Journal of Zhejiang University SCIENCE A
ISSN 1673-565X (Print); ISSN 1862-1775 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

IR study on surface chemical properties of catalytic grown carbon nanotubes and nanofibers

Li-hua TENG†1, Tian-di TANG2
([1]Institute of Biology and Environmental Science, Zhejiang Wanli University, Ningbo 315100, China)
([2]College of Chemistry, Northeast Normal University, Changchun 130024, China)
†E-mail: tlh_98@163.com

Received Sept. 21, 2007; revision accepted Dec. 26, 2007; published online Mar. 6, 2008

Abstract: In this study, the surface chemical properties of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) grown by catalytic decomposition of methane on nickel and cobalt based catalysts were studied by DRIFT (Diffuse Reflectance Infrared Fourier Transform) and transmission Infrared (IR) spectroscopy. The results show that the surface exists not only carbon-hydrogen groups, but also carboxyl, ketene or quinone (carbonyl) oxygen-containing groups. These functional groups were formed in the process of the material growth, which result in large amount of chemical defect sites on the walls.

Key words: Carbon nanotubes (CNTs), Carbon nanofibers (CNFs), Functional surface groups, Infrared (IR) spectroscopy
doi:10.1631/jzus.A071503 **Document code:** A **CLC number:** O657.3; O643.3

INTRODUCTION

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are very promising materials. They are of a great potential to be used as adsorbent, catalyst support and polymers enhancing materials capacity (Popov, 2004; Srivastava *et al.*, 2003; Qian *et al.*, 2002). Many techniques have been developed to synthesize CNTs, such as arc-discharge, laser ablation of graphite and catalytic chemical vapor deposition (CCVD). Arc-discharge and laser ablation of graphite are used for producing single-walled nanotudes, while CCVD methods are widely used for the synthesis of multi-walled CNTs and CNFs in a large scale. Therefore, the materials produced are more applicable as catalyst support and composite materials (de Jong and Geus, 2000; Serp *et al.*, 2003; Nhut *et al.*, 2003; Ros, 2002; Rodriguez, 1993; Thostenson *et al.*, 2001; Zhao *et al.*, 2007; Bezemer *et al.*, 2006; Pawelec *et al.*, 2006; Garcia *et al.*, 2006). These applications are closely related to the surface chemical properties of CNTs or CNFs and knowledge on the surface chemical properties of as-grown materials is helpful to the exploration of applications of such materials.

The infrared (IR) spectroscopy method has been adopted by many researchers to study the surface properties of CNTs, mainly focusing on the functionalized CNTs but not so much on as-grown ones (Ros, 2002; Mawhinney *et al.*, 2000; Kuznetsova *et al.*, 2000; Shaffer *et al.*, 1998; Martinez *et al.*, 2003). Ros (2002) used a transmission IR instead of DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectroscopy which detected the C-H groups on the surface and proposed that C-H groups exist on the surface defect sites. Jung and Jeon (2002) also detected the C-H groups on the surface of CNTs, and proposed that there are fewer C-H groups on the surface of CNTs prepared by arc-discharge evaporation of graphite than on that prepared by CCVD method. In this work, the surface chemical properties of CNTs and CNFs synthesized by catalytic decomposition of methane on different metal catalysts have been investigated by DRIFT and transmission IR spectroscopies. The results indicate that many oxygen-containing groups, besides the C-H groups, are possible to exist on the surface of CNTs and CNFs.

EXPERIMENTAL DETAILS

Sample preparation

Two catalysts, Ni-Cu/Al_2O_3 (marked 1#Cat) and Co/Al_2O_3 (marked 2#Cat) were prepared by co-precipitation (Li *et al.*, 1997; 1998), while Co/Al_2O_3 (marked 3#Cat) catalyst was prepared by Sol-Gel technique with supercritical drying. All the details of the preparation process can be seen in (Piao *et al.*, 2002).

The CNTs and CNFs by catalytic decomposition of methane were prepared in a horizontal tubular reactor (Tang, 2005). The condition is as follows: for 1#Cat, the reaction temperature was 650 °C; for 2#Cat and 3#Cat, the reaction temperature was 550 °C. For all the reactions, the flow rate of methane is 80 ml/min (STP (standard temperature and pressure), 99.9%). After the reaction, the system was cooled down to room temperature in N_2 atmosphere (99.99% in purity), and subsequently the product was unpacked from the reactor. The products prepared with 1#Cat and 3#Cat are CNFs with a fishbone structure (Tang, 2005) and marked as 1#CNF and 3#CNF, respectively, while the product with 2#Cat is multi-walled CNTs and marked as 2#CNT.

