



Controlled production of single-wall carbon nanotubes by catalytic decomposition of CO on bimetallic Co–Mo catalysts

B. Kitiyanan, W.E. Alvarez, J.H. Harwell, D.E. Resasco *

School of Chemical Engineering and Materials Science, University of Oklahoma, 100 East Boyd St., Norman, OK, 73019, USA

Received 16 September 1999; in final form 8 October 1999

Abstract

The term ‘controlled production’ of single-wall nanotubes (SWNT) implies the ability to control the selectivity towards SWNT by changing catalyst formulations and operating conditions, combined with a quantitative measurement of the SWNT obtained. In this contribution, a significant advancement towards the controlled production of SWNT is reported. A family of Co–Mo catalysts has been found to be able to produce SWNT with high selectivity, depending on the Co:Mo ratio, the temperature of operation, and the processing time. The optimization of the catalyst was possible by the application of a simple and direct method of quantification of the SWNT production. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Single-wall carbon nanotubes (SWNT) have shown unmatched electrical and mechanical properties [1], which might lead to a variety of new applications. However, the low availability of high-quality nanotubes and the high costs associated with the current synthesis methods would be a serious impediment for large-scale production in any commercial endeavour. The production of multi-wall nanotubes (MWNT) by catalytic hydrocarbon cracking on supported metals is now on a commercial scale [2], but the production of SWNTs by laser [3] and arc [4] techniques is still in the gram scale. A cost effective process for the production of SWNT will only emerge when today’s gram-scale technology advances to a ton-scale technology, in a way similar to the produc-

tion of chemical commodities. In fact, it is conceivable to design a continuous fluidized-bed catalytic reactor that could produce carbon nanotubes in a gas-phase process. To reach this point however, an excellent control over the activity, selectivity, and catalyst life is necessary. This goal has guided our recent research and will be the focus of this contribution.

In many catalytic processes found in the chemical industry, the separation steps that precede or follow the chemical reactor represent the largest portion of the capital and operating costs. On the other hand, while the cost of the catalyst is usually minimal in comparison to the overall cost of the plant, the catalyst is the key factor that determines how much should be spent in the separation steps. For example, a catalyst with high tolerance to the presence of impurities may reduce the costs of feed pretreatment. At the same time, a very selective catalyst can greatly reduce the separation costs involved in the

* Corresponding author. Fax: +1-405-325-5813; e-mail: resasco@ou.edu

purification of the product. Selectivity is in many cases the most important property that an efficient catalyst should exhibit. The same concepts will apply to the production of nanotubes in industrial scale, i.e., a catalyst should be designed with selectivity high enough to minimize the subsequent purification steps. This is particularly important for the catalytic production of SWNT, which in most cases produces MWNT, amorphous, and graphitic forms of carbon as by-products.

In comparison to most of the other methods currently used for the synthesis of SWNT, the potential advantage of using a gas-phase catalytic method is that the solid catalyst can be tailored to maximize selectivity. Until now however, in most attempts to produce nanotubes by the catalytic method, little attention has been paid to the optimization of the selectivity towards SWNT. In fact, the majority of the reports found in the literature disclose formation of MWNT or a combination of amorphous carbon, MWNT, and graphitic carbon [5,6]. Only a few papers [7–11] have reported the formation of SWNT by catalytic decomposition. One of the greatest limitations in the current technology is the inability to obtain a simple and direct quantification of the different forms of carbon obtained in a particular synthesis. Nowadays, electron microscopy is the characterization technique most widely employed to determine the fraction of SWNT present in a particular sample. However, TEM can only provide a qualitative description of the type of carbon species produced. It is hard to determine how representative of the overall production can a given image be. Obtaining semi-quantitative determinations of the distribution of the different carbon species in a sample, with any statistical significance is time consuming and the method could not be applied as a routine quality control to large-scale operations.

In this contribution, we describe what we believe is a breakthrough in the controlled synthesis of SWNT. We define controlled production as the ability to modify the selectivity of a catalyst by changing catalyst parameters, such as composition and support, combined with the ability to obtain a reliable quantitative measurement of the yield and selectivity of SWNT produced. This measurement should be direct and easy to conduct, so changes in selectivity during catalyst selection or steady-state production

can be readily detected, facilitating the reproducibility and quality control.

