

Synthesis of Single Walled Carbon Nanotubes Using Cobalt Grafted on MCM-41 Catalysts

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ABSTRACT

In this work single walled carbon nanotubes (SWNT) have been synthesized by high pressure CO disproportionation using cobalt grafted on MCM-41 by means of grafting method employing cobalt (II) acetylacetonate. The reduction temperature of the metal species of these catalysts and their physical properties characterized by XRD, nitrogen physisorption and temperature reduction programmed are compared to those of the catalyst prepared by in-situ incorporation.

The carbon nanotubes synthesized are characterized by Raman spectroscopy, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The results show a good and uniform dispersion of cobalt metallic particles on the MCM-41 even with higher loadings of metal than 3 wt%. The onset of reduction temperatures for the metal species as well as the pore size distribution of mesoporous catalysts decreased linearly with the increasing of metal concentration. The ratio between the G and D intensity bands for the carbon nanotubes remains constant with the metal concentrations used, however, the carbon yield increased linearly with the metal loading, without evidence of amorphous carbon corroborated by TEM and TGA.

The results also showed that a better yield for the SWNT synthesis is obtained in the catalyst prepared by grafting in comparison to the catalysts prepared by in-situ incorporation, which is an important alternative in the production of SWNTs on a bigger scale.

Keywords: carbon nanotubes, grafting, MCM-41, catalysis.

1 INTRODUCTION

The method used for the introduction of a metal in a given support is one of the principal factors that can affect the catalyst efficiency. In the case of using mesoporous silica as support, the metal has been commonly introduced by simple impregnation [1-3] or in-situ incorporation [4-10] and recently by atomic layer deposition [11] or grafting. In the first case the interactions between the metal and support are weak and all the metallic species can be reduced at temperatures below 400 °C. When the metal is introduced in the mesoporous silica by in-situ incorporation, most of the metal species are in the silica walls and their reduction required higher temperature [10, 12-18]. The reducibility of ion species of the metal in the support controls the mobility and the size of final metallic clusters, to which the interaction between the support and metal is related. In general, for the synthesis of SWNTs is necessary to ensure small metal cluster size, with very good uniformity (less than 5 nm). A very interesting alternative to achieve smaller metallic particles seems to be the bonding of the metal to the silica surfaces through covalent bonds. In this work we have compared the efficiency of catalysts prepared by grafting and impregnation methods on the synthesis of SWNT by using the CO disproportionation reaction.

2 EXPERIMENTAL

The mesoporous silica MCM-41 was synthesized using Ca-O-Sil silica and tetramethylammonium silicate (TMASi) as described elsewhere [13]. Ten grams of TMASi are diluted in 50 g of water, and then 5.2 g of Cab-O-Sil silica were dispersed in the former solution. This solution was stirred for 30 min and then adequate quantity of CaSO₄·7H₂O solution was stirred for 30 minutes more in order to incorporate Co 3 wt % in the silica (Co-MCM-41 (I)). Finally 28.79 g of

cetyltrimethylammonium bromide (CTMABr) solution at 20 wt% are added and the final pH was adjusted to 11.5 with acetic acid. The solution is stirred again for one hour. The synthesis gels were sealed in a HDPP bottle and placed in an autoclave for 6 days at 100 °C. The catalysts were washed with distilled water, and dried at 80 °C overnight. The surfactant was eliminated by heating the sample from room temperature to 540 °C in a helium flow of 30 cm³/min with a heating rate of 0.5 °C/min and held at this temperature for one hour. After that, the helium was switched to flowing air at 45 cm³/min for 5 hours more at 540 °C.

For the catalysts of cobalt grafted on MCM-41 (Co-MCM-41 (g)), the mesoporous silica without metal was synthesized with the procedure described before. After calcination, the silica was refluxed in toluene for three hours with a nitrogen purge in order to eliminate any humidity. Separately, an appropriate quantity of cobalt (II) acetylacetonate was put in toluene and stirred in a nitrogen purged reflux for three hours. After that, the solution is cooled and placed in the silica solution. The final solution is stirred and refluxed overnight in nitrogen atmosphere and then, cooled again and the catalysts is recovered by filtration and washed several times with toluene. The final product is calcinated with the same procedure described above.

The Temperature-Programmed Reduction (TPR) analyses was performed using a TCD detector of gas chromatograph (6890 plus, Agilent). One hundred mg of the catalyst was placed in a quartz cell. The sample was purged with helium at 20 cm³/min. The helium flow was switched to 5 % H₂ in argon balance. The sample cell was then heated at 5 °C/min and held for 1 h at 1000 °C to ensure complete cobalt reduction. The N₂ adsorption-desorption studies were carried out at -196 °C with a static volumetric instrument Autosorb-1C (Quantachrome) to examine the mesoporous properties of the catalysts.