Characterizations

The TEM images were obtained on a JEOL-JEM-100CX II instrument operating at 200 kV. XRD patterns were obtained with a RIGAKU D/MAX-2550 diffractometer using Cu K_{α} radiation. Nitrogen physisorption was carried out using a Thermo Finnigan 1990 apparatus. The IR spectra were obtained on a Nicolet NEXUS FT-IR spectrometer. The mixture of CNTs (or CNFs) with KBr (American Spectra Tech Company) was ground in an agate mortar up to below 400 meshes in order to achieve the well dispersion of CNTs (or CNFs) in KBr.

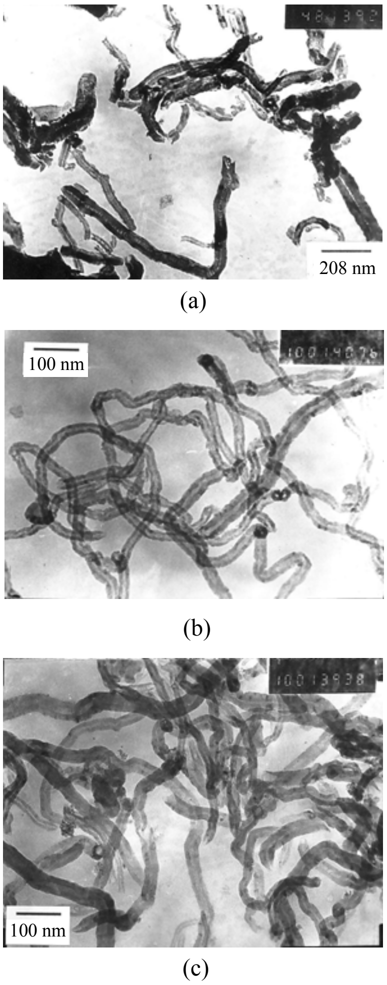
For DRIFT measurement, the specimens were submitted with a powder, and one hundred scans were collected with a resolution of 4 cm^{-1} and an MCT detector, using KBr as background. The transmission spectra were taken with a homemade stainless steel cell with KBr window; thirty-twain scans were collected with a resolution of 4 cm^{-1} and a DTGS detector. In order to eliminate the influence of water and other contaminations, both the KBr and the sample tablets were pretreated in situ with temperature of 80 °C and vacuum 3×10^{-4} Pa for 2 h. The background of KBr and the atmosphere in the cell were deduced. All the spectra baselines were corrected.

For comparison, the transmission spectra of the untreated samples were also recorded under the vacuum out gas condition. It is possible that the presence of few catalysts in CNTFs (CNTs or CNFs) result in the adsorption of IR. Thereby the spectra of catalysts in samples of CNTFs were also recorded after the catalyst was first reduced under the same conditions as those of CNTFs growth and then exposed to air.

RESULTS AND DISCUSSION

TEM, nitrogen physisorption and XRD

Fig.1 shows the images of series samples. The fibres are at a length of several tens to hundreds



(a)

(b)

(c)

Fig.1 TEM micrographs of the 1#CNF (a); 2#CNT (b) and 3#CNF (c)

microns. The diameter of the fibres mainly centered in the range of 30~60 nm and 20~40 nm for 1#CNF, and 2#CNT and 3#CNF, respectively. The BET (Brunauer-Emmett-Teller) surface area was calculated as 73, 85 and 113 m^2/g for 1#CNF, 2#CNT and 3#CNF, respectively. The porous volume was estimated at 0.14, 0.12 and 0.17 cm^3/g for 1#CNF, and 2#CNT and 3#CNF, respectively. Fig.2 shows XRD patterns of various fibers, exhibiting typical peaks at 2θ=26° associated with graphite. The d002 (graphite layer spacing) value is 0.338 nm (1#CNF), 0.346 nm (2#CNT) and 0.343 nm (3#CNF), respectively. This value is larger than that of perfect graphite (0.336 nm), indicating that the graphitization degree of these fibers is lower than that of perfect graphite.

