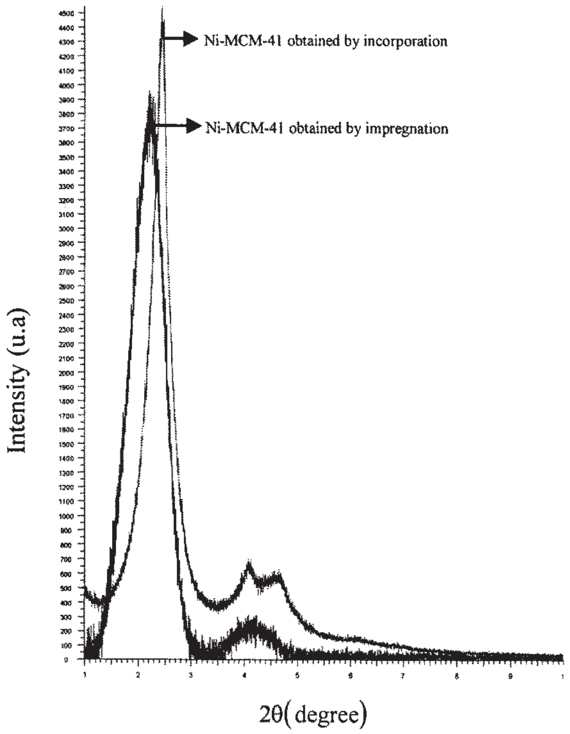

Fig. 1. X-ray diffractograms of the Ni-MCM-41 incorporated catalyst and for the Ni particles impregnated on the silica MCM-41 support

Both Ni-MCM-41 catalysts, impregnated and incorporated, were employed to grow SWNT by CO disproportionation – the Boudouard reaction – using different reaction conditions. About 200 mg of catalyst were loaded in a quartz reactor of 18 mm internal diameter placed in a ceramic radiant heater that allows accurate control of the catalytic bed temperature. The catalyst pretreatment and reaction conditions were different for the Ni-MCM-41 impregnated catalyst than for Ni-MCM-41 incorporated catalyst. For the incorporated catalyst the SWNT synthesis was carried out in two steps. The first step consisted of catalyst pre-reduction in pure flowing hydrogen (200cc/min) at atmospheric pressure during heating to 600°C at 5°C/min prior to the exposure of the Ni-MCM-41 to flowing CO. After the pre-reduction step, the catalyst was purged with pure argon for 30 min at the pre-reduction temperature and then heated to the desired reaction temperature at 5°C/min in argon flow. The second step consisted in exposing the catalyst to pure CO at different temperatures and 6 atm for the growth of SWNT for 60 min. After this second reaction step the catalyst was naturally cooled to room temperature under pure argon flow. The sample with SWNT grown on Ni-MCM-41 catalyst obtained by incorporation is further denoted as P3-Ni-MCM-41. The catalyst prepared by impregnation was heated directly to the desired reaction temperature at 5°C/min under flowing argon and then exposed to CO for 60 min, followed by cooling under flowing argon to room temperature, similar to the catalyst prepared by incorporation. The sample with SWNT grown on Ni-MCM-41 catalyst obtained by impregnation is further denoted as P7-Ni-MCM-41. Raman spectra of the SWNT produced were recorded using two excitation wavelengths (785 nm and 532 nm) on a NRS-3000 Raman instrument from Jasco.

Results and discussions

Figure 1 shows the X-ray diffractograms of the incorporated Ni-MCM-41 catalyst and for the Ni particles impregnated on the silica MCM-41 support for 2 angles from 1 to 10°. The X-Ray diffraction patterns show the typical structure for MCM-41 type materials generated by the characteristic hexagonal pore structure. Both materials show good structure; however, the main difference between the two catalysts prepared by impregnation and incorporation, respectively, is that in the incorporated catalyst fewer Ni ions are exposed to the gas phase, compared to the impregnated catalyst in which most of the Ni ions are exposed to the gas phase as NiO particles or clusters. It is therefore expected that the Ni ions in the impregnated catalyst are easier to reduce than Ni ions in the catalyst prepared by incorporation.