For the SWNT synthesis, two hundred mg of each catalyst were reduced at a 700 °C for 30 minutes in flowing hydrogen at 1atm. After reduction, the hydrogen is displaced with argon and the carbon nanotubes were synthesized by CO disproportionation at 800 °C for 30 minutes at 4.5 atm. The CO feed was first passed through a carbonyl trap to eliminate iron pentacarbonyl originating from the CO container. The oven is cooled in an argon flow and the material is recovered. The Raman spectra of nanotubes were recorded in a JASCO NRS-3100

Laser Raman Spectrophotometer with an excitation radiation at 785 cm⁻¹.

3 RESULTS AND DISCUSSIONS

Figure 1 (up) shows the pore size distribution for the catalyst prepared by grafting with different loadings of metal. As the concentration of cobalt increases the pore diameter becomes smaller, evidence of deposition of metal layer on the silica. For the TPR (down), in all cases the temperature at the maximum reduction rate was always higher than 800 °C, for the catalyst prepared by grafting and the onset of reduction decreased as the metal concentration increased. In the case of cobalt incorporated in the MCM-41 the reduction temperature began at lower values with a temperature at the maximum reduction rate about 770 °C.

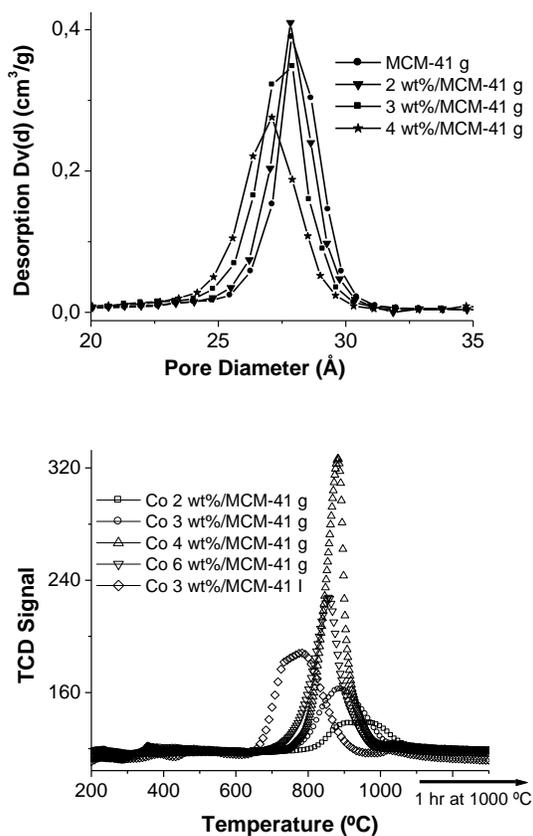


Figure 1. Up: Pore size distribution (BJH) for the catalysts prepared by grafting. Down: TPR profiles for the catalysts prepared by grafting and incorporation method with different concentrations of cobalt.

The final metal concentration after synthesis was determined by atomic absorption for the catalysts of Co 3 wt %/MCM-41 (g) and Co 3 wt%/MCM-41 (I). The final concentration of cobalt was 0.9 wt % for grafting and 1.5 wt % for incorporation. Evidently the grafting process is less effective in the incorporation of cobalt in comparison with the incorporation method. The adhesion of cobalt to the silica by grafting is determined among several factors, by the density of silanol groups on the silica surface and its availability to reaction; in the case of bonded silanol groups the probability of formation the covalent bond Si-O-Co is more limited.

Figure 2 shows the thermogravimetric analyses of the reaction products with carbon monoxide without purification, as expected an increase in the cobalt concentration provided to higher yield of carbon products. There are two weight losses both of them assigned to carbon nanotubes oxidation, as will be demonstrated by TEM. The first one may be related to oxidation of shorter tubes that are in contact with metal particles, and the second one is attributed to the oxidation of bundles of nanotubes with greater length. The second weight loss increased with the concentration of cobalt, but the first one remains almost constant, one possible explanation could be associated with part of SWNT growing within the pore and once in contact with the silica wall at the bottom of the pore, its growth could be more limited. Figure 2 (up) also shows the carbon nanotubes yield using the catalyst Co 3 wt%/MCM-41 (g) and Co 3wt%/MCM-41 (I), it is calculated as the global weight loss, the yield for cobalt grafted in just 1.5 % less than those prepared by metal incorporation, which finally has more metal available for reaction with the CO. It is also worth noting that the thermal stability of SWNT is higher when the cobalt grafted on MCM-41 catalyst is used, probably due to the formation of larger carbon nanotubes. If the yield is considered in terms of mg of cobalt per mg of carbon obtained, for 200 mg of each catalyst, 1.8 mg Co the grafted cobalt produces 28.7 mg of SWNT and 32.5 mg of SWNT are produced by

3.0 mg of Co incorporated in-situ in the MCM-41 silica.