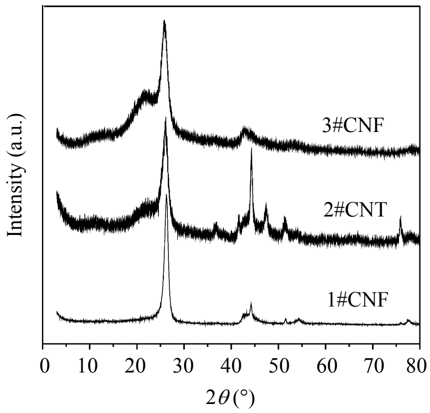


Fig.2 XRD patterns of 1#CNF, 2#CNT and 3#CNF

DRIFT spectroscopy

Fig.3 shows the DRIFT spectra of CNTFs in the 2000~800 cm^{-1} range. The band at 1630 cm^{-1} can be assigned to the absorbed water on the KBr. Due to lower sample concentrations, the contamination of water induced by KBr absorbed is significant. For 1#CNF, the small shoulder peak around 1581 cm^{-1} can be assigned to carbon skeleton vibration of aromatic ring (Ros, 2002; Mawhinney *et al.*, 2000), which cannot be detected on spectra of both 2#CNT and 3#CNF because of the water contamination. The band at 1460 cm^{-1} is assigned to CH_2 or CH_3 banding vibrations (Gomez-Serrano *et al.*, 1999; Moreno-Castilla *et al.*, 2000). Ros (2002) observed this vibration at 1454 cm^{-1} for parallel CNFs. A very weak peak at around 874 cm^{-1} only observed for sample 3#CNF can be assigned to isolated aromatic C-H out-of-plane banding vibrations.

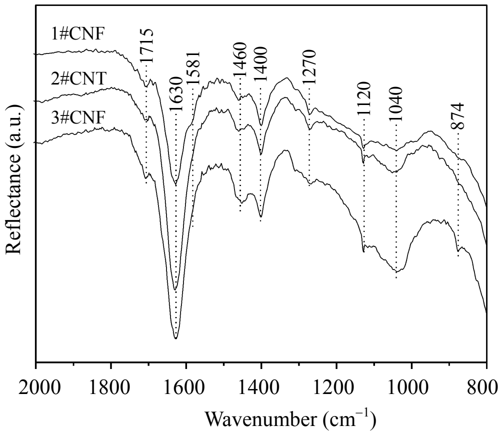


Fig.3 DRIFT spectra of samples in the range 2000~800 cm^{-1}

The 1715 cm^{-1} band may be associated with the C=O vibrations of carboxyl, lactone or ketone groups (Ros, 2002; Kuznetsova *et al.*, 2000; Chen *et al.*, 1998). Ros (2002) observed this vibration at 1717 cm^{-1} for Fishbone CNFs, but not for parallel CNFs. Martínez *et al.*(2003) also detected a very weak C=O vibration at 1720 cm^{-1} for single-walled CNTs prepared by arc-discharge evaporation of graphite method. In the range of 1300~900 cm^{-1} the IR absorption gives rich information about the oxygen-containing surface groups. The 1270, 1120 and 1040 cm^{-1} bands may be associated with C-O or C-O-C vibrations of ester, ether, phenol or carboxyl groups. Due to the overlap of absorption bands from many oxygen-containing groups in this region, an unambiguous assignment is difficult.

In Fig.4, the 3800~2600 cm^{-1} range of the DRIFT spectra provides more information about the carbon-hydrogen groups on the CNTFs. At 2922 and 2855 cm^{-1} exist two stronger absorptions and at 2960 cm^{-1} appears a weak peak shoulder. All of these IR absorption bands can be associated with CH_2 or CH_3 stretching vibrations, with positions dependent on the structure (Moreno-Castilla *et al.*, 1998; Marchon *et al.*, 1988; Boehm, 2002; Puziy *et al.*, 2002; Fanning and Vannice, 1993). Ros (2002) observed these bands at about 2947, 2917 and 2846 cm^{-1}. Jung and Jeon (2002) observed the asymmetric stretching vibration that appeared at 2960 and 2930 cm^{-1}, and the symmetric stretching vibration of CH_2 and CH_3 occurred at 2873 and 2862 cm^{-1}, respectively, for CNTs produced by chemical vapor deposition method. The IR absorption in the range of 3600~3200 cm^{-1} with the minimum at 3424 cm^{-1} is associated with hydroxyl stretching vibration in adsorbed water or surface carboxylic and phenolic groups (Gomez-Serrano *et al.*, 1999; Boehm, 2002; Puziy *et al.*, 2002; Fanning and Vannice, 1993; Zielke *et al.*, 1996; Aguilar *et al.*, 2003; Yang and Lua, 2003).

