3

Synthesis of Carbon Nanotubes Using Metal-Modified Nanoporous Silicas

Pezhman Zarabadi-Poor and Alireza Badiei
School of Chemistry, College of Science, University of Tehran, Tehran, Iran

1. Introduction

Some years ago a scientist, Sumio Iijima, who was working in NEC laboratories in Japan as an electron microscopist has discovered a new class of carbon allotropes which attracted a lot of interests among material science investigators. Briefly, after some investigation on the produced soot on walls of arc discharge reactor he examined the precipitated soot on cathode and has found really interesting graphitic structures. The taken transmission electron microscopy (TEM) images revealed a tubular graphitic structure that has fascinated the scientist due its extraordinary physical and chemical properties (Iijima, 1991).

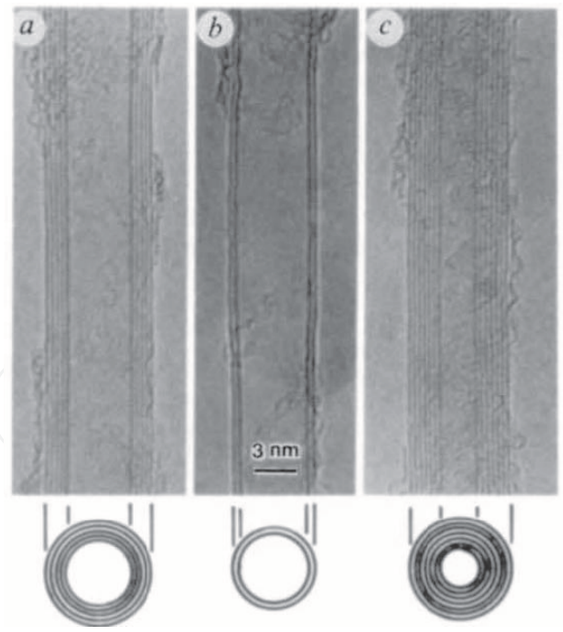


Fig. 1. TEM micrographs of carbon nanotubes consisting (a) five, (b) two, (c) seven graphitic sheets (Iijima, 1991)

After 1991, considerable attention of scientists to carbon nanotubes (CNTs) caused remarkable increase of publication around carbon nanotube related subjects of interests (Fig. 2). Increasing the number of publications from 77 in 1995 to 5619 in 2010 and total number

of 37112 publications until the end of 2010, all shows that there are some interesting points in carbon nanotubes which led to this enormous attention of researchers. Basically, unique electronic, optoelectronic, and mechanical properties of carbon nanotubes (Saito & Dresselhaus, 1998) are among the most important reasons for this huge attention to them. These properties make CNTs suitable for a lot of applications such as electronic devices (Fuhrer et al., 2000), chemical sensors (Kong et al., 2000), hydrogen storage (Dillon et al., 1997), mechanical devices (Frank et al., 1998), field emission tips (Fan et al., 1999), nanotweezers (Kim & Lieber, 1999), and so on.

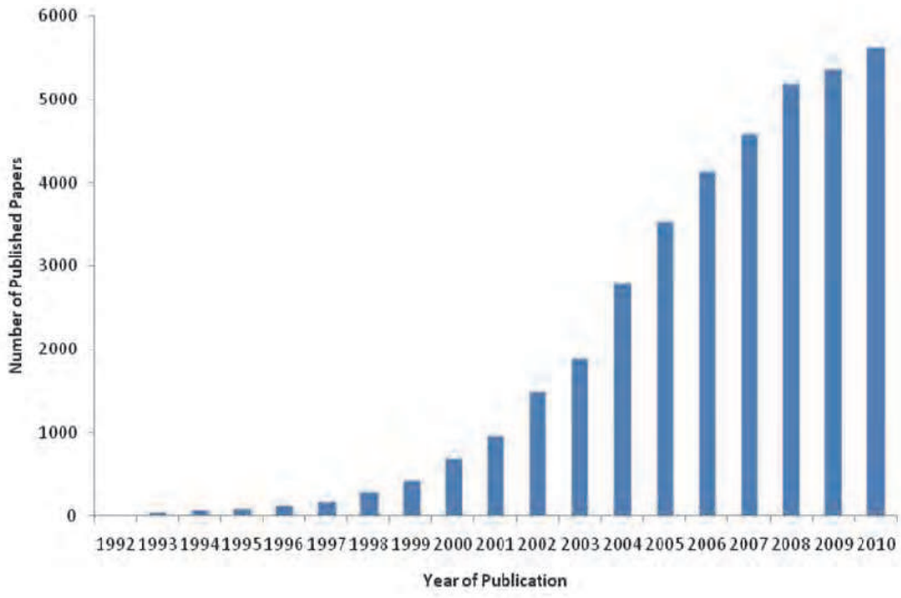


Fig. 2. The annual number of published papers on carbon nanotubes since their discovery until the end of 2010. Data were taken from www.scopus.com using carbon nanotubes* as keyword for article title.

Accordingly, application of carbon nanotubes in aforementioned and other devices needs production of CNTs. Up to know, several synthetic approaches such as arc discharge (Iijima, 1991; Iijima & Ichihashi, 1993; Tans et al., 1997), laser ablation (Guo et al., 1995; Thess et al., 1996), chemical vapor deposition (CVD) (Jose-Yacaman et al., 1993), were introduced to produce carbon nanotubes. Based on the related scientific literature, each of these methods has its charasteristics, advantageous and disadvantageous which define the applicability of mentioned methods. Among these methods, CVD has been shown to be of more industrial interest due to its lower reaction temperature in comparison with arc discharge and laser ablation (Morgan & Mokaya, 2008) and also possibility for industrial scale up (Geng et al., 2002; Somanathan et al., 2006). Indeed, catalytic CVD synthesis of CNTs can be accomplished via two general approaches, fluidized bed method (García-García et al., 2008; Wei et al., 2008) or fixed solid supported metal catalysts (Zarabadi-Poor et al., 2010). Therefore, these procedures need supporting of metals on solid supports to catalyze the carbon nanotubes preparation. Alumina (Zarabadi-Poor et al., 2010), nanoporous silica (Somanathan et al., 2006), MgO (Steplewska & Borowiak-Palen, 2010), and silicon (Mizuno et al., 2005) are among the most studied substrates.

In this chapter, the application of metal-modified nanoporous silicas for CNT growth in a CVD reactor will be reviewed. Herein, different nanoporous silicas which were used for production of carbon nanotubes considering different metals and catalyst preparation methods are the main subjects of following discussions.