Figure 3 shows the TEM images for carbon nanotubes synthesized on Co 3 wt % grafted in MCM-41. It is possible to see bundles of carbon nanotubes with high purity and homogenous diameters and no carbon amorphous carbon is observed by TEM. The diameter of nanotubes is about 1 nm, which is corroborated by Raman spectroscopy. It is still possible to see atomic layer of MCM-41 silica template after reaction; the small dark dots correspond to the metallic clusters of cobalt of nanometric size. For the SWNT synthesized on Co 3wt % (1.5)/MCM-41 (I) no amorphous carbon was observed.

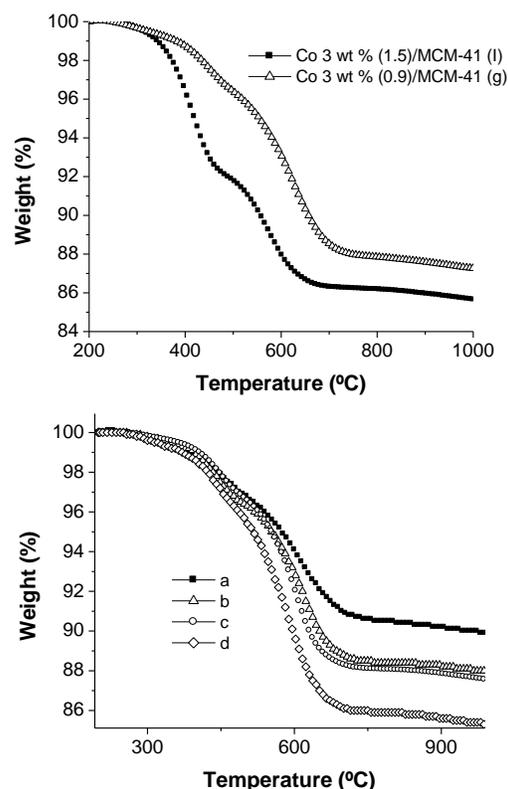


Figure 2. Up: TGA of SWNT synthesized using Co 3 wt % (0.9)/MCM-41 (g) and Co 3wt % (1.5)/MCM-41 (I). The number in parenthesis represent the actual concentration determined by chemical analysis, g = grafting, I= In-situ Incorporation. Down: TGA of SWNT synthesized on Co grafted in MCM-41 with a nominal concentration of 2 wt % (a), 3 wt % (b), 4 wt % (c) and 6 wt % (d).

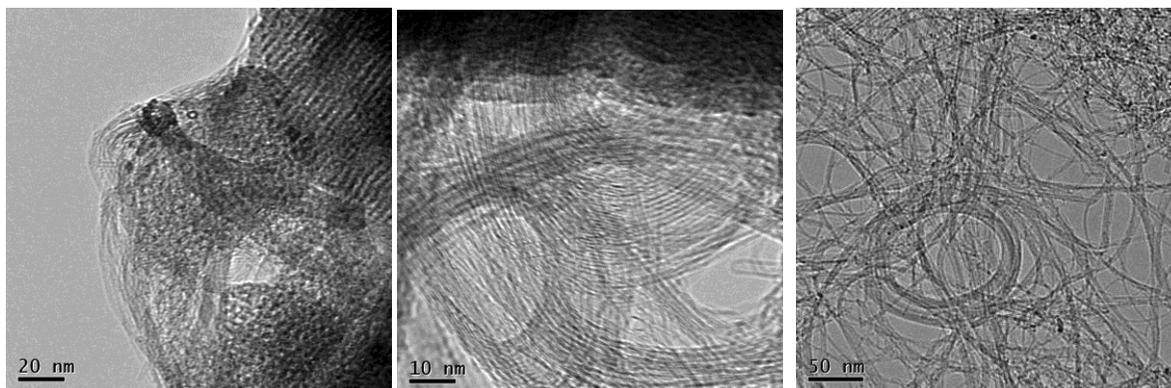


Figure 3. TEM images of the SWNT as-synthesized using Co 3 wt% grafted in MCM-41.

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