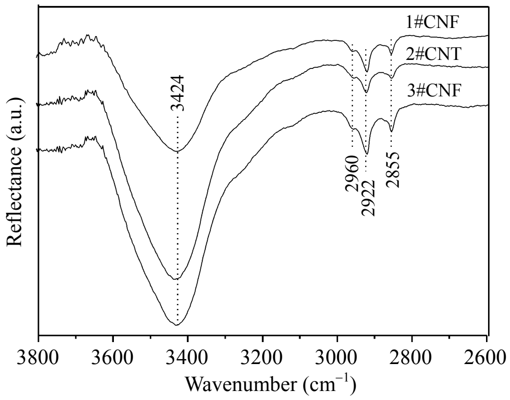


Fig.4 DRIFT spectra of sample in the range 3800~2600 cm^{-1}

Transmission spectroscopy

DRIFT spectroscopy is a sensitive surface technique, as the CNTFs are highly opaque which may induce the loss of IR light, resulting in a weak IR activity. Therefore we recorded the result of transmission IR spectra and compared that with that of a DRIFT spectra. Fig.5 and Fig.6 present the transmission spectra of CNTFs in the range of 2000~800 cm^{-1} and 3800~2600 cm^{-1} (the samples are not treated by out gas in cell). Compared to the DRIFT spectra, the stretching vibration of carbon skeleton of 1#CNF was shown up at 1586 cm^{-1}, and the positions of the other absorption bands are almost the same in the DRIFT spectra.

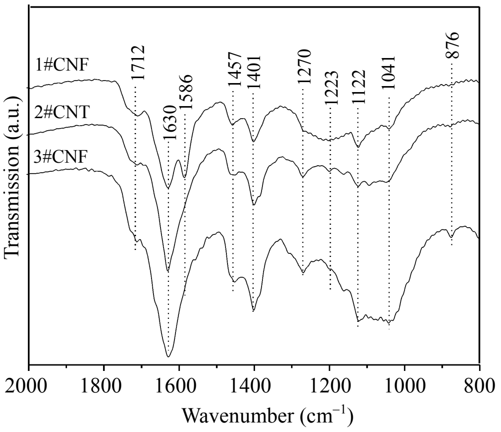


Fig.5 Transmission spectra of samples in the range 2000~800 cm^{-1}

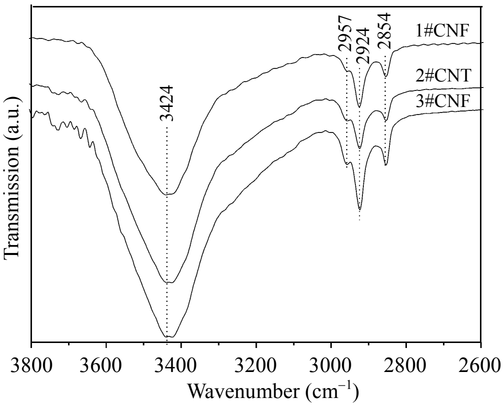


Fig.6 Transmission spectra of samples in the range 3800~2600 cm^{-1}

Fig.7 and Fig.8 show the spectra of CNTFs in the ranges of 2000~800 cm^{-1} and 3800~2600 cm^{-1}, respectively (the samples are treated by out gas in cell with vacuum). Due to pretreating the samples in the cell, the influence of water on the spectra can be eliminated. The carbon skeleton stretching vibrations of the three samples were shown up, and strong absorptions appeared at about 1582 and 1555 cm^{-1}, 1582 cm^{-1} corresponding to 1#CNF and 2#CNT, and 1555 cm^{-1} to 3#CNF. For most carbon materials, the carbon skeleton stretching vibrations can be found (Moreno-Castilla *et al.*, 2000; Dandekar *et al.*, 1998). Because of the history of carbon materials, it is possible that some heteroatoms, such as oxygen, can be incorporated in the structure during synthesis. The C=C band conjugated with adjacent C=O, results in the IR absorption of this band varying more strongly or weakly (Moreno-Castilla *et al.*, 2000; de la Puente *et al.*, 1998). For instance, Ros (2002) observed this band at 1570 cm^{-1} for parallel CNFs, while Shaffer *et al.*(1998) detected this band at 1550 cm^{-1} for multi-walled CNTs.