2. Experimental results

Several transition metal catalysts have been shown to be active for generation of carbon nanotubes [12,13]. Among the various formulations that we have investigated, a Co–Mo/SiO₂ catalyst, containing 6 wt % total metals and a Co:Mo molar ratio of 1:2, exhibited the highest selectivity towards SWNT. This catalyst was prepared by incipient wetness impregnation of aqueous solutions of Cobalt Nitrate and Ammonium Heptamolybdate, followed by drying in an oven at 80°C and calcination in flowing air at 500°C. For the production of nanotubes, 100–500 mg of calcined catalyst was placed in a horizontal quartz tubular reactor, heated in H₂ up to 500°C, and then in He to 700°C. Subsequently, CO was introduced at this temperature and at a flowrate of 100 cm³/min for the production of nanotubes. The product was inspected in a TEM, model JEOL JEM-2000FX at 200 kV. As shown in Fig. 1A, SWNTs were observed in large quantities, most of them aligned as bundles. From the TEM pictures, it was observed that the diameter of the individual tubes was about 1 nm. From inspection of the TEM micrographs, it appears that the SWNT produced by the catalytic method contain more defects than those produced by the laser ablation or arc discharge methods. At the same time, small quantities of amorphous carbon were observed covering the bundles of SWNT, but no evidence of MWNT or graphitic carbon was observed on this sample. The presence of SWNT on this sample was further confirmed by Raman spectroscopy, conducted at room temperature and using 532 nm excitation. The spectrum exhibited a strong line in the range 1580–1590 cm⁻¹, normally observed in SWNT [14].

It is important to note here that not all Co–Mo formulations investigated were equally effective in producing SWNT. For example, while Mo samples produced no SWNT at 700°C, when Mo was added to Co, the selectivity towards SWNT greatly increased, which indicates that some sort of synergism between Co and Mo makes the combination of the two metals effective. As illustrated in Fig. 1B, the

TEM image shows that the catalyst with a Co:Mo molar ratio of 2:1 resulted in a significant fraction of MWNT, as opposed to the catalyst with a molar ratio of 1:2, which mainly produced SWNT.

The method that we have developed for quantifying the amount of SWNT produced is based on the standard temperature programmed oxidation (TPO) technique, commonly employed in catalysis research.

We have used this method in the past to characterize carbonaceous deposits on heterogeneous catalysts [15,16]. To conduct the TPO, a continuous flow of 5% O₂/He is passed over the catalyst containing the carbon deposits while the temperature is linearly increased (11°C/min). The evolution of CO₂ produced by the oxidation of the carbon species is monitored by a mass spectrometer. Quantification of

