Carbon Nanofibers with Controlled Size and Morphology Synthesized with a Ni-MgO Catalyst Treated by Mechnochemical Process

Yuan Fangli* , 류호진**

*Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100080, China

** Advance Materials Division, Korea Research Institute of Chemical TechnologyO.Box 107, Daejeon 305-600,South Korea

Abstract

Carbon nanofibers (CNF) with uniform diameter and controlled size could be prepared from catalytic decomposition of C_2H_2 with the catalyst treated by mechnochemical(MC) process. The distribution and size of Ni catalyst can be governed by tuning grinding time using MC process. As a result, size and structure of CNF can be controlled. The effect of grinding time to the as-grown CNF was checked. CNFs with diameter from 10-70nm can be synthesized. CNFs with bundle formation sharing one tip were found for MC treated catalyst.

1. Introduction

Carbon nanofiber (CNF) has excellent electric conductivity, absorbability and mechanochemical property applicable to polymer reinforcement [1], electrode materials [2], catalyst support materials [3-5], and energy storage [6-8].

The growth of CNF by a catalytic pyrolysis of hydrocarbon gases requires the transition metal catalyst such as Ni, Co, Fe, etc. It suggests that catalyst characteristics such as the shapes, size and surface area are one of the most keys for preparation of carbon nanofiber using CVD process [9-11]. Three types of CNFs which possess "platelet", "ribbon" and "herring-bone" structures can be produced by tuning the catalyst condition and process parameters [12]. Surface science studies have revealed that certain faces favor precipitation of carbon in the form of graphite, whereas less order carbon will be deposited from other faces [13-15]. So by judicious choice of the catalyst and careful control of the reaction conditions, it is possible to tailor the growth of CNF to generate structure of a desired conformation.

The catalyst for the growth of CNF is conventionally prepared by impregnation or ion exchange process. However, it is not easy to control the dispersion of catalyst particles on the support. In addition, several-step procedures such as stirring, drying and heat-treating are demanded. In this study, mechnochemical process was used to treat the catalyst, which was speculated to govern the size and structure of as-grown CNF.

2. Experimental

$Ni(OH)_2$ and $Mg(OH)_2$ were used as the staring materials to prepare catalyst, and the mol ratio of Ni and Mg was 1:1. They were well mixed by grinding under dry condition using a mixer mill(MM200,Retsch). The grinding was done at approximately 1800rpm, and the duration of grinding was 120-360 min. In order to compare, $Ni(OH)_2$ and $Mg(OH)_2$ mixtures were also ground in ethanol with an agate mortar and pestle. The catalysts were labeled as MC and MP, respectively.

Carbon nanofibers were grown by thermal CVD in quartz-tube electric furnace with C_2H_2 as a carbon source. An argon stream was first introduced into when heating from room temperature to 500℃. Then H_2 of 100 sccm flowed to reduce the surface of mixture to obtain Ni particle used as a catalytic active site for 30min. Next, C_2H_2 gas at 10 sccm and H_2 gas at 100 sccm were simultaneously flowed for 30 min to prepare CNFs. Finally, the sample was cooled down to room temperature under an argon stream.

Morphology of as-grown carbon nanofibres and Pt loaded carbon nanofibers was observed by the scanning electron microscope (SEM, JSM-840A and Phillips XL 30S FEG).