2. Nanoporous silicas

In 1992, researchers of Mobil introduced a family of ordered nanoporous materials named M41S (Beck et al., 1992; Kresge et al., 1992). Then attraction of other scientists to this materials caused discovery of other types of nanoporous materials such as SBA-15 (Zhao et al., 1998), LUS-1 (Bonneviot et al., 2003),FSM-16 (Inagaki et al., 1993), KIT-1 (Ryoo et al., 1996), MSU (Bagshaw et al., 1995), and HSM (Tanev & Pinnavaia, 1995)which were synthesized within highly acidic to strongly basic pH range using cationic, anionic, neutral and nonionic structure directing agents. Among these materials, MCM-41, LUS-1 and SBA-15 are most studied ones in our previous researches such as studies on metal modification (Badiei & Bonneviot, 1998; Béland et al., 1998), pre-concentration of metals (Ganjali et al., 2006; Javanbakht et al., 2009b; Javanbakht et al., 2010), modification with 8-hydroxyquinoline (Badiei et al., 2011b; Badiei et al., 2011a), carbon paste electrodes (Ganjali et al., 2010; Javanbakht et al., 2007a; Javanbakht et al., 2007b; Javanbakht et al., 2009a), solid phase micro extraction (Hashemi et al., 2009) and hydroxylation catalysts (Arab et al.). Therefore, these materials are the major subject in the coming discussions about catalytic synthesis of CNTs.

One of most important application of solid supports such as nanoporous silicas is related to the heterogenization of transition metals (Cornils & Herrmann, 1996). Briefly, several methods have been used in this manner such as adsorption or encapsulation of homogenous catalyst (Coronado et al., 2000; Goettmann et al., 2006; Kuil et al., 2006; Zhu et al., 2004), covalent immobilization (Pagar et al., 2006), modification of supported metal catalysts (Marchetti et al., 2004) and etc. To the best of our knowledge, iron, cobalt and nickel are the most studied metals in catalytic production of carbon nanotubes and therefore they will be reviewed in following sections.

3. Synthesis of CNTs using Fe-modified nanoporous silicas

Several reports have been published on the synthesis of CNTs using iron-modified nanoporous silicas up to now. Duxiao et al. (Duxiao et al., 2001) investigated the CVD synthesis of carbon nanotubes on hexagonal nanoporous silica (HMS). They used acetylene as carbon precursor and showed that in the case of HMS the formation of CNTs started at the internal surface of Fe-HSM. In 2005, Lu et al. (Lu et al., 2005) addressed a rare report on the synthesis of carbon nanotubes. It was remarkable because it is related to the synthesis of amorphous carbon nanotubes via CVD procedure and using SBA-15 as the solid support for the iron based catalysts. They have employed impregnation method for introduction of iron species using $Fe(acac)_3$ as iron precursor into the structure of SBA-15 nanoporous silica. The main purpose of using SBA-15 as the solid support in the as mentioned published letter is the porous structure of SBA-15. They believe that it can lead the formation of metal catalysts with well-controlled particle size. They concluded from the formation of carbon nanotubes on the outer side (Fig. 3) of channels that particle migration happened during the CVD process and proposed "top growth mechanism" herein. Also, they mentioned that the outer

diameter of CNTs (about 20nm) is much higher than pore diameter of SBA-15 (about 7nm) which caused by the thickness of nanotubes.

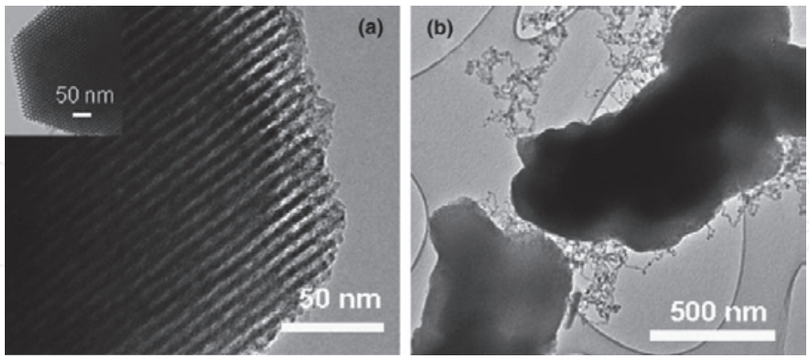


Fig. 3. TEM micrographs of a) Fe-SBA-15 and b) grown CNTs on the outer surface of catalyst (Lu et al., 2005)

Wang and his co-workers presented the synthesis of CNTs using Fe-SBA-15 catalysts (Wang et al., 2005a; Wang et al., 2005b). They, (Wang et al., 2005a), have synthesized Fe-SBA-15 via direct synthesis approach. Iron species were introduced into the structure through addition of iron nitrate nonahydrate during the synthesis of SBA-15 besides the increasing of pH to 7. According to their research, synthesis of multi-walled carbon nanotubes (MWNTs) by CVD decomposition of acetylene on the Fe-SBA-15 produced straight, uniform, open and highly graphitized CNTs. Increasing the amount of iron in the catalysts caused obtaining CNTs with larger diameters and as a conclusion the best CNTs can be obtained using catalysts with 3.5% iron content. A typical high resolution transmission electron microscopy (HRTEM) image of this sample is given in Fig. 4.

Fig. 4. HRTEM image of carbon nanotube prepared using catalyst with 3.5% iron (Wang et al., 2005a)

The same research group (Wang et al., 2005b), have tried to obtain Fe-SBA-15 with higher thermal stability. The synthesis procedure for the catalysts is similar to their previous works (Wang et al.,2005a). Their efforts to obtain more thermal stable catalysts have been accomplished by calcination of catalysts in the temperature ranging from 550 to 950 °C. Synthesis of carbon nanotubes were again done via similar procedure to the first article. They have concluded that the obtained CNTs are more uniformed with outer and inner diameters about 35nm and 15nm, respectively. In the other research Barreca et al. (Barreca et