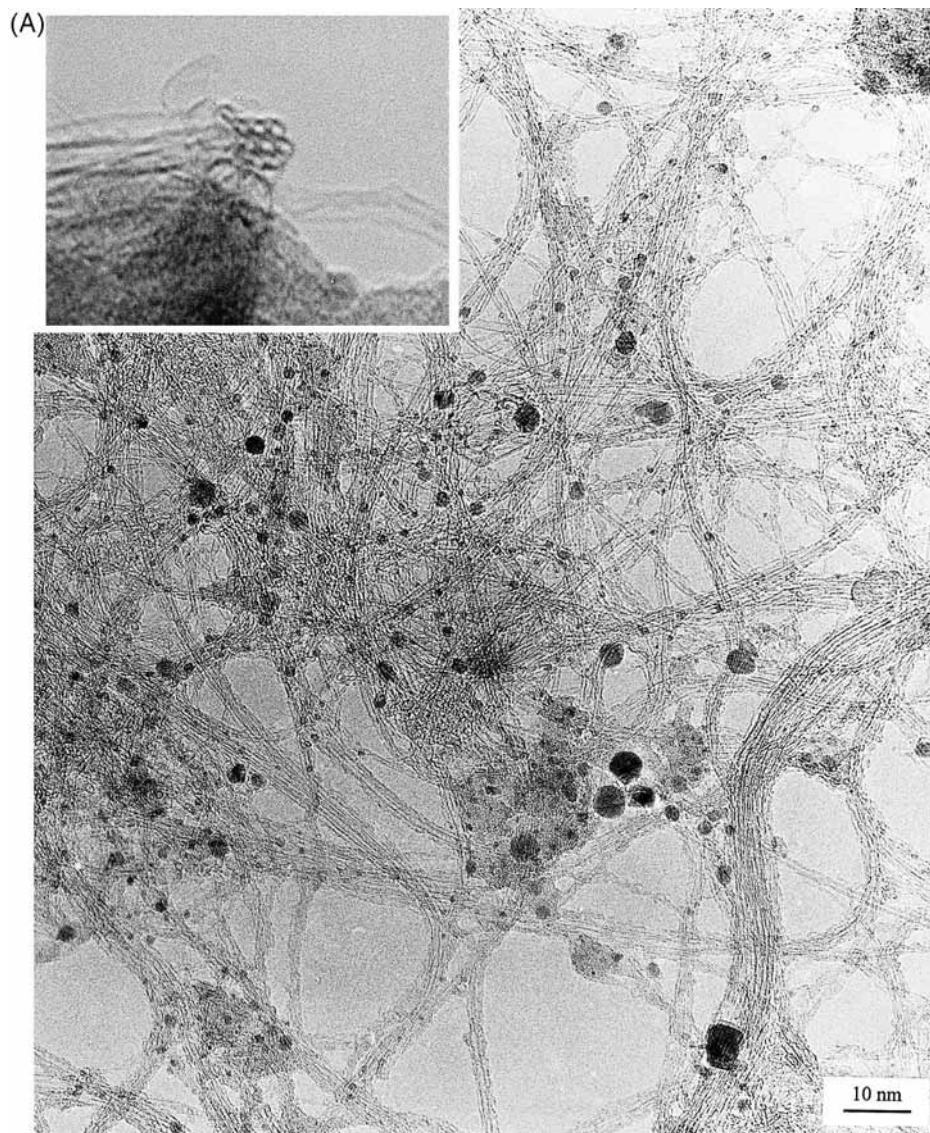


Fig. 1. TEM images showing (A) SWNT produced by decomposition of 50% CO/He at 700°C on a Co–Mo/SiO₂ catalyst, 6 wt % total metals, Co:Mo molar ratio of 1:2. Inset shows the detail of a front view of a SWNT bundle; (B) mixture of SWNT and MWNT produced on a Co–Mo/SiO₂ catalyst, 6 wt % total metals, Co:Mo molar ratio of 2:1, under the same conditions as that of (A).