Compared to the DRIFT spectra (Fig.3), it is interesting that a new peak appeared at about 1652 cm^{-1} (Fig.7), which can be attributed to C=O stretching vibration in quinine or conjugated ketone (Mawhinney *et al.*, 2000; Moreno-Castilla *et al.*, 1998; 2000; Shin *et al.*, 1997; Starsinic *et al.*, 1983). But this information did not appear in the DRIFT spectra. The band at 1735 cm^{-1} can be associated with C=O

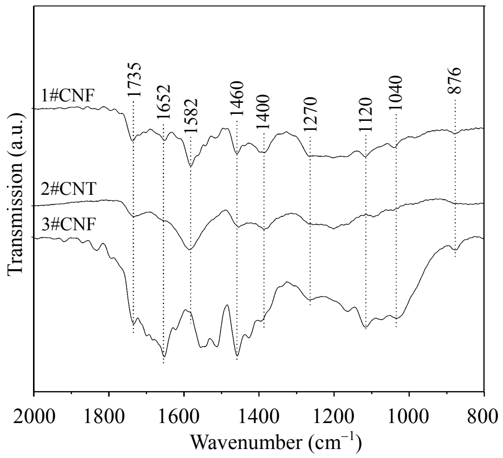


Fig.7 Transmission spectra of samples in the range 2000~800 cm^{-1}

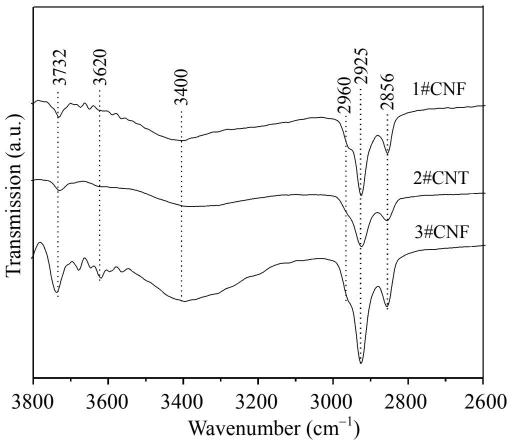


Fig.8 Transmission spectra of samples in the range 3800~2600 cm^{-1}

stretching vibration in carboxyl, lactone or ketone groups, while this peak was at 1715 cm^{-1} in the DRIFT spectra due to the hydrogen bond formed between the absorbed water and this group. As only carboxyl group can interact with water to form hydrogen bond and it cannot be occurred between water and lactone or ketone groups, we conclude that the band at 1735 cm^{-1} should be assigned to the stretching vibrations of carboxyl. CH_3 or CH_2 banding vibration at 1460 cm^{-1}, C-H out-of plane banding vibration at about 876 cm^{-1} and C-O (or C-O-C) stretching vibration in the range of 1300~900 cm^{-1} are almost the same as those in the DRIFT spectra.

Because the samples have been pretreated and made the influence from water decrease obviously, the strength of IR absorption in the range of 3600~3200 cm^{-1} became unsharp, and the peak minimum moved to lower wavenumber (Fig.8). It is worth to note that all three samples appeared a weak but sharp absorption band at 3732 cm^{-1}, and sample 3#CNF showed an absorption band at about 3620 cm^{-1}, which are assigned to isolated O-H stretching vibration temporarily (Fig.8).

It must be noted that the preparation of CNTFs catalyst still exists in the CNTFs samples. We must deduct this influence on spectrum of CNTFs. Fig.9 shows the spectra of in the range of 2000~400 cm^{-1} for catalyst of CNTFs growth and pure KBr samples. It can be seen that the sharp peak at 1400 cm^{-1} is also present in the catalysts and KBr samples, and this peak can be attributed to trace of nitrate that formed from NO_x take up from the air (Zielke *et al*., 1996). The band at 470 cm^{-1} is attributed to vibration of crystal lattice of NiO, and the bands at 664 and 574 cm^{-1} are the vibration of crystal lattice of CoO in catalysts. The result indicated that the IR adsorption of CNTFs growth catalyst did not appear in the range of 2000~800 cm^{-1}.

