Thermal Stability of Carbon Nanotubes produced by Catalytic Chemical Vapor Deposition of Ethylene on Different Supports

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ABSTRACT

We have studied thermal stability and the morphology of MWCNTs obtained by catalytic chemical vapor deposition (CCVD) of ethylene as hydrocarbon precursor of nanotubes, using 6% iron and 12 % cobalt as bimetallic catalysts on calcium carbonate, magnesium oxide and mesoporous silica MCM41 as supports. The results show that when bimetallic catalyst of Fe-Co is supported on $CaCO_3$ a higher amount of carbon nanotubes is produced, but they have a broad diameter size distribution varying from 40 nm to 85 nm, depending on the ethylene flow. At higher concentration of ethylene, the diameter of MWCNTs became higher and the thermal stability of the carbonaceous material is increased. Otherwise the carbon nanotubes synthesized using MgO and mesoporous silica MCM41 as supports present lower diameter with a better structural regularity. The diameter of nanotubes varies from 15 to 33 nm when mesoporous silica support is used and from 7 to 18 nm for MgO support. If the iron on mesoporous support is previously reduced, the efficiency of carbon nanotubes production increases.

Keywords: *Carbon nanotubes, CCVD, support, ethylene.*

1 INTRODUCTION

The carbon nanotubes are an interesting material due to its extraordinaire properties as high module tensile, thermal and electric conductivity among others [1,2]. One of the techniques more promissory in the synthesis of carbon nanotubes is without doubt CCVD. In this synthesis technique many parameters has been studied as the temperature effect and reaction time [3-9], the type of metallic catalyst and its concentration [10-20] as well as the hydrocarbon source [21], however relatively few works has been devoted in the study the effect that support has over the nature and yield of carbon nanotubes.

In this work we make a comparative study that the kind of support has in the quality of final carbon nanotubes obtained using always the same amount of bimetallic catalyst on the more common supports used in the literature, namely; calcium carbonate, magnesium oxide and mesoporous silica. We study also the effect of the concentration of ethylene, and the effect of the previous reduction of iron catalyst particles on mesoporous silica supports.

2 EXPERIMENTAL

The MgO and $CaCO_3$ are from Merck. The mesoporous silica MCM41 used as support is prepared from sodium silicate (Merck) as silica source and cetyltrimethylammonium bromide (Acros) as template.

The catalysts are prepared by the impregnation method by dissolving in distilled water the appropriate quantity of $Fe(NO_3).9H_2O$ and $Co(NO_3)_2.6H_2O$ salts (Merck) in order to generate 6 % and 12 % in weight of iron and cobalt respectively in relation with the support weight. The catalyst solution is added to a suspension that contained the support and stirred during 30 minutes, then, the solvent is evaporated, the final material is grinded and heated at 120 ºC overnight.

The MWCNTs are synthesized in an oven with temperature control. In a typical procedure 500 mg of catalyst are placed inside of a quartz tube (U form) under nitrogen flow of 100 sccm and heating to 750 ºC. To start nanotubes carbon reaction, different concentrations of ethylene diluted in a 100 sccm nitrogen are supplied by 30 minutes; finally the oven is cooled a room temperature. The materials synthesized by using $CaCO_3$ and MgO as supports are dissolved in 30 % nitric acid overnight and then filtrated and washed with plenty distilled water and dry in oven at 100 ºC. In the case of mesoporous silica hydrofluoric acid is used to eliminate the support. When the iron catalysts is supported on mesoporous silica, the iron is reduced by supplying 50 sccm hydrogen in 150 sccm nitrogen flow during 15 minute, then 100 sccm nitrogen is flowed during the 15 minute more to eliminate the remnant hydrogen.

The samples are characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), X-ray diffraction and nitrogen adsorption desorption.

