CO$_2$-Assisted SWNT Growth on Porous Catalysts

Qian Wen, Weizhong Qian,* Fei Wei, Yi Liu, Guoqing Ning, and Qiang Zhang

*Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of
Chemical Engineering, Tsinghua University, Beijing, 100084, China*

The effect of CO$_2$ on the synthesis of single-walled carbon nanotubes (SWNTs) by methane decomposition on a Fe/Mo/MgO porous catalyst was investigated. Characterizations of the change in methane conversion with time, XRD and SSA of the catalyst, Raman spectroscopy, TGA, and the specific surface area (SSA) of SWNTs showed that CO$_2$ inhibited the formation of amorphous carbon around the catalyst and also interacted with the MgO support of the catalyst, which decreased its particle size and increased the SSA of the catalyst. The result was an increase in the yield, purity, and SSA of SWNTs. These results indicated that the limited and small space in the pores of the porous catalyst made it difficult to increase the SWNTs in high yield. The addition of CO$_2$, by destroying the structure of the catalyst and decreasing the catalyst size, provides a new route to increase the yield, purity, and SSA of SWNTs.

Introduction

There is continuous interest in the synthesis of single-walled carbon nanotubes (SWNTs)[1] because of their extraordinary electrical and mechanical properties and many possible applications.[2−7] SWNTs can be prepared efficiently in chemical vapor deposition (CVD) processes[8] using the decomposition of hydrocarbon or CO on metal crystallites (1−3 nm) deposited on flat substrates or supported on porous catalysts and other agglomerate forms. The CVD processes using porous catalysts are attractive because there is a wide and cheap catalyst selection from the varieties of metal species (mainly Ni, Co, and Fe), supports (Al$_2$O$_3$, SiO$_2$, and MgO), and relatively mature preparation technologies, which gives the potential of SWNT synthesis at low cost. However, despite many efforts made in this field, a high yield of SWNTs has still not been achieved, as compared with that from using catalysts on flat substrates, especially assisted by water[9−12] or oxygen.[13−15]

On looking at the growth processes of SWNTs on different catalysts, it can be noticed that SWNTs grow up from a flat substrate with relative ease. However, on agglomerate porous catalysts, the SWNTs first grow in the inner pores of the catalyst, and the catalyst texture becomes destroyed gradually during the SWNT growth, which is normally observed in the growth of carbon filaments or multiwalled CNTs (MWNTs) on porous catalysts.[16,17] In this case, it is clear that the SWNTs suffer large stresses during their growth. Since carbon nanotubes are extraordinarily flexible under large strains,[18] and the stiffness of SWNTs is even smaller than MWNTs,[19] we suggest here that the relatively stable porous catalyst texture, resulting in the large resistance during the lift up of SWNTs, is the cause of the low yield of SWNTs.

To confirm this hypothesis and find a way to increase the SWNT yield, CO$_2$ was introduced into the SWNT synthesis system that used a Fe/Mo/MgO model catalyst to decompose methane. Conventionally, CO$_2$ has been used in the synthesis[20,21] and postprocessing of CNTs.[22−24] The effects of CO$_2$