al., 2007) used the advantages of direct synthesis approach for preparation of catalysts. They have used P85 triblock copolymer to synthesize hexagonal nanoporous silica under acidic condition. The iron phthalocyanine was used as iron precursor to incorporate the iron nanoparticles into the nanoporous structure. The acid treatment was applied to eliminate the Fe_2O_3 particles from the outer surface of nanoporous silicas. In the acid washed catalysts, MWNTs with narrow diameter distribution (5 and 15 nm) were obtained. On the other hand, unwashed catalysts produced CNTs on the outer surface with a broad diameter distribution ranging from 20 to 90nm. Also, higher metal content in both catalysts caused higher CNT density. The most recent report on the synthesis of carbon nanotubes using iron-modified nanoporous silica has been published by Gokulakrishnan and co-workers (Somanathan et al., 2011). KIT-6 type nanoporous silica was synthesized following typical routes through using P123 structure directing agent under acidic condition. Iron species were incorporated into the structure by impregnation of KIT-6 with iron nitrate solution. They have mentioned that 1-3% iron was loaded into KIT-6 which caused decreasing the specific area from 745 $m^2.g^{-1}$ (for KIT-6) to 653, 551, and 377 $m^2.g^{-1}$for 1%Fe, 2%Fe and 3%Fe, respectively. The CNT synthesis was carried using acetylene as carbon source at 800 °C. The best yield was obtained by 2% Fe loaded catalyst (91%). The 1% Fe catalysts did not show significant activity through the synthesis of CNTs. It was expected to obtain higher production yield when using catalyst with higher iron contents than 2% but it has not been observed. The observed yield for 3% Fe catalyst was reported 79% which is attributed to the agglomeration of iron particles. It has been concluded from TEM micrographs which 10 nm graphene layers consists of 29 graphene sheets. As a main conclusion the Fe-modified KIT-6 has been introduced as a potential for large scale production of multi-walled carbon nanotubes.

4. Synthesis of CNTs using Co-modified nanoporous silicas

To the best of our knowledge, MCM-41 is the major solid support in the most of the researches on the synthesis of CNTs using Co metal as the active site.

Lim et al. (Lim et al., 2003) utilized direct synthesis method to incorporate Co species into the structure of MCM-41. Quaternary ammonium surfactants, $C_nH_{2n+1}(CH_3)_3NBr$, with n= 10, 12, 14, 16, and 18 were used as structure directing agents in this research. Investigation of Co atoms status inside the Co-MCM-41 materials revealed that about 30-40 atoms uniformly exist in each pore as well as they present as a mixture of tetrahedral and distorted tetrahedral structures like Co_3O_4. The crystallization time (20-160 hr) and temperature (100 and 150 °C) were monitored in order to obtain optimums for both MCM-41 and Co-MCM-41. It has been mentioned that for MCM-41 4 days and 100 °C are optimum synthetic conditions, however, for Co-MCM-41 6 days and 100 °C produce better products.

In the next step, C16 Co-MCM-41 has been selected for further catalytic activity evaluation on the synthesis of single-walled carbon nanotubes (SWNTs). It exhibited good results in this manner with 90% selectivity over SWNT and 4 wt% over carbon deposition. TEM micrograph and corresponding Raman spectra (Fig. 5) shows the successful synthesis of CNTs. Gary L. Haller's research group continued the aforementioned research by following works. They have investigated the effect of catalyst pre-reduction, nanotube growth temperatures (Chen, 2004b), CO pressure, and reaction time (Chen, 2004a) using Co-MCM-41 catalysts. Chen et al. used C16 Co-MCM-41 with 1 wt% cobalt as catalyst (Lim et al., 2003). As pointed out in (Chen, 2004b), single-walled carbon nanotubes were synthesized by

CO disproportionation under following conditions: reaction time, 60 min; reaction temperature, 650-900 °C; and CO pressure, 6 atm. Basically, the influence of catalyst pre-reduction condition and growth temperature on the selectivity and uniformity of SWNT were observed. In order to investigate the effect of pretreatment on the catalyst, two techniques were applied: *in-situ* X-ray Absorption Near-Edge Structure (XANES) for investigation of cobalt state during pretreatment, and *ex-situ* Extended X-ray Absorption Fine Structure (EXAFS) to monitor the formation of cobalt clusters during SWNT growth. The aim of this research, obtaining SWNTs with narrow diameter distribution have been accomplished by applying optimized condition; pre-reducing of catalysts at 500-600 °C and growing SWNTs at 750 -800 °C. Figure 6 indicates the correlation between quality and yield of synthesized carbon nanotubes which shows the optimum synthesis condition. The I_D/I_G ratio in Figure 6a indicates the ratio between two major peaks in Raman spectrum of CNTs. D-band appears around 1340 cm^{-1} and is related to disordered graphite. High frequency G-band appears around 1580 cm^{-1} and is attributed to splitting of the E_{2g} stretching mode of graphite.

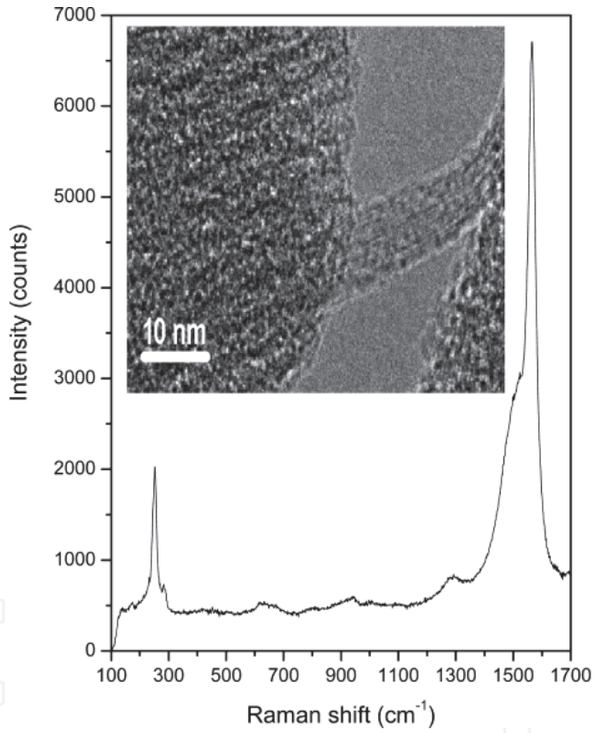


Fig. 5. Raman spectrum and TEM image of CNT synthesized using C16 Co-MCM-41 (Lim et al., 2003)

In the second article (Chen, 2004a), Chen et al. applied the optimized pretreatment and reaction temperature (500 and 800 °C, respectively) to monitor the effect of CO pressure and reaction time on disproportional decomposition of CO in SWNT synthesis. They have chosen 2-6 atm. range for CO partial pressure and 5-120 min. for reaction time. It has been concluded that following processes affects both selectivity and diameter uniformity of SWNTs under applied synthetic conditions: 1) reduction of cobalt, 2) nucleation of the reduced cobalt atoms into clusters and 3) initiation and growth of the SWNTs.