3 RESULTS

3.1 Effect of the support and the ethylene flow

The figure 1 (a) shows the TGA thermograms of raw material produced by deposition of ethylene using 6 % Fe and 12 % Co as catalysts on different supports. Only one weight lost is presents around 600 ºC. The $CaCO_3$ support present the higher weight lost of 69.7 %, followed by 52.9 % of the mesoporous silica support and 36.9 % of MgO. This weight lost is assigned principally to carbon nanotubos, but even at this temperature some amorphous carbon is present as confirmed by TEM images (not showed). It can be deduced that when MgO is used as support the carbon nanotubes exhibit lower diameter and they degrades at lower temperature and more amorphous carbon is present.

For the mesoporous silica support which has high surface area, it is deduced that an adequate dispersion of metallic cluster on the support reflects a more uniform diameter of carbon nanotubes, the external diameters vary from 15 to 33 nm and internal diameter is about 10 nm. However when the same concentration of metal is introduced on calcium carbonate under the same experimental condition, due to its lower surface area, a poor dispersion of the metallic clusters generate a broad distribution in the diameter of nanotubes from 40 to 80 nm.

When MgO support is used, the carbon nanotubes diameters are thinner compare with other supports (7-18 nm) but the efficiency of carbon nanotubes mass production respect to the initial mass of the catalyst is only 32.2 % (52.9 % for MCM41 and 69.8 % for $CaCO_3$)and more amount of amorphous carbon is observed in the final material. This support seems more adequate in the synthesis of single wall carbon nanotubes as it has been reported elsewhere [22-25].

Apparently in this support the metallic clusters are well dispersed but the activity of these is reduced in the experimental conditions worked. We are studying the relation between the chemical structure of the metallic species and the degree of dispersion.

The influence of ethylene concentration in the efficiency and nature of carbon obtained is also evaluated. In the figure 1b we can see that when the ethylene flow increases, the temperature of degradation of carbon nanotubes is higher and the total decomposition takes place in broad temperature range indicating the presence of different carbon phases. When only 200 sccm of ethylene without nitrogen dilution is supplied a higher yield near to 85.7 % carbon is obtained, however the nanotubes are too thick with more defects in the surface and its diameters are about 85 nm. Instead of, the carbon nanotubes synthesized using a ethylene/nitrogen relation of 100/100 produces carbon nanotubes with a lower average diameter (48 nm).

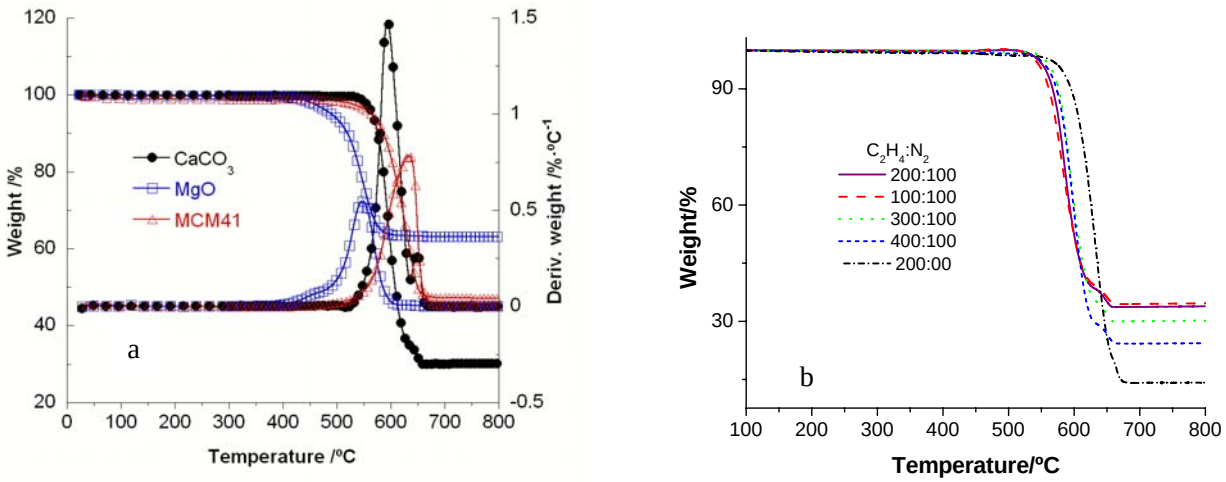

Figure 1. Thermo gravimetric analysis of raw material synthesized by CCVD using 6 % Fe-12 % Co as catalyst (a) Carbon nanotubes supported on MgO, MCM41 and $CaCO_3$ using 300 sccm C_2H_4 in 100 sccm of N_2 (b) Carbon nanotubes synthesized supported on $CaCO_3$ with different ethylene flows