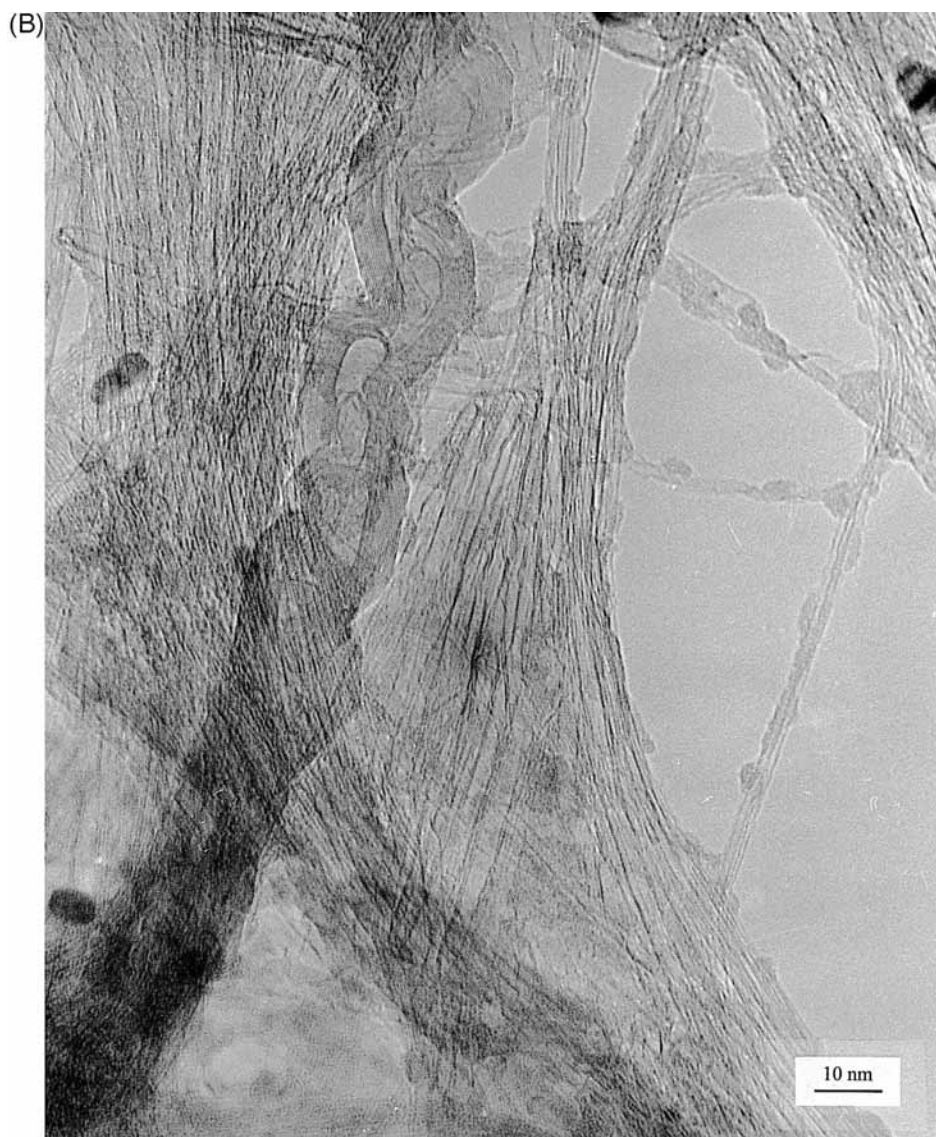


Fig. 1 (continued).

the evolved CO_2 , calibrated with 100 μl pulses of pure CO_2 and oxidation of known amounts of graphite, gives a direct measurement of the amount of carbon that gets oxidized at each temperature. This method appears particularly suitable for the quantitative characterization of SWNT because SWNT are oxidized in a relatively narrow temperature range, which lies above the temperature of oxidation of amorphous carbon and below the oxida-

tion of MWNT and graphitic carbon. In agreement with our results, previous TGA studies, [3,17] have shown that, in the absence of a catalyst, the ignition temperature of SWNT is 100°C higher than that of C_{60} fullerenes and 100°C lower than that of MWNT.

Fig. 2 illustrates the TPO profiles of the carbon species produced on the Co–Mo/ SiO_2 catalyst, which, as described above, exhibited the highest selectivity towards SWNT. This sample presented a

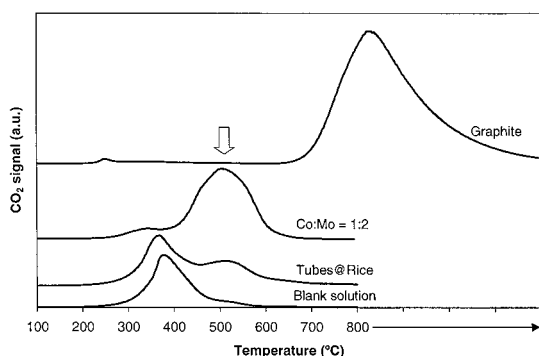


Fig. 2. Temperature programmed oxidation (TPO) of all the carbonaceous species present in the Co–Mo/SiO₂ catalyst (Co:Mo = 1:2) after decomposition of 50% CO/He at 700°C, compared to similar TPOs of a graphite reference and commercial SWNT obtained from Tubes@Rice. Also included is the TPO of the blank solution, containing a surfactant, in which the commercial SWNT are dispersed. All the references were physically mixed with bare Co–Mo/SiO₂ catalyst. The temperature ramp was 11°C/min.