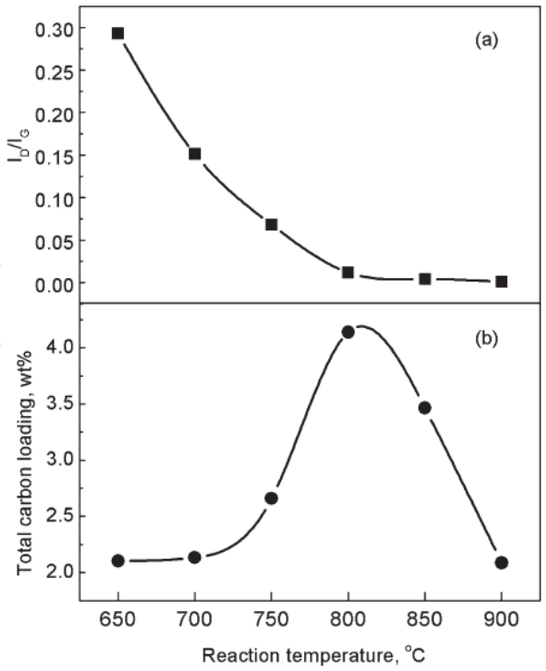


Fig. 6. Correlation diagram between synthesis temperatures (°C), quality index (I_D/I_G), and total carbon loading (%) (Chen, 2004b)

TEM images of synthesized CNTs under different CO pressures are given in Fig. 7. According to these images, it is obvious that higher CO pressures causes better uniformity of synthesized CNTs. Therefore, synthesis of SWNTs under different CO partial pressures revealed two remarkable results. Applying low CO pressures in the synthesis provides SWNTs with broad diameter distribution. It has been explained that in such circumstances reduction of cobalt species and growth of SWNTs are slow (Chen, 2004a). Therefore, cobalt clusters, which are the sites of SWNT formation, are allowed to grow into larger sizes. On the other hand, synthesis of SWNTs under high pressure of CO provides SWNTs with uniform and narrow diameter distribution. Considering the aforementioned discussion about low pressure of CO, it is reasonable.

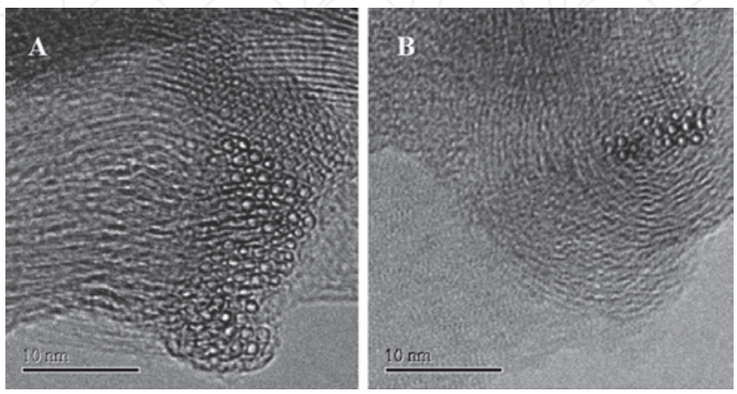


Fig. 7. TEM micrographs synthesized CNTs under CO pressure of a) 2 and b) 6 atm (Chen, 2004a)

After above remarkable researches (Yang et al., 2004), Garry Haller and co-workers have carried out a comprehensive statistical research to recognize how different variable parameters affect the synthesis of Co-MCM-41 catalysts in order to obtain aligned SWNTs. The independent variables which have been considered in this article are: *alkyl chain length, initial cobalt concentration, surfactant silica ratio, TMA silica ratio, water silica ratio, pore diameter, metal composition and structural order.* Considering these variables, several material synthesis have been designed, ID: Co01-Co28, which has produced a scatter plot matrix for analyzing the effect of main synthesis variables. It has been raised to a normalized model which is helpful in quantitative measurement of interaction between different variables considering corresponding correlation coefficients. The most important correlation coefficients are given in Table 1.

Correlation coefficient	Considered variables
0.9974	Metal composition in Co-MCM-41 and initial Co concentration in the synthesis solution
0.9261	Pore size and alkyl chain length of surfactant
0.5756	Structural order and alkyl chain length of surfactant

Table 1. Correlation coefficients between different variables in Yang et al. paper (Yang et al., 2004)

It has been concluded that the presented model can be used to produce samples with varying pore size and constant cobalt content while having a high degree of structural order.

As it has mentioned above regarding Chen et al.'s articles (Chen, 2004b; a), the size of cobalt clusters has a strong effect on the properties of resulting carbon nanotubes. Ciuparu et al.'s paper (Ciuparu et al., 2004) presents a deeper investigation on the mechanism of cobalt cluster size control. The interesting result of this work is the effect of hydrogen pretreatment of catalyst which facilitates the synthesis of SWNTs with small diameters.

Another statistical analysis following Haller research group works addresses investigation of C10 Co-MCM-41 catalyst in order to obtain SWNTs with smaller diameters (Yang et al., 2005). This work is similar to their previous published article (Yang et al., 2004). Herein, Yang et al. defined experimental parameters as follows: *surfactant to silica ratio, pH, TMASi to Si ratio, Co concentration, water to Si ratio, slope of isotherm capillary condensation step and ratio of peak intensity of (110) to (100) of X-ray diffraction pattern.* Considering the first five variables (independent variables) synthesis condition for 27 samples have been designed and carried out. It has been concluded that the most significant effects on the structural order of C10 Co-MCM-41 samples rise from the first three variables. The other independent variables may negatively affect the structural order of mentioned catalyst. Raman spectra of synthesized SWNTs using C10 Co-MCM-41 and C16 Co-MCM-41 are shown in Fig. 8. Appearing the small peak at 301 cm^{-1} reveals the successful synthesis of SWNTs with C10 Co-MCM-41 (3 wt% cobalt) with 0.77 nm diameter.

The effect of cobalt content on the synthesis of SWNTs via CO disproportion on Co-MCM-41 catalysis was presented in L. D. Pfefferle co-workers paper (Chen et al., 2006). Chen et al. synthesized Co-MCM-41 samples with Co concentration ranging from 0.5 to 4 %. The lowest concentration of Co leads to obtain few Co clusters which are large enough to initiate the growth of single-walled carbon nanotubes. While using Co concentration higher than 3 % causes the formation of large cobalt clusters and consequently production of undesired products.