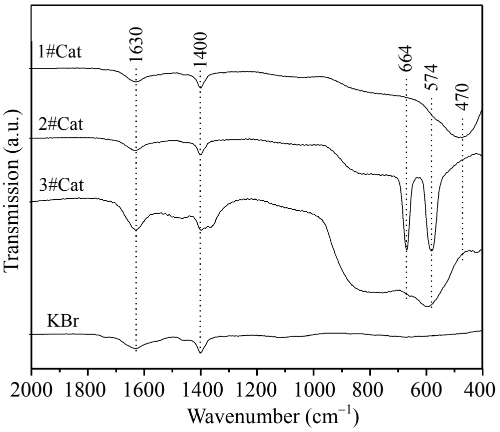


Fig.9 Transmission spectra of catalysts and KBr
1#Cat: Ni-Cu/Al_2O_3; 2#Cat: Co/Al_2O_3; 3#Cat: Co/Al_2O_3 (SG)

From the above spectra, it is shown that the IR adsorption of 3#CNF at about 1735, 2925 and 2855 cm^{-1}, notably stronger than other samples. It seems that the concentration of carboxyl and carbon-hydrogen groups on the surface of 3#CNF is higher than those of 1#CNF and 2#CNT. Compared to the other two samples, the adsorption of oxygen-containing surface groups on 3#CNF in the range of 1300~900 cm^{-1} is also stronger. These results reveal that the concentration of oxygen-containing surface groups on 3#CNF is higher. 2#Cat and 3#Cat are both made of cobalt due to different preparation methods; the concentrations of the oxygen-containing surface groups and the carbon-hydrogen groups on surface of CNTFs from these two catalysts are different. Finally, from the spectra of Fig.7, we found that the stretching vibration of quinone or ketone present on 1#CNF and 3#CNF, but for 2#CNT, this vibration is not obvious.

CONCLUSION

The results of IR spectroscopy allow us to conclude that different kinds of chemical groups exist on the surface of CNTs and CNFs. Firstly, there are many carbon-hydrogen groups on the surface of CNTs and CNFs produced by catalytic method; secondly, because of trace oxygen in methane and catalyst, it is possible to induce oxygen atom to graphitic shell during the production process of CNTs and CNFs. Finally, the difference between catalysts and growth conditions may also have effect on the amounts and types of surface chemical groups, thus resulting in different surface reactivity.

References

Aguilar, C., García, R., Soto-Garrido, G., Arriagada, R., 2003. Catalytic wet air oxidation of aqueous ammonia with activated carbon. *Applied Catalysis B: Environmental*, **46**(2):229-237. [doi:10.1016/S0926-3373(03)00229-7]

Bezemer, G.L., Radstake, P.B., Falke, U., Oosterbeek, H., Kuipers, H.P.C.E., van Dillen, A.J., de Jong, K.P., 2006. Investigation of promoter effects of manganese oxide on carbon nanofibers supported cobalt catalysts for Fischer-Tropsch synthesis. *J. Catal.*, **237**(1):152-161. [doi:10.1016/j.jcat.2005.10.031]

Boehm, H.P., 2002. Surface oxides on carbon and their analysis: a critical assessment. *Carbon*, **40**(2):145-149. [doi:10.1016/S0008-6223(01)00165-8]

Chen, J., Hamon, M.A., Hu, H., Chen, Y., Rao, A.M., Eklund, P.C., Haddon, R.C., 1998. Solution properties of single-walled carbon nanotubes. *Science*, **282**(5386):95-98. [doi:10.1126/science.282.5386.95]

Dandekar, A., Baker, R.T.K., Vannice, M.A., 1998. Characterization of activated carbon, graphitized carbon fibers and synthetic diamond powder using TPD and DRIFTS. *Carbon*, **36**(12):1821-1831. [doi:10.1016/S0008-6223(98)00154-7]

de Jong, K.P., Geus, J.W., 2000. Carbon nanofibers: Catalytic synthesis and applications. *Catalysis Reviews*, **42**(4):481-510. [doi:10.1081/CR-100101954]

de la Puente, G., Centeno, A., Gil, A., Grange, P., 1998. Interactions between molybdenum and activated carbons on the preparation of activated carbon-supported molybdenum catalysts. *Journal of Colloid and Interface Science*, **202**(1):155-166. [doi:10.1006/jcis.1998.5461]