The Raman spectra in figures 2 and 3 recorded for samples exposed to CO at 750°C indicated that the Ni-MCM-41 catalysts prepared following the two methods initiate the growth of carbon nanotubes. This is especially important for the impregnated catalyst as incorporation of transition metal ions in the silica framework of the MCM-41 materials is not trivial and the metal loading is often limited by structural stability of the resulting material, as discussed by other authors [10]. If catalysts can be produced by impregnation for the synthesis of SWNT, the price per unit of product should drop significantly.

While the incorporated catalyst is not reducible under CO atmosphere, as demonstrated elsewhere [11], the impregnated catalyst is easily reduced upon exposure to CO at temperatures of 750°C or higher producing SWNT, consistent with the Ni ions being exposed to the gas phase, as discussed above. However, SWNT produced with the catalyst obtained by impregnation have a wider diameter distribution centered towards larger diameters and the catalyst shows lower selectivity for SWNT and higher selectivity for graphite. All these results suggest larger Ni particles form on the impregnated catalyst than on the incorporated one, consistent with a faster reduction rate and higher mobility of Ni clusters on the catalyst prepared by impregnation. Indeed, TEM images showed in figures 4 and 5 show larger metallic clusters on the impregnated catalyst compared with the incorporated one.

Raman spectroscopy represents a powerful tool providing useful structural information on the quasi one-dimensional SWNT. Raman spectra of the SWNT samples were recorded using the 785 nm and 532 nm laser lines for excitation. Figures 2 and 3 show the Raman spectra collected at 785 nm and 532 nm laser wavelengths, respectively, for the SWNT produced by CO disproportionation on catalyst samples prepared by incorporation and impregnation. The Raman Breathing Mode peaks (RBM) under 450 cm^{-1} are characteristic for SWNT and provide information on the diameter and electronic properties of these materials; the D band around 1300 cm^{-1} correlates with the disordered carbon species, and the G band around 1600 cm^{-1} is the peak assigned to the tangential vibration mode of ordered carbon species such as carbon nanotubes and graphite. The RBM region is particularly of interest since the spectral features in this region are resonant and the peak intensities have a strong dependence on the tube diameters. There are several reports showing the SWNT diameter correlates with the position of the RBM peak by the following equation: RBM (cm^{-1}) = $234/d_t + 10$ where d_t is the tube diameter in nm [12]. This equation was used to calculate the diameters shown in table 1.

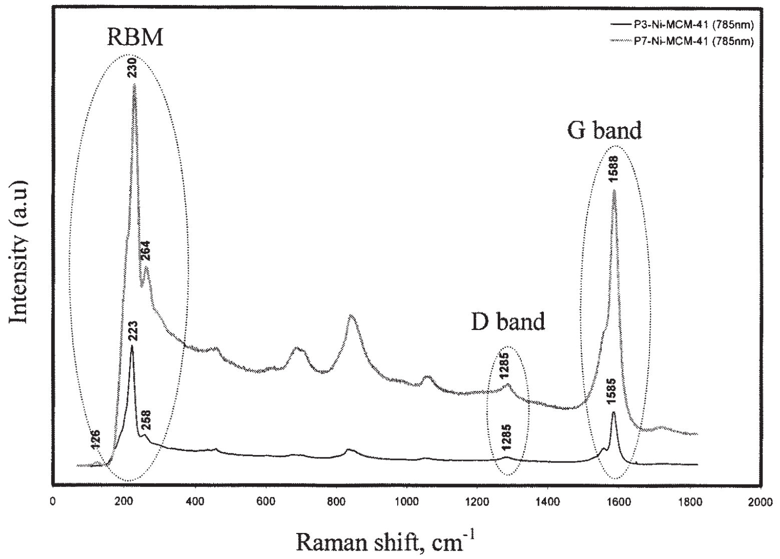

Fig. 2. Raman spectra recorded using the 785 nm laser wavelength for SWNT samples synthesized at 750°C on Ni-MCM-41 catalysts