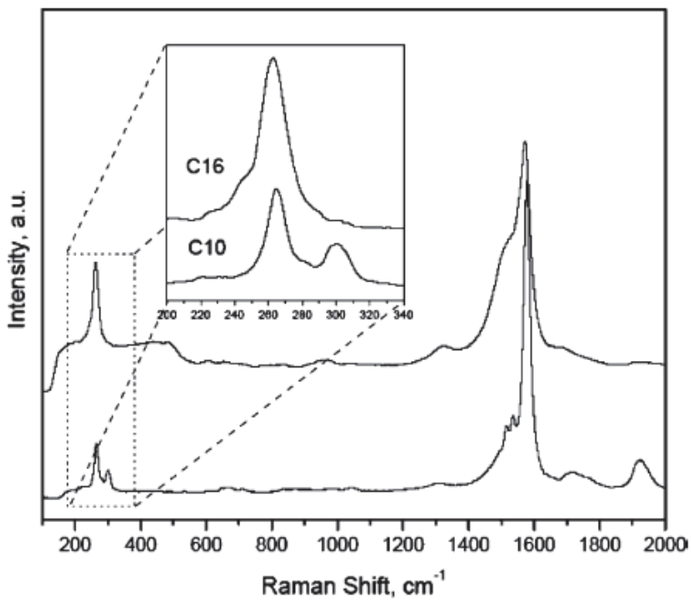


Fig. 8. Raman spectra of synthesized SWNTs using C10 Co-MCM-41 and C16 Co-MCM-41 (Yang et al., 2005)

The last article which has been reviewed here is a report on the application of Co-MCM-41 materials for the synthesis of SWNTs via CVD method. Somanathan et al. (Somanathan et al., 2006) incorporated Co species into the structure of MCM-41 through direct synthesis approach with different Si/Co ratios ranging from 25 to 100. SWNTs were synthesized at 750 °C using acetylene as carbon source with 40 ml.min^{-1} flow rate for 10 min. They have concluded that Co-MCM-41 is very stable under severe reaction condition as well as the obtaining high selectivity toward SWNT using Co-MCM-41 with Si/Co =100 (Fig. 8). The proposed growth mechanism is mentioned top-growth considering different evidences such as TEM image (Fig. 10).

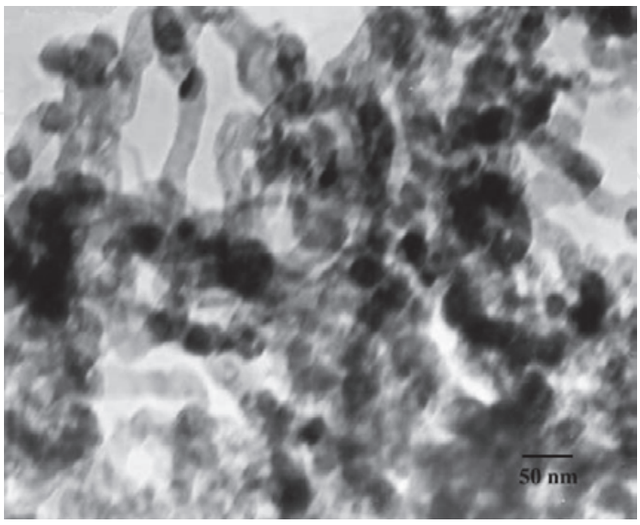


Fig. 9. TEM image of CNTs synthesized using Co-MCM-41 (100) (Somanathan et al., 2006)

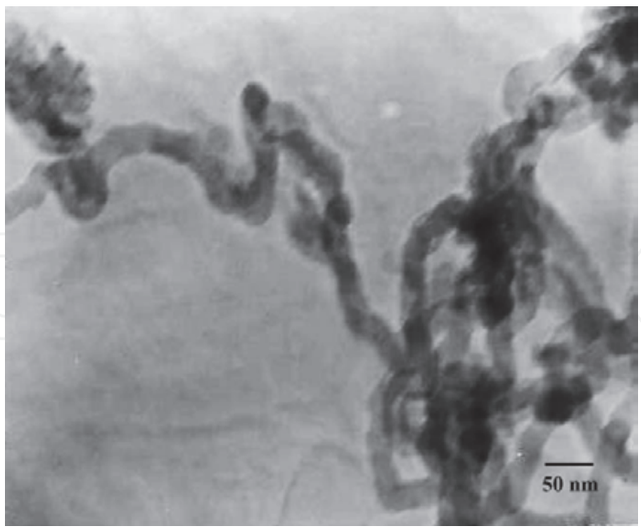


Fig. 10. TEM micrographs with cobalt particles at the tip of nanotubes (Somanathan et al., 2006)

5. Synthesis of CNTs using Ni-modified nanoporous silicas

Herein, some other articles which address application of Ni-MCM-41 in the synthesis of carbon nanotubes are presented.

Chen et al. besides their researches on the Co-MCM-41 catalysts also have carried out research on the Ni-MCM-41 materials. In some of their works (Chen et al., 2005), Ni (1 wt%) have been incorporated into the structure of MCM-41 based on their previous report (Lim et al., 2003). The SWNT synthesis approach is also similar. It has been concluded that using Ni-MCM-41 in comparison with Co-MCM-41 produces SWNTs with broader diameter distribution and lower carbon deposition. This has been related to the tendency of Ni to CO which causes faster reduction of nickel particles and migration of nickel clusters. Chen et al also proposed, Ni-MCM-41 catalyst, while using other carbon sources can improve the properties of SWNTs. Then, Chen et al. tried to investigate the effect of various carbon sources on the synthesis of SWNTs using Ni-MCM-41 (Chen et al., 2007). Synthesis of SWNTs using Ni-MCM-41 using CO, ethanol and methane under similar conditions revealed that CO produced SWNTs with narrower diameter distribution than ethanol. On the other hand, using methane as the carbon precursor was not a successful experiment under same conditions to produce CNTs .

Somanathan et al. also followed their previous works on Co-MCM-41 catalysts by reporting synthesis of SWNTs over Ni-MCM-41 nanoporous materials (Somanathan & Pandurangan, 2006). Herein, Ni-MCM-41 materials were synthesized through similar methods mentioned in their work on Co-MCM-41 (Somanathan et al., 2006). Performing experiments using catalysts with different Si/Ni ratios and reaction conditions provided optimum synthesis circumstances. It has been mentioned that using Ni-MCM-41 with Si/Ni=100 at 750 °C for 10 min at N_2 and acetylene flow rates of 140 and 60 ml.min^{-1} gives the highest carbon yield (71.01%). Presence of metal particles at the tip of grown carbon nanotubes brought authors to the "tip-growth" mechanism occurring in these experiments.