* To whom correspondence should be addressed. Tel: +86-10-62788984. Fax: +86-10-62772051. E-mail: qwz@flotu.org.
(1) Iijima, S.; Ichihashi, T. *Nature* **1993,** *363,* 603.
(2) Tans, S. J.; Devoret, M. H.; Dai, H. J.; Thess, A.; Smalley, R. E.; Geerligs, L. J.; Dekker, C. *Nature* **1997,** *386,* 474.
(3) Dresselhaus, M. S.; Dresselhaus, G.; Avouris, P. *Carbon Nanotubes Synthesis, Structure, Properties, and Applications*; Springer: New York, 2001.
(4) Chen, R. J.; Bangsaruntip, S.; Drouvalakis, K. A.; Kam, N. W. S.; Shim, M.; Li, Y. M.; Kim, W.; Utz, P. J.; Dai, H. J. *Proc. Natl. Acad. Sci. U.S.A.* **2003,** *100,* 4984.
(5) Li, Y. J.; Wang, K. L.; Wei, J. Q; Gu, Z. Y.; Wang, Z. C.; Luo, J. B.; Wu, D. H. *Carbon* **2005,** *43,* 31.
(6) Chen, X.; Tam, U. C.; Czlapinski, J. L.; Lee, G. S.; Rabuka, D.; Zettl, A.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2006,** *128,* 6292.
(7) Shofner, M. L.; Khabashesku, V. N.; Barrera, E. V. *Chem. Mater.* **2006,** *18,* 906.
(8) Su, M.; Zheng, B.; Liu, J. *Chem. Phys. Lett.* **2000,** *322,* 321.
(9) Zhu, H. W.; Li, X. S.; Jiang, B.; Xu, C. L.; Zhu, Y. F.; Wu, D. H.; Chen, X. H. *Chem. Phys. Lett.* **2002,** *366,* 664.
(10) Liu, J. X.; Ren, Z.; Duan, L. Y.; Xie, Y. C. *Acta Chimica Sinica (Chin. Ed.)* **2004,** *62,* 775.
(11) Hata, K.; Futaba, D. N.; Mizuno, K.; Namai, T.; Yumura, M.; Iijima, S. *Science* **2004,** *306,* 1362.
(12) Futaba, D. N.; Hata, K.; Namai, T.; Yamada, T.; Mizuno, K.; Hayamizu, Y.; Yumura, M.; Iijima, S. *J. Phys. Chem. B* **2006,** *110,* 8035.
(13) Nagasawa, S.; Yudasaka, M.; Hirahara, K.; Ichihashi, T.; Iijima, S. *Chem. Phys. Lett.* **2000,** *328,* 374.
(14) Rummeli, M. H.; Borowiak-Palen, E.; Gemming, T.; Pichler, T.; Knupfer, M.; Kalbac, M.; Dunsch, L.; Jost, O.; Silva, S. R. P.; Pompe, W.; Buchner, B. *Nano Lett.* **2005,** *5,* 1209.
(15) Fan, J.; Yudasaka, M.; Miyawaki, J.; Ajima, K.; Murata, K.; Iijima, S. *J. Phys. Chem. B* **2006,** *110,* 1587.
(16) Fenelonov, V. B.; Derevyankin, A. Y.; Okkel, L. G.; Avdeeva, L. B.; Zaikovskii, V. I.; Moroz, E. M.; Salanov, A. N.; Rudina, N. A.; Likholobov, V. A.; Shaikhutdinov, S. K. *Carbon* **1997,** *35,* 1129.
(17) Qian, W. Z.; Liu, T.; Wei, F.; Wang, Z. W.; Luo, G. H.; Yu, H.; Li, Z. F. *Carbon* **2003,** *41,* 2613.
(18) Falvo, M. R.; Clary, G. J.; Taylor, R. M.; Chi, V.; Brooks, F. P.; Washburn, S.; Superfine, R. *Nature* **1997,** *389,* 582.
(19) Wang, C. Y.; Ru, C. Q.; Mioduchowski, A. *J. Nanosci. Nanotechnol.* **2003,** *3,* 199.
(20) Chen, S. Y.; Chang, L. W.; Peng, C. W.; Miao, H. Y.; Lue, J. T. *J. Nanosci. Nanotechnol.* **2005,** *5,* 1887.
(21) Albert, G. N.; David, P. B.; Paula, Q.; David, G.; Hua, J.; Esko, I. K. *Chem. Phys. Lett.* **2006,** *417,* 179.

CO₂-Assisted SWNT Growth on Porous Catalysts

Chem. Mater., Vol. 19, No. 6, 2007 1227

observed in previous works include the regeneration of the catalysts,[21] help in giving more uniform SWNT samples,[22] and thinning and opening of the ends of the tubes,[23] which are similar effects to oxygen or water on the growth of CNTs.[11,25] However, in the present work, in addition to looking at the previous effects of the presence of small amounts of CO_2 on the purity of the SWNT products, the effects on the catalyst support and the catalyst texture were also examined. It is well-known that CO_2 can interact with MgO to form $MgCO_3$ species. Notably, the bulk $MgCO_3$ phase is an unstable phase that decomposes again into MgO and CO_2 at temperatures higher than 913 K (at atmospheric pressure). Thus, it can be expected that the formation and decomposition of the $MgCO_3$ phase at the high-temperature condition of SWNT synthesis can result in the gradual cracking of the catalyst texture and decrease of the catalyst particle size, which are favorable for SWNT growth. In addition, we also present evidence that CO_2 is ineffective on affecting other catalyst supports such as SiO_2 and Al_2O_3 that do not interact with CO_2. A relatively low yield of SWNTs resulted from using these supports as compared with that using a MgO support, which further confirmed our hypothesis.