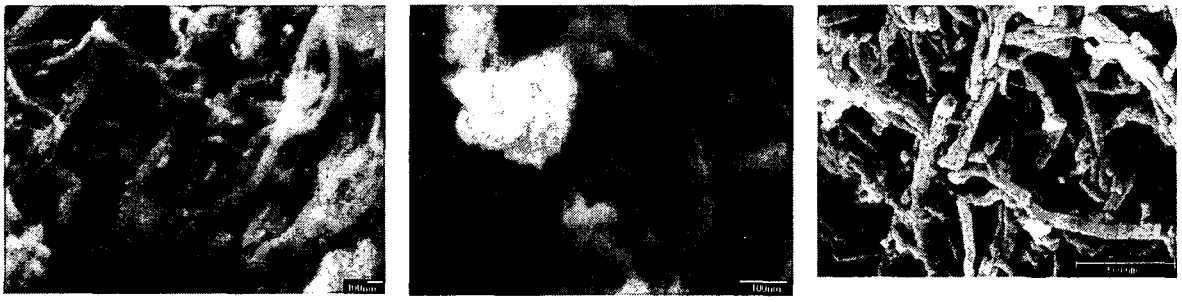
3. Results and Disscusion

Fig.1 shows the SEM images of as-grown nanofibers. As shown for MP catalyst in Fig.1(A), two morphological types of linear and spiral were mixed CNFs due to only simple mixing. It can be seen that the size in diameter distribution of CNFs prepared with MP catalyst is broad. In addition to greater diameter and shorter length CNFs, there are some thin CNFs. However, the morphology changes to linear types and the diameter also becomes more homogeneous with MC catalyst. It becomes homogeneous and linear for CNFs prepared with MC catalyst ground for 120min, and the diameter is about 150-200 nm. In addition to homogeneous, the diameter becomes finer with the grinding time increasing to 360min, and the diameter of CNFs is about 50-100nm. It is believed that the homogeneous distribution and finer size of CNFs are due to the homogeneous distribution and smaller size of Ni particles treated with mechanochemical process. Therefore homogeneous diameter and controlled size CNFs can be tuned with catalyst treated by mechnochemcal process.

A B C

Fig.1 SEM images of as-grown nanofibers
(A - MP, B - MC with 120min, C - MC with 360min)

Fig.2 shows bundle formation of CNFs prepared with MC catalyst. As the arrow indicated in Fig.2(A), there are many CNF bundles, and CNFs in these bundles are combined close. However there are no CNF bundles found in the MP catalyst. Fig.2(B) shows the bundles with four CNFs. It is also seen that the four CNFs share the one tip as arrow A indicated. Fig.2(C) shows bundles with two CNFs. As the arrow indicated, the two CNFs share one tip.

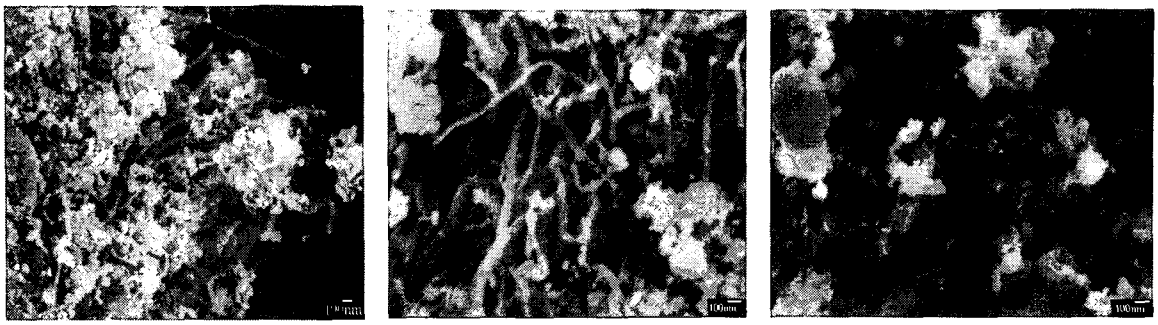


A B C

Fig.2 Bundle formation of CNFs prepared with MC catalyst
(A – bundles with two CNFs, B – bundles with four CNFs, C – bundles shared one tip)

Mechnochemical process using a high-energy ball-mill has been widely used for preparing nonequilibrium materials like nanocrystalline and amorphous materials. It is an effective way to rapidly refine the particle microstructure, i.e., grain size or crystallite size, during milling [16-17]. It is clear that Ni particles can be refined using MC process, so that the size of as-grown CNFs decreases with the grinding time increase. More over, Ni particles can be distributed on the support MgO homogeneously which results in the uniform CNFs. The most important aspect is that Ni particles can be grind to supply some faces favoring precipitation of carbon and embeded on the support materials using mechnochemical process. It is maybe the embedding that prevents the catalyst Ni particles from agglomerating at high temperature. At the same time, different face in one Ni particles would help to grow bundles with one tip.