6. Concluding remarks and future directions

Basically, reviewing mentioned articles here has shown that using metal-modified nanoporous silica as catalysts for the synthesis of CNTs was interesting for scientists to improve the synthetic approaches in order to obtain CNTs with desired properties and conditions. Although there are a lot of published works in this manner, taking a look at these researches reveals that still there are a lot of points which need to being studied for further development on the synthesis procedures of CNTs.

Briefly, industries need different class of carbon nanotubes such as single-walled, multiwalled, with junction and so on. Therefore, future studies should be done in order to improve the current methods. These researches should consider two major points, 1) obtaining CNTs with desired properties, 2) decreasing the cost of production. In this manner, studying the effect of different methods for introducing metal species into the structure of nanoporous silicas, effect of calcination of the metal-modified nanoporous silicas, influence of different carbon precursors, combination of two metals and etc. were subject of some few previous reports and can be the interesting subject of research for upcoming works.

7. Acknowledgment

The authors thank the University of Tehran Research Council for support of this work.

8. References

Arab, P., Badiei, A., Koolivand, A. & Mohammadi Ziarani, G. Direct Hydroxylation of Benzene to Phenol over Fe3O4 Supported on Nanoporous Carbon, *Chin. J. Catal.* 32:258-263.

Badiei, A. & Bonneviot, L. (1998). Modification of Mesoporous Silica by Direct Template Ion Exchange Using Cobalt Complexes, *Inorg. Chem.* 37:4142-4145.

Badiei, A., Goldooz, H. & Ziarani, G. M. (2011a). A novel method for preparation of 8-hydroxyquinoline functionalized mesoporous silica: Aluminum complexes and photoluminescence studies, *Appl. Surf. Sci.* 257:4912-4918.

Badiei, A., Goldooz, H., Ziarani, G. M. & Abbasi, A. (2011b). One pot synthesis of functionalized SBA-15 by using an 8-hydroxyquinoline-5-sulfonamide-modified organosilane as precursor, *J. Colloid Interface Sci.* 357:63-69.

Bagshaw, S. A., Prouzet, E. & Pinnavaia, T. J. (1995). Templating of Mesoporous Molecular Sieves by Nonionic Polyethylene Oxide Surfactants, *Science* 269:1242-1244.

Barreca, D., Blau, W. J., Croke, G. M., Deeney, F. A., Dillon, F. C., Holmes, J. D., Kufazvinei, C., Morris, M. A., Spalding, T. R. & Tondello, E. (2007). Iron oxide nanoparticle impregnated mesoporous silicas as platforms for the growth of carbon nanotubes, *Microporous Mesoporous Mater.* 103:142-149.

Beck, J. S., Vartuli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. D., Chu, C. T. W., Olson, D. H. & Sheppard, E. W. (1992). A new family of mesoporous molecular sieves prepared with liquid crystal templates, *J. Am. Chem. Soc.* 114:10834-10843.

Béland, F., Echchahed, B., Badiei, A. & Bonneviot, L. 1998. EXAFS multiple scattering characterization of metal modified mesoporous sieves. Pages 567-574 in: Stud. Surf. Sci. Catal. L. Bonneviot, F. Beland, C. Danumah, S. Giasson and S. Kaliaguine, eds. Elsevier.

Bonneviot, L., Morin, M. & Badiei, A. (2003). Mesostructured metal or non-metal oxides and method for making same, US 2003/0133868.

Chen, Y. (2004a). Synthesis of uniform diameter single wall carbon nanotubes in Co-MCM-41: effects of CO pressure and reaction time, *J. Catal.* 226:351-362.

Chen, Y. (2004b). Synthesis of uniform diameter single-wall carbon nanotubes in Co-MCM-41: effects of the catalyst prereduction and nanotube growth temperatures, *J. Catal.* 225:453-465.

Chen, Y., Ciuparu, D., Yang, Y., Lim, S., Wang, C., Haller, G. L. & Pfefferle, L. D. (2005). Single-wall carbon nanotube synthesis by CO disproportionation on nickel-incorporated MCM-41, *Nanotechnology* 16:S476-S483.

Chen, Y., Ciuparu, D., Lim, S., Haller, G. & Pfefferle, L. (2006). The effect of the cobalt loading on the growth of single wall carbon nanotubes by CO disproportionation on Co-MCM-41 catalysts, *Carbon* 44:67-78.

Chen, Y., Wang, B., Li, L., Yang, Y., Ciuparu, D., Lim, S., Haller, G. & Pfefferle, L. (2007). Effect of different carbon sources on the growth of single-walled carbon nanotube from MCM-41 containing nickel, *Carbon* 45:2217-2228.

Ciuparu, D., Chen, Y., Lim, S., Yang, Y., Haller, G. L. & Pfefferle, L. (2004). Mechanism of Cobalt Cluster Size Control in Co-MCM-41 during Single-Wall Carbon Nanotubes Synthesis by CO Disproportionation, *J. Phys. Chem. B* 108:15565-15571.

Cornils, B. & Herrmann, W. A. (1996). *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, New York.

Coronado, J. M., Coloma, F. & Anderson, J. A. (2000). Styrene hydroformylation over modified Rh/SiO2·Al2O3 catalysts, *J. Mol. Catal. A: Chem.* 154:143-154.

Dillon, A. C., Jones, K. M., Bekkedahl, T. A., Kiang, C. H., Bethune, D. S. & Heben, M. J. (1997). Storage of hydrogen in single-walled carbon nanotubes, *Nature* 386:377-379.

Duxiao, J., Nongyue, H., Yuanying, Z., Chunxiang, X., Chunwei, Y. & Zuhong, L. (2001). Catalytic growth of carbon nanotubes from the internal surface of Fe-loading mesoporous molecular sieves materials, *Mater. Chem. Phys.* 69:246-251.

Fan, S., Chapline, M. G., Franklin, N. R., Tombler, T. W., Cassell, A. M. & Dai, H. (1999). Self-Oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties, *Science* 283:512-514.

Frank, S., Poncharal, P., Wang, Z. L. & Heer, W. A. d. (1998). Carbon Nanotube Quantum Resistors, *Science* 280:1744-1746.

Fuhrer, M. S., Nygård, J., Shih, L., Forero, M., Yoon, Y.-G., Mazzoni, M. S. C., Choi, H. J., Ihm, J., Louie, S. G., Zettl, A. & McEuen, P. L. (2000). Crossed Nanotube Junctions, *Science* 288:494-497.