The change in methane conversion with time, XRD and SSA of the catalyst, SSA, Raman spectroscopy, TGA, SEM, and HRTEM characterizations of SWNTs are combined in the present work to provide a comprehensive analysis of the SWNT growth process and the effect of CO_2 on the yield and purity of SWNTs.

Experimental Procedures

Catalyst Preparation. The Fe/Mo/MgO catalyst was prepared by an impregnation method. An iron nitrate hydrate ($Fe(NO_3)_3 \cdot 9H_2O$) and ammonium molybdate ((NH_4)$_6Mo_7O_{24} \cdot 4H_2O$) solution with MgO powder was ultrasonicated to a gel, dried at 383 K, ground to a fine powder, and then calcined at 823 K. The catalyst mol ratio was 0.02 mol of Fe and 0.0013 mol of Mo per mol of MgO. The catalysts using other supports, such as SiO_2 and Al_2O_3, were prepared in the same manner.

Synthesis of SWNTs. The synthesis of SWNTs at 1173 K performed with adding and not adding CO_2 were compared. The catalyst was packed into a quartz tube reactor. The reactant gas was 5% H_2 and 95% CH_4, with and without a CO_2 mixture (10% CO_2 + 90% Ar, premixed). The concentration of CO_2 was controlled to 0.1−2.0% in the reactant gas (CH_4). The reaction system included an on-line BET SSA measurement system[26] and on-line gas chromatography to perform the in situ characterizations of the catalyst, as-grown carbon products, and product gases. The SWNT growth was carried out for 15 min, and the products were cooled in Ar to ambient conditions.

Characterization. The SSAs of the catalyst and SWNT products in the reaction processes were in situ analyzed by the online BET measurement system. Thus, we can evaluate the changes in the catalyst and SWNTs in the presence and absence of CO_2. Catalysts
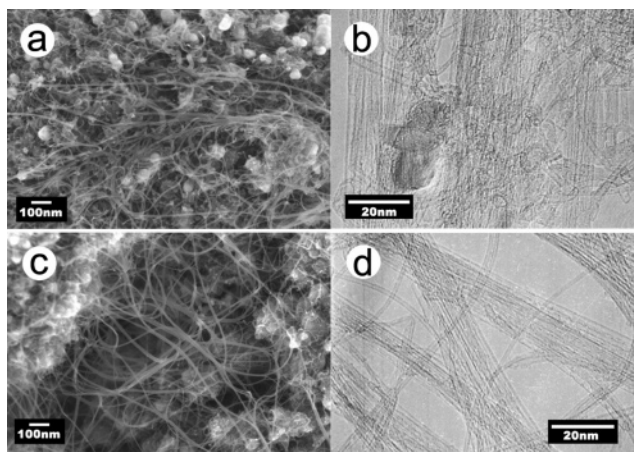

Figure 1. SEM and TEM images of the materials prepared by methane cracking on the Fe/Mo/MgO catalyst. (a) SEM of SWNT product synthesized in the absence of CO_2, (b) TEM of SWNTs synthesized in the absence of CO_2, (c) SEM of SWNT product synthesized in the presence of CO_2, and (d) TEM of SWNTs synthesized in the presence of CO_2.

before and after reaction were characterized by XRD (D8-Discover). The SWNT products were further characterized by SEM (JSM7401F, 3 kV), TEM (JEOL-2010, 120 kV), Raman spectroscopy (Renishaw, RM2000, 633 nm), and TGA (TGA-2050) analysis.