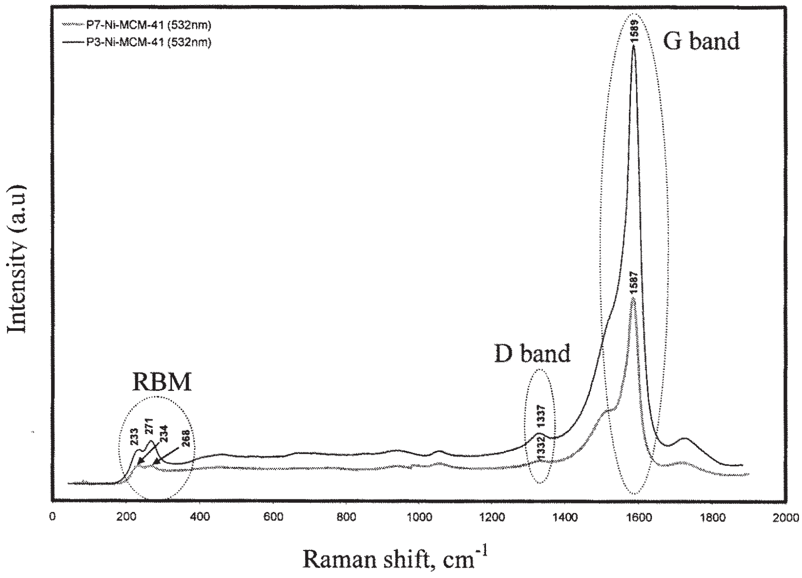

Fig. 3. Raman spectra recorded using the 532 nm laser wavelength for SWNT samples synthesized at 750°C on Ni-MCM-41 catalysts

Table 1
CALCULATION OF THE SWNT DIAMETER

P3-Ni-MCM-41 (the sample with SWNT grown on Ni-MCM-41 catalyst obtained by incorporation)				**P7-Ni-MCM-41 (the sample with SWNT grown on Ni-MCM-41 catalyst obtained by impregnation)**		
λ(nm)	**RBM, cm^{-1}**	**D_t, nm**	**G/D**	**RBM, cm^{-1}**	**D_t, nm**	**G/D**
532	233	1.05	6.76	234	1.04	4.83
	271	0.90		268	0.91	
785	223	1.09	3.27	126	2.02	2.95
				230	1.06	
	258	0.94		264	0.88	

The G/D peak intensity ratios can be employed to assessing the quality of the SWNT sample. Ratios higher than 1 are determined for both catalysts suggesting that the SWNT obtained have a good structure.

Transmission Electron Microscopy imaging with atomic scale resolution remains the most powerful tool to image nanoscale materials. TEM images of SWNT were collected on a Tecnai F20 200 kV microscope and are depicted in figures 4 and 5.

Figures 4 and 5 show TEM images of the SWNT grown on Ni-MCM-41 catalysts obtained by incorporation and impregnation, respectively. The samples investigated by TEM are pristine samples, without any treatment for removal of silica or metal particles. Some of the MCM-41 template and metal particles are also visible. All images show good structure of the SWNT produced, with no evidence for MWNT.

In figure 4 we observe that most of the nanotubes grow bundled, even they originate from different pores of the catalyst. The SWNT grown from the incorporated catalyst look more uniform in diameter, consistent with the Raman results. For this sample, the average diameter of the Ni crystallites is around 4 nm.