Ganjali, M., Daftari, A., Hajiagha-Babaei, L., Badiei, A., Saberyan, K., Ziarani, G. & Moghimi, A. (2006). Pico Level Monitoring of Silver with Modified Hexagonal Mesoporous Compound (MCM-41) and Inductively Coupled Plasma Atomic Emission Spectrometry, *Water, Air, Soil Pollut.* 173:71-80.

Ganjali, M., Asgari, M., Faridbod, F., Norouzi, P., Badiei, A. & Gholami, J. (2010). Thiomorpholine-functionalized nanoporous mesopore as a sensing material for Cd²⁺ carbon paste electrode, *J. Solid State Electrochem.* 14:1359-1366.

García-García, F. R., Pérez-Cabero, M., Nevskaia, D. M., Rodríguez-Ramos, I. & Guerrero-Ruiz, A. (2008). Improving the synthesis of high purity carbon nanotubes in a catalytic fluidized bed reactor and their comparative test for hydrogen adsorption capacity, *Catal. Today* 133-135:815-821.

Geng, J., Singh, C., Shephard, D. S., Shaffer, M. S. P., Johnson, B. F. G. & Windle, A. H. (2002). Synthesis of high purity single-walled carbon nanotubes in high yield, *Chem. Commun.*:2666-2667.

Goettmann, F., Le Floch, P. & Sanchez, C. (2006). Highly regioselective terminal alkynes hydroformylation and Pauson-Khand reaction catalysed by mesoporous organised zirconium oxide based powders, *Chem. Commun.*:180-182.

Guo, T., Nikolaev, P., Thess, A., Colbert, D. T. & Smalley, R. E. (1995). Catalytic growth of single-walled manotubes by laser vaporization, *Chem. Phys. Lett.* 243:49-54.

Hashemi, P., Shamizadeh, M., Badiei, A., Zarabadi-Poor, P., Ghiasvand, A. R. & Yarahmadi, A. (2009). Amino ethyl-functionalized nanoporous silica as a novel fiber coating for solid-phase microextraction, *Anal. Chim. Acta* 646:1-5.

Iijima, S. (1991). Helical microtubules of graphitic carbon, *Nature* 354:56-58.

Iijima, S. & Ichihashi, T. (1993). Single-shell carbon nanotubes of 1-nm diameter, *Nature* 363:603-605.

Inagaki, S., Fukushima, Y. & Kuroda, K. (1993). Synthesis of highly ordered mesoporous materials from a layered polysilicate, *J. Chem. Soc., Chem. Commun.*:680-682.

Javanbakht, M., Badiei, A., Ganjali, M. R., Norouzi, P., Hasheminasab, A. & Abdouss, M. (2007a). Use of organofunctionalized nanoporous silica gel to improve the lifetime of carbon paste electrode for determination of copper(II) ions, *Anal. Chim. Acta* 601:172-182.

Javanbakht, M., Ganjali, M. R., Norouzi, P., Badiei, A., Hasheminasab, A. & Abdouss, M. (2007b). Carbon Paste Electrode Modified with Functionalized Nanoporous Silica Gel as a New Sensor for Determination of Silver Ion, *Electroanalysis* 19:1307-1314.

Javanbakht, M., Divsar, F., Badiei, A., Fatollahi, F., Khaniani, Y., Ganjali, M. R., Norouzi, P., Chaloosi, M. & Ziarani, G. M. (2009a). Determination of picomolar silver concentrations by differential pulse anodic stripping voltammetry at a carbon paste electrode modified with phenylthiourea-functionalized high ordered nanoporous silica gel, *Electrochim. Acta* 54:5381-5386.

Javanbakht, M., Khoshsafar, H., Ganjali, M. R., Badiei, A., Norouzi, P. & Hasheminasab, A. (2009b). Determination of Nanomolar Mercury(II) Concentration by Anodic-Stripping Voltammetry at a Carbon Paste Electrode Modified with Functionalized Nanoporous Silica Gel, *Curr. Anal. Chem.* 5:35-41.

Javanbakht, M., Rudbaraki, H., Sohrabi, M. R., Attaran, A. M. & Badiei, A. (2010). Separation, pre-concentration and determination of trace amounts of lead(II) ions in environmental samples using two functionalised nanoporous silica gels containing a dipyridyl sub-unit, *International Journal of Environmental Analytical Chemistry* 90:1014 - 1024.

Jose-Yacaman, M., Miki-Yoshida, M., Rendon, L. & Santiesteban, J. G. (1993). Catalytic growth of carbon microtubules with fullerene structure, *Appl. Phys. Lett.* 62:202-204.

Kim, P. & Lieber, C. M. (1999). Nanotube Nanotweezers, *Science* 286:2148-2150.

Kong, J., Franklin, N. R., Zhou, C., Chapline, M. G., Peng, S., Cho, K. & Dai, H. (2000). Nanotube Molecular Wires as Chemical Sensors, *Science* 287:622-625.

Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C. & Beck, J. S. (1992). Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, *Nature* 359:710-712.

Kuil, M., Soltner, T., van Leeuwen, P. W. N. M. & Reek, J. N. H. (2006). High-Precision Catalysts: Regioselective Hydroformylation of Internal Alkenes by Encapsulated Rhodium Complexes, *J. Am. Chem. Soc.* 128:11344-11345.

Lim, S., Ciuparu, D., Pak, C., Dobek, F., Chen, Y., Harding, D., Pfefferle, L. & Haller, G. (2003). Synthesis and Characterization of Highly Ordered Co−MCM-41 for Production of Aligned Single Walled Carbon Nanotubes (SWNT), *J. Phys. Chem. B* 107:11048-11056.

Lu, A.-H., Schmidt, W., Tatar, S.-D., Spliethoff, B., Popp, J., Kiefer, W. & Schüth, F. (2005). Formation of amorphous carbon nanotubes on ordered mesoporous silica support, *Carbon* 43:1811-1814.

Marchetti, M., Paganelli, S. & Viel, E. (2004). Hydroformylation of functionalized olefins catalyzed by SiO2-tethered rhodium complexes, *J. Mol. Catal. A: Chem.* 222:143-151.

Mizuno, K., Hata, K., Saito, T., Ohshima, S., Yumura, M. & Iijima, S. (2005). Selective Matching of Catalyst Element and Carbon Source in Single-Walled Carbon Nanotube Synthesis on Silicon Substrates, *J. Phys. Chem. B* 109:2632-2637.

Morgan, S. & Mokaya, R. (2008). Aligned Bundles of Carbon Nanotubes Are Easily Grown on As-Synthesized Mesoporous Silicate Substrates, *J. Phys. Chem. C* 112:15157-15162.