Fanning, P.E., Vannice, M.A., 1993. A DRIFTS study of the formation of surface groups on carbon by oxidation. *Carbon*, **31**(5):721-730. [doi:10.1016/0008-6223(93)90009-Y]

Garcia, J., Gomes, H.T., Serp, P., Kalck, P., Figueiredo, J.L., Faria, J.L., 2006. Carbon nanotube supported ruthenium catalysts for the treatment of high strength wastewater with aniline using wet air oxidation. *Carbon*, **44**(12): 2384-2391. [doi:10.1016/j.carbon. 2006.05.035]

Gomez-Serrano, V., Piriz-Almeida, F., Duran-Valle, C.J., Pastor-Villegas, J., 1999. Formation of oxygen structures by air activation. A study by FT-IR spectroscopy. *Carbon*, **37**(10):1517-1528. [doi:10.1016/S0008-6223(99)00025-1]

Jung, Y.S., Jeon, D.Y., 2002. Surface structure and field emission property of carbon nanotubes grown by radio-frequency plasma-enhanced chemical vapor deposition. *Appl. Surf. Sci.*, **193**(1-4):129-137. [doi:10.1016/S0169-4332(02)00227-1]

Kuznetsova, A., Mawhinney, D., Naumenko, B.V., Yates, J.T.Jr., Liu, J., Smalley, R.E., 2000. Enhancement of adsorption inside of single-walled nanotubes opening the entry ports. *Chem. Phys. Lett.*, **321**(3-4):292-296. [doi:10.1016/S0009-2614(00)00341-9]

Li, Y.D., Chen, J.L., Chang, L., 1997. Catalytic growth of carbon fibers from methane on a nickel-alumina composite prepared from Feiknecht compound precursor. *Applied Catalysis A: General*, **163**(1-2):45-57. [doi:10.1016/S0926-860X(97)00116-6]

Li, Y.D., Chen, J.L., Chang, L., Qin, Y.N., 1998. The doping effect of copper on the catalytic growth of carbon fibers from methane over a Ni/Al_2O_3 catalyst prepared from Feitknecht compound precursor. *J. Catal.*, **178**(1):76-83. [doi:10.1006/jcat.1998.2119]

Marchon, B., Carrazza, J., Heinemann, H., Somorjai, G.A., 1988. TPD and XPS studies of O_2, CO_2, and H_2O adsorption on clean polycrystalline graphite. *Carbon*, **26**(4):507 -514. [doi:10.1016/0008-6223(88)90149-2]

Martinez, M.T., Callejas, M.A., Benito, A.M., Cochet, M., Seeger, T., Anson, A., Schreiber, J., Gordon, C., Marhic, C., Chauvet, O., Fierro, J.L.G., Maser, W.K., 2003. Sensitivity of single wall carbon nanotubes to oxidative processing: structural modification, intercalation and functionalisation. *Carbon*, **41**(12):2247-2256. [doi:10.1016/S0008-6223(03)00250-1]

Mawhinney, D.B., Naumenko, V., Kuznetsova, A., Yates, J.T.Jr., 2000. Infrared spectral evidence for the etching of carbon nanotubes: ozone oxidation at 298 K. *J. Am. Chem. Soc.*, **122**(10):2383-2384. [doi:10.1021/ja994094s]

Moreno-Castilla, C., Carrasco-Marin, F., Maldonado-Hodar, F.J., Rivera-Utrilla, J., 1998. Effects of non-oxidant and oxidant acid treatments on the surface properties of an activated carbon with very low ash content. *Carbon*,

36(1-2):145-151. [doi:10.1016/S0008-6223(97)00171-1]

Moreno-Castilla, C., Lopez-Ramon, M.V., Carrasco-Marin, F., 2000. Changes in surface chemistry of activated carbons by wet oxidation. *Carbon*, **38**(14):1995-2001. [doi:10.1016/S0008-6223(00)00048-8]

Nhut, J.M., Pesant, L., Tessonnier, J.P., Wine, G., Guille, J., Pham-Huu, C., Ledoux, M.J., 2003. Mesoporous carbon nanotubes for use as support in catalysis and as nanosized reactors for one-dimensional inorganic material synthesis. *Applied Catalysis A: General*, **254**(2):345-363. [doi:10.1016/S0926-860X(03)00482-4]