In addition to controlling MC grinding time, other parameters such as H_2 flow rate, pyrolytic temperature, ratio of H_2/C_2H_2 can also affect the morphology and size of as-grown CNFs. Fig.3 shows CNFs with different diameter prepared with MC catalyst. It shows that CNFs with different diameter would be governed by tuning the parameters of MC process and pyrolytic process.



A B C

Fig.3 CNFs with different diameter prepared with MC catalyst

A – 10-30nm, MC 360min, 700℃, H_2 100sccm at 700℃;

B – 30-50nm, MC 720min, 700℃, H_2 100sccm from 200℃

C – 50-70nm, MC 720min, 600℃, H_2 100sccm at 600℃

4. Conclusions

Carbon nanofibers with controlled size and morphology can be synthesized with catalyst treated using mechnochemical process. The size and uniformity of CNFs can be governed by tuning the grinding time using MC process. The diameter of CNFs can be controlled from 10-70nm by modulating the grinding time in MC process and parameters in pyrolytic process. Bundle formation of CNFs with one tip can be synthesized with the catalyst treated using MC process. It would be the MC process that makes Ni particles embeded on the support materials and several faces favoring precipitation of carbon on one Ni particle.

Acknowledgments

One of the authors (Yuan Fangli) is thankful for the Brain Pool Program fellowship of KOFST.

References

[1] Wang,X.; Wang,S.; Chung, D.D.L. J.Mater.Sci. 1999,34,2703

[2] Endo,E., Kim Y.A., Hayashi T., Nishimura K, Matusita T., Miyashiya K, Dresselhaus M.S. Carbon 2001,39,1287

[3] Rodriguez,N.M.; Kim,M.S.;Baker,R.T.K. J.Phys.Chem. 1994,98,13108

[4] Park,C.; Baker,R.T.K. J.Phys.Chem.B 1998,102,5168

[5] Baker,R.T.K.; Laubernds,K.; Wootsch,A.; Paal,Z. J.Catal. 2000,193,165

[6] Park,C.; Anderson,P.E.; Chambers,A.; Tan,C.D,; Hidalgo,R.; Rodriguez,N.M. J.Phys.Chem.B 1999,103,10572

[7] Fan,Y.Y.; Liao,B.; Liu,M.; Wei,Y.L.; Lu,M.Q.; Cheng,H.M. Crabon 1999,37,1649

[8] Gupta,B.K.;Srivastava,O.N. Int.J.Hydrogen Energy 2000,25,825

[9] N.M.Rodriquez, J.Mater.Res. 8 (1993) 3233

[10] N.M.Rodriquez, A.Chambers, R.T.K. Baker, J.Phys.Chem. B 102 (1998) 2551

[11] M.Takizawa, S.Bandow, M.Yudasaka, Y.Ando, H.Shimoyama, S.Iijima, Chem. Phys.Lett.

326 (2000) 351
[12] Rodriguez,N.M.; Chambers,A.;Baker,R.T.K. Langmuir 1995,11,3862
[13] Goodman,O.W.; Kelley,R.D.; Madey,T.E.; Yates,J.T. J.Catal. 1980, 63, 226
[14] Nakamura,J.; Hirano,H.; Xie M.; Matsuo,I.; Yamada T.; Tanaka K. 1989 Surf.Sci. 222,L809
[15] Yang R.T.; Chen J.P. J.Catal. 1989,115,52
[16] C.Surayanarayana, Prog Materi Sci 46(2001) 1
[17] C.C.Koch, Nanostructureed Mater. 9 (1997) 13