Pagar, N., Deshpande, R. & Chaudhari, R. (2006). Hydroformylation of olefins using dispersed molecular catalysts on solid supports, *Catal. Lett.* 110:129-133.

Ryoo, R., Kim, J. M., Ko, C. H. & Shin, C. H. (1996). Disordered Molecular Sieve with Branched Mesoporous Channel Network, *J. Phys. Chem.* 100:17718-17721.

Saito, M. S. D. R. & Dresselhaus, G. (1998). *Physical Properties of Carbon Nanotubes*, World Scientific Publishing, Singapore.

Somanathan, T. & Pandurangan, A. (2006). Effective Synthesis of Single-Walled Carbon Nanotubes Using Ni−MCM-41 Catalytic Template through Chemical Vapor Deposition Method, *Ind. Eng. Chem. Res.* 45:8926-8931.

Somanathan, T., Pandurangan, A. & Sathiyamoorthy, D. (2006). Catalytic influence of mesoporous Co-MCM-41 molecular sieves for the synthesis of SWNTs via CVD method, *J. Mol. Catal. A: Chem.* 256:193-199.

Somanathan, T., Gokulakrishnan, N., Chandrasekar, G. & Pandurangan, A. (2011). Fabrication of multiwalled carbon nanotubes in the channels of iron loaded three dimensional mesoporous material by catalytic chemical vapour deposition technique, *Appl. Surf. Sci.* 257:2940-2943.

Steplewska, A. & Borowiak-Palen, E. (2011). Study on the effect of the metal–support (Fe-MgO and Pt-MgO) interaction in alcohol-CVD synthesis of carbon nanotubes, *J. Nanopart. Res.* 13:1987-1994.

Tanev, P. T. & Pinnavaia, T. J. (1995). A Neutral Templating Route to Mesoporous Molecular Sieves, *Science* 267:865-867.

Tans, S. J., Devoret, M. H., Dai, H., Thess, A., Smalley, R. E., Geerligs, L. J. & Dekker, C. (1997). Individual single-wall carbon nanotubes as quantum wires, *Nature* 386:474-477.

Thess, A., Lee, R., Nikolaev, P., Dai, H., Petit, P., Robert, J., Xu, C., Lee, Y. H., Kim, S. G., Rinzler, A. G., Colbert, D. T., Scuseria, G. E., Tománek, D., Fischer, J. E. & Smalley, R. E. (1996). Crystalline Ropes of Metallic Carbon Nanotubes, *Science* 273:483-487.

Wang, X., Wang, M., Jin, H., Li, Z. & He, P. (2005a). Preparation of carbon nanotubes at the surface of Fe/SBA-15 mesoporous molecular sieve, *Appl. Surf. Sci.* 243:151-157.

Wang, X. Q., Ge, H. L., Jin, H. X. & Cui, Y. J. (2005b). Influence of Fe on the thermal stability and catalysis of SBA-15 mesoporous molecular sieves, *Microporous Mesoporous Mater.* 86:335-340.

Wei, F., Zhang, Q., Qian, W.-Z., Yu, H., Wang, Y., Luo, G.-H., Xu, G.-H. & Wang, D.-Z. (2008). The mass production of carbon nanotubes using a nano-agglomerate fluidized bed reactor: A multiscale space–time analysis, *Powder Technol.* 183: 10-20.

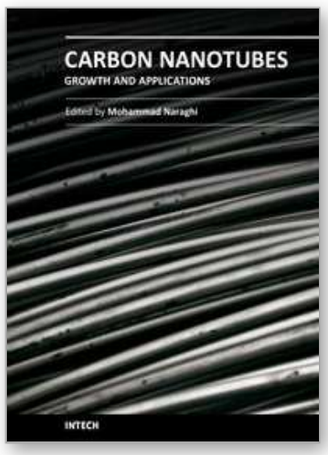
Yang, Y., Lim, S., Wang, C., Du, G. & Haller, G. L. (2004). Statistical analysis of synthesis of Co-MCM-41 catalysts for production of aligned single walled carbon nanotubes (SWNT), *Microporous Mesoporous Mater.* 74:133-141.

Yang, Y., York, J. D., Xu, J., Lim, S., Chen, Y. & Haller, G. L. (2005). Statistical design of C10-Co-MCM-41 catalytic template for synthesizing smaller-diameter single-wall carbon nanotubes, *Microporous Mesoporous Mater.* 86:303-313.

Zarabadi-Poor, P., Badiei, A., Yousefi, A. A., Fahlman, B. D. & Abbasi, A. (2010). Catalytic chemical vapour deposition of carbon nanotubes using Fe-doped alumina catalysts, *Catal. Today* 150:100-106.

Zhao, D., Huo, Q., Feng, J., Chmelka, B. F. & Stucky, G. D. (1998). Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures, *J. Am. Chem. Soc.* 120:6024-6036.

Zhu, H. J., Ding, Y. J., Yan, L., Xiong, J. M., Lu, Y. & Lin, L. W. (2004). The PPh3 ligand modified Rh/SiO2 catalyst for hydroformylation of olefins, *Catal. Today* 93-95:389-393.



Carbon Nanotubes - Growth and Applications

Edited by Dr. Mohammad Naraghi

ISBN 978-953-307-566-2
Hard cover, 604 pages
Publisher InTech
Published online 09, August, 2011
Published in print edition August, 2011

Carbon Nanotubes are among the strongest, toughest, and most stiff materials found on earth. Moreover, they have remarkable electrical and thermal properties, which make them suitable for many applications including nanocomposites, electronics, and chemical detection devices. This book is the effort of many scientists and researchers all over the world to bring an anthology of recent developments in the field of nanotechnology and more specifically CNTs. In this book you will find:
- Recent developments in the growth of CNTs
- Methods to modify the surfaces of CNTs and decorate their surfaces for specific applications
- Applications of CNTs in biocomposites such as in orthopedic bone cement
- Application of CNTs as chemical sensors
- CNTs for fuelcells
- Health related issues when using CNTs

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Pezhman Zarabadi-Poor and Alireza Badiei (2011). Synthesis of Carbon Nanotubes Using Metal-Modified Nanoporous Silicas, Carbon Nanotubes - Growth and Applications, Dr. Mohammad Naraghi (Ed.), ISBN: 978-953-307-566-2, InTech, Available from: http://www.intechopen.com/books/carbon-nanotubes-growth-and-applications/synthesis-of-carbon-nanotubes-using-metal-modified-nanoporous-silicas

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

IntechOpen