small oxidation peak centered at around 330°C, which we ascribe to amorphous carbon, and a major peak marked in the figure with an arrow, centered at about 510°C, which we ascribe to the oxidation of SWNT. Two important reference samples were investigated by TPO and their profiles are included in Fig. 2. The first reference was a graphite powder physically mixed with the bare Co–Mo catalyst. The oxidation of this form of carbon occurred at very high temperatures, starting at about 700°C, and completed after 30 min at 800°C. The second important reference sample investigated was a commercial sample of purified SWNT, obtained from Tubes@Rice (Rice University). This sample comes in a liquid suspension of 5.9 g/l, containing a non-ionic surfactant Triton X-100. To conduct the TPO experiment, this suspension was impregnated on the Co–Mo/SiO₂ catalyst to get 0.6 wt % SWNT on the sample. As shown in Fig. 2, the TPO of this impregnated sample exhibited two peaks, a low-temperature one that corresponds to the oxidation of the surfactant and a second one centered at 510°C, which corresponds exactly to the position that we ascribed to the oxidation of SWNT. To corroborate that the first peak was indeed due to the oxidation of Triton, we prepared an identical sample with a blank solution containing only the surfactant in the same concentration. The TPO shows

that indeed that was the case. The quantification of the amount of SWNT in the sample from the CO₂ produced gave a value of 0.64 wt %, in good agreement with the amount of SWNT loaded in the sample (0.6 wt %).

By using TPO, we have been able to quickly test different formulations and obtain SWNT selectivities when varying Co:Mo ratios and type of catalyst supports. For example, Fig. 3 shows the clear synergistic effect exhibited by Co and Mo. In the first place, Mo alone does not produce carbon nanotubes, and only exhibits a small low-temperature peak corresponding to amorphous carbon. The term ‘amorphous carbon’ implies carbonaceous deposits, which are not in the form of ordered nanotubes or graphite. The claim that the Mo-alone sample only produced amorphous carbon was substantiated by the absence of graphite or nanotubes in the TEM observations. On the other hand, Co alone is not selective for the production of SWNT, and generates mainly graphitic carbon and MWNT. Again, these observations were corroborated by TEM. By contrast, the combination of the two metals in appropriate ratio results in high selectivity for SWNT. By using TPO we have been able to investigate the effect of varying the Co:Mo molar ratio in the Co–Mo/SiO₂ catalysts. Fig. 4 shows that, in agreement with the TEM characterization, the TPO of the Co:Mo = 1:2 sample indicates that this sample produced mostly SWNT, with a small amount of amorphous carbon.

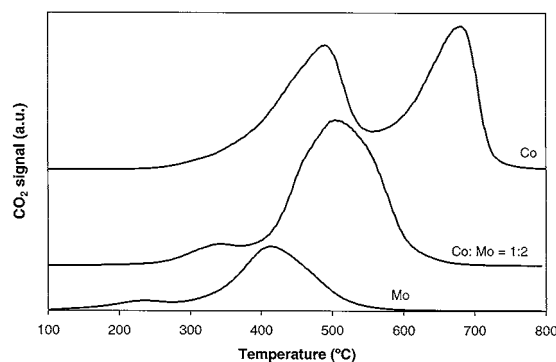


Fig. 3. Temperature programmed oxidation (TPO) of all the carbonaceous species present in the Co–Mo/SiO₂ catalyst (Co:Mo = 1:2) after decomposition of 50% CO/He at 700°C for 1 h, compared to monometallic Co/SiO₂ and Mo/SiO₂ catalysts, treated in identical way.

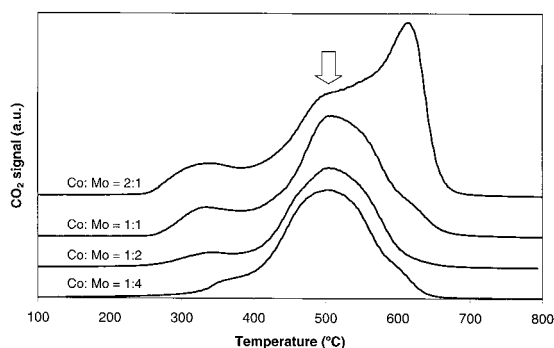


Fig. 4. Effect of Co:Mo ratio in the distribution of different carbonaceous species produced by decomposition of 50% CO/He at 700°C for 1 h, as measured by TPO, using a temperature ramp of 11°C/min. The arrow indicates the center of the peak corresponding to the oxidation of SWNT.