Results and Discussion

SEM and TEM images revealed that the SWNT products, synthesized by methane decomposition with and without CO_2, both formed straight bundles with diameters of several nanometers and lengths of several micrometers (Figure 1). In some localized regions, the SWNTs interacted tightly with the catalyst support (Figure 1a,c). Comparatively, the synthesis in the absence of CO_2 gave SWNT products that contained some very short tubes and relatively more broken carbon sheets (Figure 1b). The SWNT bundles from the synthesis with CO_2 (SWNTs-CO_2) were of high density and uniformly long length (Figure 1d). Notably, the outer walls of the SWNT-CO_2 products were all smooth and clean, that is, free of amorphous carbon (Figure 1d), and their TGA analysis also showed only one peak corresponding to SWNTs (see Supporting Information), indicating its relatively high purity. In addition, the Raman characterization showed that the intensity ratios of the D band (centered at about 1340 cm^{-1}) to the G band (centered at about 1590 cm^{-1}) of the SWNTs synthesized in the presence and absence of CO_2 were 0.06 and 0.2, respectively (Figure 2), which also indicated the much higher purity of SWNTs-CO_2. Furthermore, the SSA for SWNTs-CO_2 was 691.1 m^2/g, which was much larger than that (442.8 m^2/g) synthesized in the absence of CO_2. Since the SSA of pure SWNTs (about 800 m^2/g) is far larger than those of MWNTs and amorphous carbon (both smaller than 300 m^2/g), the results indicated that the content of SWNTs was higher in the synthesis with CO_2. If we assume that the SSAs of pure MWNTs and pure SWNT bundles are 250 and 750 m^2/g, respectively, as in previous reports,[27,28] the purities of the SWNTs synthesized in the

(22) Smith, M. R., Jr.; Hedges, S. W.; Lacount, R.; Kern, D.; Shah, N.; Huffman, G. P.; Bockrath, B. *Carbon* **2003**, *41*, 1221.

(23) Tsang, S. C.; Harris, P. J. F.; Green, M. L. H. *Nature* **1993**, *362*, 520.

(24) Chen, Y.; Liu, C.; Li, F.; Chen, H. M. *J. Porous Mater.* **2006**, *13*, 141.

(25) Osswald, S.; Flahaut, E.; Gogotsi, Y. *Chem. Mater.* **2006**, *18*, 1525.

(26) Ning, G. Q.; Wei, F.; Luo, G. H.; Jin, Y. *Carbon* **2005**, *43*, 1439.

(27) Peigney, A.; Laurent, C.; Flahaut, E.; Bacsa, R. R.; Rousset, A. *Carbon* **2001**, *39*, 507.

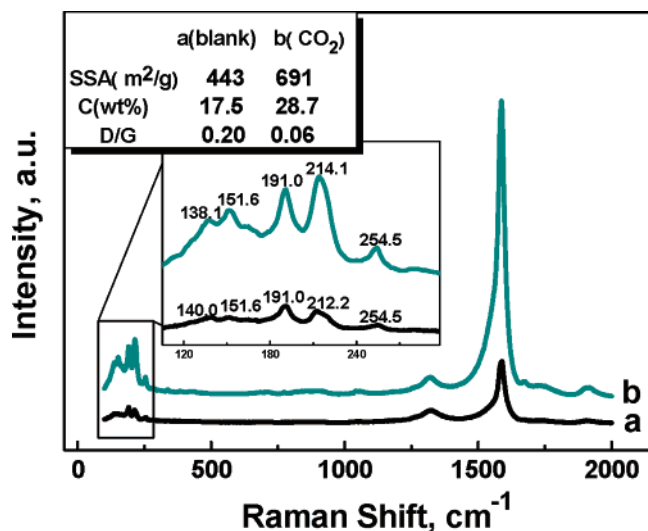(28) Williams, K. A.; Eklund, P. C. *Chem. Phys. Lett.* **2000**, *320*, 352.

Figure 2. Raman spectroscopy of the materials prepared by methane cracking on the Fe/Mo/MgO catalyst (a) in the absence of CO_2 and (b) in the presence of CO_2 (0.26% in volume fraction).
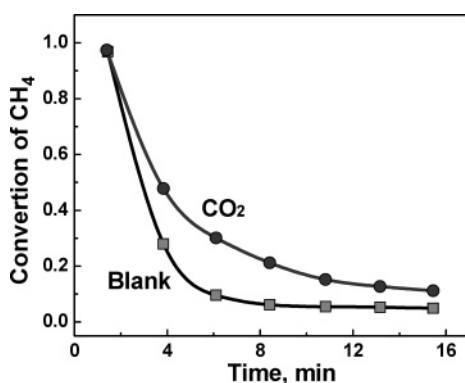

Figure 3. Methane conversion vs time at 1173 K on the Fe/Mo/MgO catalyst in the absence and presence of CO_2 (0.26% in volume fraction).

presence and absence of CO_2, roughly estimated, were 88.3 and 38.7%, respectively. Thus, the SSA value of the SWNTs-CO_2, together with their TGA result and Raman scattering characterization, showed that SWNTs with much higher purity and fewer defects were produced in the presence of CO_2.