In figure 5 is readily observed that SWNT produced by chemical vapor deposition on Ni-MCM-41 synthesized by impregnation have a wider distribution of tube diameters, consistent with the Raman spectra in figure 3. The Ni particles observed in figure 5 are larger size than the one observed in figure 4 and seem covered with graphite, which

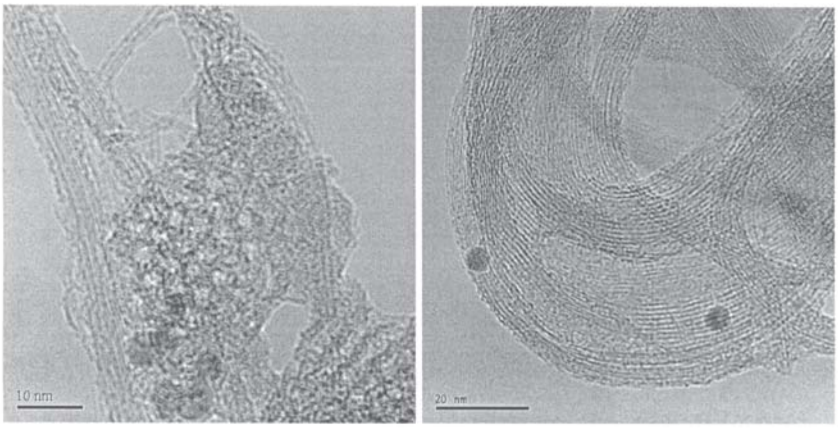

Fig. 4. TEM images of the SWNT grown on Ni-MCM-41 catalyst obtained by incorporation

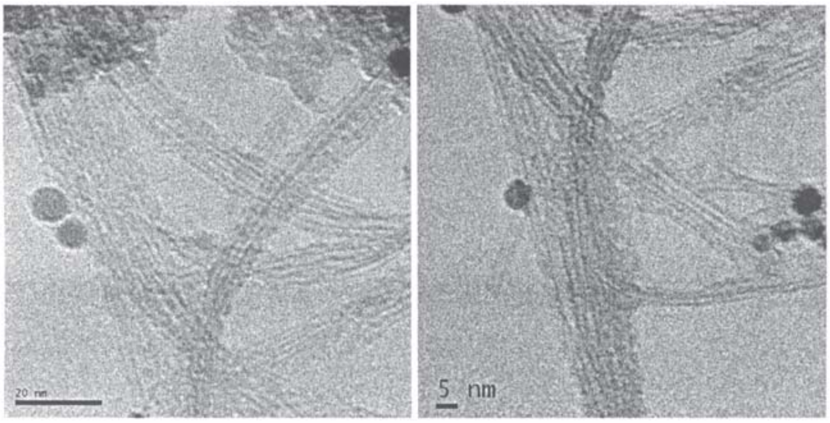

Fig. 5. TEM images of the SWNT grown on Ni-MCM-41 catalyst obtained by impregnation

may be a good explanation for the relatively high G/D ratio also observed with this catalyst. We may therefore state that the TEM images showed in the figure 4 and 5 indicate a low content of disordered carbon consistent with the Raman results.

Conclusions

The results of our investigations suggest that mesoporous molecular sieve templates with Ni incorporated in the framework exhibit good structural stability and can be used for growth of SWNT. Raman spectra show that SWNT were synthesized with a narrow diameter distribution and high selectivity.

The method of adding the metal to the catalyst – impregnation and incorporation, respectively – influences the structure of the SWNT produced, as well as the selectivity of the nanotubes produced. The results obtained by Raman and TEM suggest that SWNT produced by chemical vapor deposition on Ni-MCM-41 synthesized by incorporation have a rather narrow diameter distribution, while the catalyst prepared by impregnation of Ni precursors on silica MCM-41 produces SWNT with a wider distribution of tube diameters. Anchoring of the nickel clusters on the silica surface seems to be the determining factor in the SWNT diameter control most likely because Ni exhibits a strong affinity for CO and adsorption of CO molecules make the metallic clusters more mobile on the surface such that Ni particles grow larger and faster, initiating the growth of larger tubes with a wider diameter distribution.

It was also shown that catalyst prepared by impregnation produces more amorphous and disordered carbon than that synthesized by incorporation, likely requiring more complicated purification procedures. However, we have shown that by adding Ni species through impregnation, the catalysts still initiate the growth of single walled carbon nanotubes and, controlling the reaction conditions, they may prove to be an alternative to the catalysts prepared by incorporation that are more difficult to synthesize.

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