3.2 Effect of the Fe/MCM41 catalyst reduction

The effect of iron catalyst reduction supported on mesoporous silica on the thermal stability of the final product is studied. The figure 2a showed that when the iron catalyst is reduced only one weight lost of 50.1 % near to 600 ºC is observed corresponding to carbon nanotubes decomposition. But, when the catalyst is not reduced two lost of weight are seen, the first one of 18.7 % at 263 ºC and second one of 47.8 % near 600 ºC corresponding to amorphous carbon and carbon nanotubes respectively. This suggests that when iron oxides are present on mesoporous support, they can interact with the silica surface decreasing the catalyst efficiency and more carbon amorphous is produced as can be seen in the TEM micrographs (figure 3a). The particles of metal oxides can be also occluded inside the porous of the material, making more difficult the growing of carbon nanotubes.

The purification of the final product obtained without catalyst reduction requires the treatment with hydrofluoric acid to eliminate the mesoporous silica support and metallic particles, after a heating at 500 ºC to eliminate the amorphous carbon and finally a treatment with nitric acid to eliminate metallic particles that were inside the amorphous carbon. The purification of the final product obtained with catalyst reduction only requires treatment with hydrofluoric acid. It is found that the product obtained with catalyst reduction presents 98 % purity in comparison with 85 % for the product obtained without any previous catalyst reduction process (figure 2b), in addition the decomposition temperature range is wider and presents lower thermal stability indicating still presence of amorphous carbon and a higher quantity of metal particles inside of nanotubes which are not eliminate by acid treatments because they are cover by grapheme sheets.

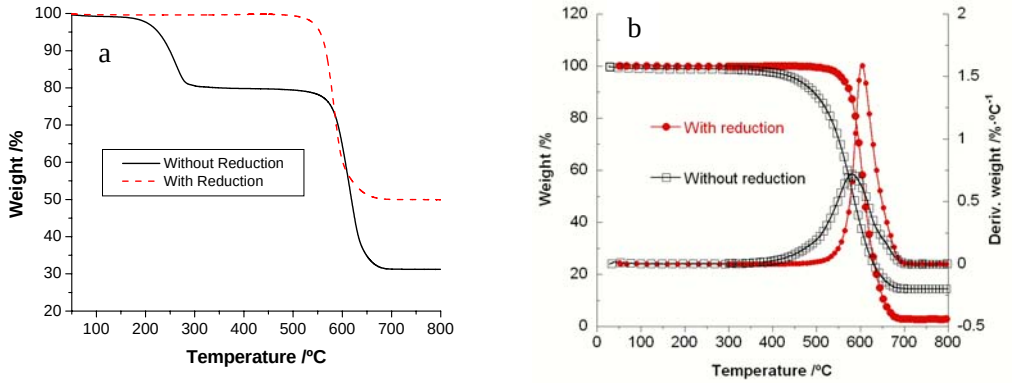

Figure 2. TGA thermograms of the carbon nanotubes obtained by CCVD of ethylene to 300 sccm in nitrogen to 100 sccm over 6 % Fe-MCM41 (a). The unpurified product with and without reduction of catalyst. b).After purification treatments.