Pawelec, B., la Parola, V., Navarro, R.M., Murcia-Mascar, S., Fierro, J.L.G., 2006. On the origin of the high performance of MWNT-supported Pt-Pd catalysts for aromatic hydrogenation. *Carbon*, **44**(1):84-98. [doi:10.1016/j.carbon.2005.07.004]

Piao, L.Y., Li, Y.D., Chen, J.L., Chang, L., Lin, Y.S., 2002. Methane decomposition to carbon nanotubes and hydrogen on an alumina supported nickel aerogel catalyst. *Catal. Today*, **74**(1-2):145-155. [doi:10.1016/S0920-5861(01)00540-5]

Popov, V.N., 2004. Carbon nanotubes: properties and application. *Materials Science and Engineering: R: Reports*, **43**(3):61-102. [doi:10.1016/j.mser.2003.10.001]

Puziy, A.M., Poddubnaya, O.I., Martinez-Alonso, A., Suarez-Garcia, F., Tascon, J.M.D., 2002. Synthetic carbons activated with phosphoric acid I. Surface chemistry and ion binding properties. *Carbon*, **40**(9):1493-1505. [doi:10.1016/S0008-6223(01)00317-7]

Qian, D., Wagner, G.J., Liu, W.K., Yu, M.F., Ruoff, R.S., 2002. Mechanics of carbon nanotubes. *Appl. Mech. Rev.*, **55**(6):495-533. [doi:10.1115/1.1490129]

Rodriguez, N.M., 1993. A review of catalytically grown carbon nanofibers. *J. Mater. Res.*, **8**(12):3233-3250. [doi:10.1557/JMR.1993.3233]

Ros, T.G., 2002. Rhodium Complexes and Particles on Carbon Nanofibres. Ph.D Thesis, Utrecht University, The Netherlands.

Serp, P., Corrias, M., Kalck, P., 2003. Carbon nanotubes and nanofibers in catalysis. *Applied Catalysis A: General*, **253**(2):337-358. [doi:10.1016/S0926-860X(03)00549-0]

Shaffer, M.S.P., Fan, X., Windle, A.H., 1998. Dispersion and packing of carbon nanotubes. *Carbon*, **36**(11):1603-1612. [doi:10.1016/S0008-6223(98)00130-4]

Shin, S., Jang, J., Yoon, S.H., Mochida, I., 1997. A study on the effect of heat treatment on functional groups of pitch based activated carbon fiber using FTIR. *Carbon*, **35**(12):1739-1743. [doi:10.1016/S0008-6223(97)00132-2]

Srivastava, D., Wei, C., Cho, K., 2003. Nanomechanics of carbon nanotubes and composites. *Appl. Mech. Rev.*, **56**(2):215-230. [doi:10.1115/1.1538625]

Starsinic, M., Taylor, R.L., Walker, P.L.Jr., Painter, P.C., 1983. FTIR studies of saran chars. *Carbon*, **21**(1):69-74. [doi:10.1016/0008-6223(83)90158-6]

Tang, T.D., 2005. Study on Carbon Nanofibers Supported Pd-Pt Catalyst for Naphthalene Hydrogenation. Ph.D Thesis, Tianjin University, China (in Chinese).

Thostenson, E.T., Ren, Z., Chou, T.W., 2001. Advances in the science and technology of carbon nanotubes and their composites: a review. *Composites Science and Technology*, **61**(13):1899-1912. [doi:10.1016/S0266-3538(01)00094-X]

Yang, T., Lua, A.C., 2003. Characteristics of activated carbons prepared from pistachio-nut shells by physical activation. *Journal of Colloid and Interface Science*, **267**(2):408-417. [doi:10.1016/S0021-9797(03)00689-1]

Zhao, Y., Li, C.H., Yu, Z.X., Yao, K.F., Ji, S.F., Ji, L., 2007. Effect of microstructures of Pt catalysts supported on carbon nanotubes (CNTs) and activated carbon (AC) for nitrobenzene hydrogenation. *Materials Chemistry and Physics*, **103**(2-3):225-229. [doi:10.1016/j.matchemphys.2007.02.045]

Zielke, U., Huttinger, K.J., Hoffman, W.P., 1996. Surface-oxidized carbon fibers: I. Surface structure and chemistry. *Carbon*, **34**(8):983-998. [doi:10.1016/0008-6223(96)00032-2]