From the change in methane conversion with time (Figure 3), it is clear that the catalyst during the synthesis in the absence of CO_2 lost its activity rapidly. Comparatively, the addition of 0.26% CO_2 (in volume fractions) was effective on keeping the catalyst stable and active. Specifically, the conversion of methane above 10% from 6 to 15 min of the reaction time indicated the effective regeneration of the catalyst due to the addition of CO_2. The result indicated that CO_2 effected an increase in the yield of SWNTs. According to the TGA results, the SWNT yields in the experiments with and without CO_2 were 28.7 and 17.5%, respectively, which was a significant 64% increase due to the addition of CO_2 (see Supporting Information). The product gas contained CO, which indicated that CO_2 reacted with carbon to give CO. Thus, CO_2 was able to remove amorphous carbon to regenerate the catalyst, which is a similar effect to oxygen and water.[11] Meanwhile, we also compared the effect of the presence of a small amount of oxygen in the reactant gas by repeating the same experiment. However, the carbon yield
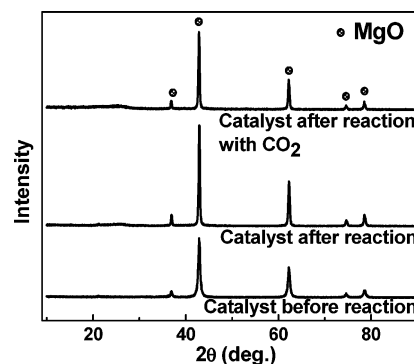

Figure 4. XRD spectra of the Fe/Mo/MgO catalyst before and after the reaction without CO_2 and after the reaction with CO_2.

was only increased from 17.5 to 20.3% by using oxygen as a regenerating agent (see Supporting Information). From the viewpoint of removing amorphous carbon to regenerate the catalyst, the effect of CO_2 and oxygen appears similar, and the significantly higher SWNT yield effected by CO_2 suggests another undiscovered effect.

To understand this, we carefully examined the state of the catalyst obtained from the experiments performed in the presence and absence of CO_2. XRD results (Figure 4) confirmed that the average crystallite size of MgO in the fresh catalyst was 23 nm, but it sintered to 40 nm after being used for SWNT growth without CO_2. However, in the presence of CO_2, the after-reaction crystallite size was smaller and was 32 nm, which is an effect of CO_2 that has not been previously reported. It is suggested that this effect of CO_2 on the MgO support is mainly due to that CO_2 is able to interact with MgO to form $MgCO_3$. Since the decomposition temperature of bulk $MgCO_3$ is only 913 K (at atmospheric pressure), the newly formed $MgCO_3$ is an unstable phase and will redecompose at the high-temperature conditions used for SWNT synthesis. Also, there is an obvious difference between the MgO and the $MgCO_3$ crystal lattices (see Supporting Information). Since phase separation is always observed in alloys with mismatched ratios and lattice characteristics, this mismatch between $MgCO_3$ and MgO lattices would gradually destroy the structure of the MgO support in the cycle of formation and redecomposition of the $MgCO_3$ phase in the main MgO lattice. Thus, a size decrease from 40 to 32 nm is reasonable, considering that the CO_2 concentration was only about 0.1% and that the reaction time was only 15 min. To further support this result, we also tested the effect of CO_2 on a pure MgO support and obtained a similar size decrease effect (see Supporting Information). Meanwhile, together with the size decrease of the MgO support, a SSA increase was also observed in the experiment using the pure MgO support. The SSA of a fresh MgO support was 124 m^2/g at ambient conditions, and it decreased to 57.2 m^2/g at 1173 K in Ar. But, this was improved to 66.4 m^2/g by the addition of 0.1% CO_2. The result suggested that in the SWNT synthesis system, CO_2 was also effective on increasing the SSA of the catalyst support, which allowed an effective redispersion of the metal species on them and the subsequent growth of SWNTs in high yield and with a high SSA. On the other hand, although the presence of CO_2 is helpful with decreasing the size of the MgO support and increasing the SSA of the catalyst