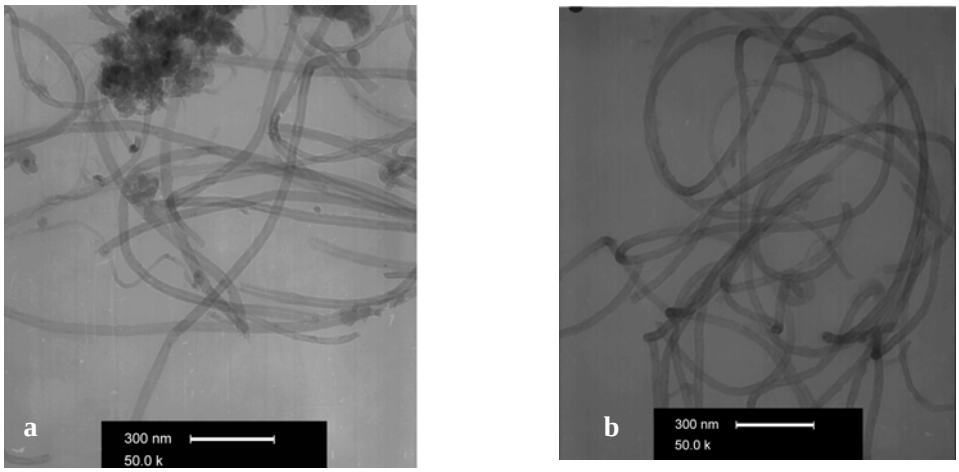

Figure 3. TEM micrographs of MWCNTs synthesized on 6%Fe/MCM41 a). Without Fe catalyst reduction b) After Fe catalyst reduction

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REFERENCES

1. V.N. Popov, Materials Science and Engineering, R43, 61 (2004)
2. T. W. Odom, J. Huang, P. Kim, and C. Lieber, J. Phys. Chem B, 104, 2794 (2000)
3. C. Klinke, R. Kurt, J. M. Bonard, K. Kern, J. Phys. Chem. B 106, 11191 (2002).
4. Y. Li et al., Carbon 43, 1325 (2005).
5. H. Igarashi, H. Murakami, S. Maruyama, N. Nakashima, Chemical Physics Letters 392, 529 (2004).
6. A. Huczko, Applied Physics A Materials Science & Processing 74, 617 (2002).
7. J. H. Hafner et al., Chemical Physics Letters 296, 195 (1998).
8. A.-C. Dupuis, Progress in Materials Science 50, 929 (2005).
9. P. Mauron et al., Diamond and Related Materials 12, 780 (2003).
10. P. Ramesh, N. Kishi, T. Sugai, H. Shinohara, J. Phys. Chem. B 110, 130 (2006).
11.Y. Yang, Z. Hu, Y. N. Lu, Y. Chen, Materials Chemistry and Physics 82, 440 (2003).
12. J. Cheng et al., Materials Chemistry and Physics 95, 5 (2006).
13.B. C. Liu, B. Yu, M. X. Zhang, Chemical Physics Letters 407, 232 (2005).
14. C. J. Lee, J. Park, S. Y. Kang, J. H. Lee, Chemical Physics Letters 323, 554 (2000).
15. A. M. Cassell, S. Verma, L. Delzeit, M. Meyyappan, J. Han, Langmuir 17, 260 (2001).
16. A. K. M. Fazle Kibria, Y. H. Mo, K. S. Nahm, M. J. Kim, Carbon 40, 1241 (2002)
17. E. Couteau et al., Chemical Physics Letters 378, 9 (2003).
18. J W Seo et al., New Journal of Physics 120, 1367 (2003).
19. K. V. Katok, V. A. Tertykh, G. P. Prikhod'ko, Materials Chemistry and Physics 96, 396 (2006)
20. Y. Chen, D. Ciuparu, S. Lim, G. L. Haller, L. D. Pfefferle, Carbon 44, 67 (2006).
21. A. Fonseca et al., Applied Physics A Materials Science & Processing 67, 11 (1998).
22. B. C. Liu et al., Chemical Physics Letters 383, 104 (2004).
23. E. Flahaut, A. Peigney, Ch. Laurent, A. Rousset, Journal of Materials Chemistry 10, 249 (2002).
24. S. C. Lyu et al., J. Phys. Chem. B 108, 1613 (2004).
25. H. Ago, K. Nakamura, N. Uehara and M. Tsuji, J. Phys. Chem. B., 108, 18908 (2004).