CO₂-Assisted SWNT Growth on Porous Catalysts

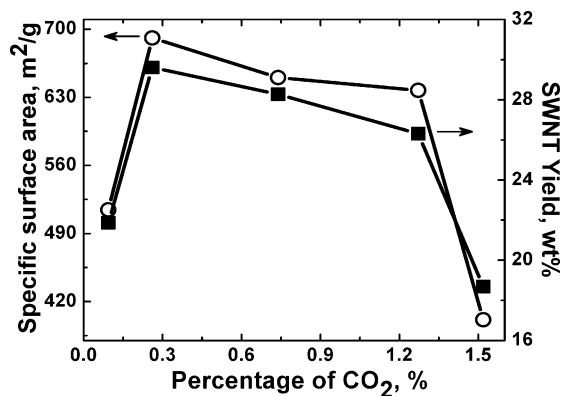*Chem. Mater., Vol. 19, No. 6, 2007* 1229

Figure 5. BET SSAs and carbon yield of the nanotubes prepared by methane cracking on the Fe/Mo/MgO catalyst with different percentage composition of CO_2 in the reactant gases.
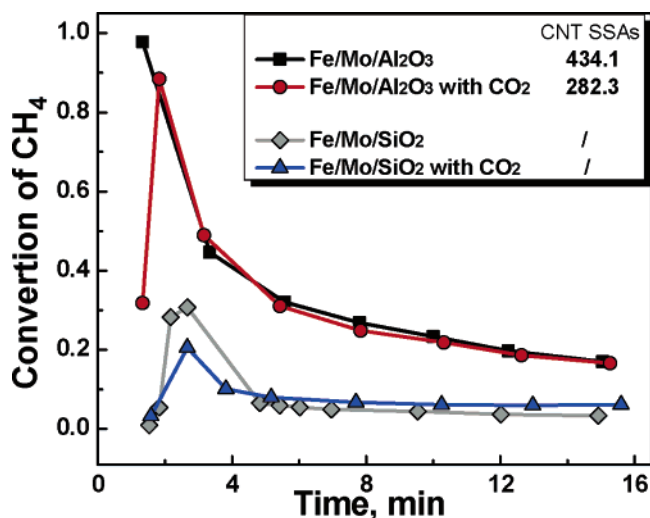

Figure 6. Methane conversion vs time at 1173 K on the Fe/Mo/Al₂O₃ and Fe/Mo/SiO₂ catalysts in the absence and presence of CO_2.

effectively, too much CO_2 will also react with the SWNTs to decrease the yield. From a quantitative viewpoint, an appropriate concentration of CO_2 was between 0.1 and 1.2% (Figure 5). In this range, the SSA of the SWNTs was about $600-700$ m²/g, and the yield of SWNTs was about 30% of the catalyst weight.

To further confirm the effect of CO_2 on the catalyst support, we also used other catalyst supports such as Al_2O_3 and SiO_2 that are generally used in CNT synthesis but that do not interact with CO_2. After the same CNT growth process as with the use of the Fe/Mo/MgO catalyst stated previously, we obtained methane conversions in the absence and presence of CO_2 (Figure 6). The initial conversion of methane on the Fe/Mo/Al₂O₃ catalyst was much higher than that on the Fe/Mo/SiO₂ catalyst, but these catalysts all deactivated within 3.5 min. Notably, the addition of CO_2 seemed ineffective on improving the conversion of methane and the activity of the catalysts on Al_2O_3 and SiO_2 supports. Even worse, the SSA of the carbon products decreased from 434 m²/g (without CO_2) to 282 m²/g (with CO_2) with the use of the Fe/Mo/Al₂O₃ catalyst, which seemed to indicate that carbon products were destroyed by CO_2. From the TEM characterization, it was observed that the content of SWNTs in the carbon products was very low on these catalyst supports in the synthesis performed without using CO_2.

Furthermore, the carbon products were mostly MWNTs with the use of the Fe/Mo/Al₂O₃ catalyst when CO_2 was introduced, probably because of the easier oxidation of SWNTs by CO_2, as compared with MWNTs. These results further support our deduction on the effect of using CO_2 to tailor the MgO supported catalyst to increase the purity and SSA of the SWNT products.

From the previous results, it is clear that the effect of CO_2 is not only to remove the amorphous carbon but also to modify and improve the catalyst properties by decreasing the size of the support and increasing the BET SSA of the catalyst. The new finding of the size and SSA changes of the MgO support suggests a reconsideration of the growth process of SWNTs. For the agglomerated porous catalysts used in the present work, the metal particles are dispersed in the inner pores of the catalyst, and the initial SWNT growth mainly occurs on the active metal sites in the inner pores of the catalyst. Hence, the growth of SWNTs to a length of several hundred micrometers must overcome the metal−support interaction that keeps the metal particles in the pores by destroying the structure of catalyst first, as in the MWNT and carbon filament synthesis.[16−18] Here, we propose that the initially grown SWNTs containing only one carbon layer may be not well graphitized. Thus, they are of low mechanical strength and unable to overcome the metal−support and support−support interactions of the catalyst and need to destroy the catalyst structure. On this view, if the size of the catalyst support becomes larger and the SSA of the catalyst becomes smaller at high temperatures, SWNT growth will be inhibited seriously.[29] Consequently, with such catalysts, it is more probable that amorphous carbon or defective nanotubes will be produced due to the deformation of the nanotubes in the limited inner space of the catalyst, which is a similar effect to the heavy stress exerted on the SWNTs during the intentional bending of nanotubes.[30] Such deduction is further supported by the magnification of the TEM images (Figure 1b and Supporting Information). Thus, it is proposed that the free growth resistance from the pore wall is responsible for the low yield and purity of the SWNTs. On comparing the increase in the previous yield of SWNTs affected by the addition of oxygen and CO_2, it can be seen that the limitation imposed by the catalyst structure was at least as limiting as the carbon encapsulation that caused catalyst deactivation and the inhibition of SWNT growth. Comparatively, the growth of SWNTs from the metal particles on a flat substrate is a relatively simple process with low resistance. Furthermore, these results also imply that if catalysts with small-sized metal particles and support, similar to the nanoarchitecture catalysts with large SSA, can be prepared, the SWNT growth process on them may be simplified, and a relatively high SWNT yield can be expected. From this viewpoint, the findings in the present work are of both scientific and technical importance for the further controlled production of SWNTs.

(29) Ago, H.; Imamura, S.; Okazaki, T.; Saito, T.; Yumura, M.; Tsuji, M. *J. Phys. Chem. B* **2005**, *109*, 10035.
(30) Lourie, O.; Cox, D. M.; Wagner, H. D. *Phys. Rev. Lett.* **1998**, *81*, 1638.

We have further tested the effect of CO_2 on the SWNT growth on a Fe/MgO porous catalyst and obtained similar results. These results indicate that the addition of a small amount of CO_2 is a novel and general method to increase the yield and purity of SWNTs synthesized on porous catalysts that have a support that easily reacts with CO_2. It can be noted that our catalyst in this work was only a model catalyst used to unravel the mechanism. More improvement can be expected with the use of the actual highly active catalysts. Since CO_2 is easily available and controllable in the CVD process, this method is suitable for the production of SWNTs with a high yield and purity at low cost.

Conclusion

CO_2 was introduced into a SWNT synthesis system comprising a Fe/Mo/MgO model catalyst that decomposed methane. A small amount of added CO_2 was effective on removing amorphous carbon to regenerate the catalyst, decreasing the size of the MgO support and increasing the SSA of the catalyst. The results showed the importance of keeping the particle size small and the SSA of the catalyst high for the production of SWNTs with high yield, purity, and SSA. A previously unreported effect of CO_2 was proved operative on the catalysts using a MgO support but not on the catalysts using a Al_2O_3 or SiO_2 support. The range of CO_2 added should be $0.1-1.5\%$ in the feed gas. The SWNT product synthesized using the addition of CO_2 was $600-700$ m^2/g SSA, with a yield of 30% of the catalyst weight, and the purity was 88% of the carbon products. The results are useful for a better understanding of the SWNT growth process on porous catalysts and controlled production of SWNTs.

Supporting Information Available: General experimental procedures; magnification of TEM images of the carbon materials prepared using the Fe/Mo/MgO catalyst; TGA curves of the SWNT products; gas chromatography characterization of the product gas during SWNT synthesis; XRD spectra of the Fe/Mo/MgO catalyst; general view of the crystal lattices of MgO and $MgCO_3$; TEM images of pure MgO materials; and calculation of the purities of SWNTs synthesized in the presence and absence of CO_2. This material is available free of charge via the Internet at http://pubs. acs.org.

CM062339B