An increase in the Co:Mo ratio did not enhance the production of SWNT, but it did accelerate the formation of MWNT and graphitic carbon, as shown by the increasing size of the peaks in the region 600–700°C. From the TPO data, selectivity values were estimated by curve fitting. They were 57% SWNT and 31% MWNT for the Co:Mo (2:1), 80% SWNT and 4% MWNT for the Co:Mo (1:1), and 88% SWNT and 4% MWNT for the Co:Mo (1:2). It is important to note that, in all cases, the quantitative data agreed very well with the qualitative observations made by TEM.

The use of TPO also allows for a systematic screening of operating conditions. For example, the TPO profiles from products run at different reaction temperatures showed that the selectivity to SWNT had a maximum at about 700°C. Similar analysis were done to investigate the effects of gas phase concentration and reaction time at a given temperature.

Even though the results presented in this contribution demonstrate that the TPO method is a very efficient way of quantifying the production of carbon nanotubes, it is important to be aware of some limitations of the method. The TPO is a catalytic process in which the metals present in the sample catalyze the oxidation of the carbon species. Therefore, if the nature of the catalyst is significantly changed, the position of the oxidation peaks may appear shifted even when the carbon structures are the same. We have observed such shifts when the

catalyst support was modified. Therefore, in order to use this method properly, a complete analysis of the family of catalysts and the operating conditions needs to be done together with known references, as we have done in the present paper.

By a proper quantification of the amount of SWNT produced as a function of time at varying temperatures and gas phase concentrations we will be able to obtain reliable kinetic parameters that will shed some light into the mechanism of SWNT formation. Several interesting trends are already apparent in the present data. For example, the clear synergism shown by Co and Mo illustrates the complexity of the SWNT growth mechanism, which is today much less understood than the growth of MWNT. Previous studies [10] have shown that the decomposition of CO on Mo catalysts yield SWNT at 1200°C. However, at the much lower temperatures employed in this study, 700°C, Mo alone was unable to form any carbon nanotube. By contrast, Co alone formed significant amounts of MWNT, some graphite, and relatively small amounts of SWNT. Interestingly, when Mo and Co were simultaneously present in the catalyst, the production of MWNT was drastically suppressed while the production of SWNT was enhanced. In separate experiments [18], conducted on mechanical mixtures of Co-alone and Mo-alone samples, the enhanced selectivity displayed by the Co–Mo catalysts was not observed. Rather, the TPO of the mechanical mixtures were similar to the sum of the independent contributions of Co and Mo. These results demonstrate that an intimate contact between Co and Mo is necessary to generate the synergism responsible for the high selectivity towards SWNT. Recent studies [19] have reported the appearance of SWNT during the decomposition of hydrocarbons on multi-metallic Ni–Co–Fe catalysts. Unfortunately, in that report TEM was the only characterization technique employed and it was not indicated whether a large fraction of MWNT was simultaneously present.

3. Conclusions

In summary, in this contribution we have demonstrated a methodology that we call ‘controlled production’ of SWNT, based on a simple quantification

method that allows us to conduct systematic screening of catalyst formulations and operating conditions. By this methodology we have identified a Co–Mo catalyst formulation that yields high selectivity towards SWNT. Also, through the application of this quantitative analysis, kinetics studies can be carried out, which will provide relevant mechanistic information about the growth of SWNT.

Acknowledgements

This research was conducted with financial support from the Oklahoma Center for Advancement of Science and Technology (OCAST) and the College of Engineering at the University of Oklahoma. The authors wish to acknowledge Dr. R. Frech and his group for the measurement of the Raman spectra.

References

- [1] B.I. Yakobson, R.E. Smalley, *Am. Sci.* 85 (1997) 324.
- [2] H.G. Tennent, J.J. Barber, R. Hoch, US Patent 5,578,543, 1996.
- [3] A.G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodriguez-Macias, P.J. Boul, A.H. Lu, D. Heymann, D.T. Colbert, R.S. Lee, J.E. Fischer, A.M. Rao, P.C. Eklund, R.E. Smalley, *Appl. Phys. A* 67 (1998) 29.
- [4] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M.L. De La Chapelle, S. Lefrant, P. Deniard, R. Lee, J.E. Fischer, *Nature* 388 (1997) 756.
- [5] N. Krishnankuty, C. Park, N.M. Rodriguez, R.T.K. Baker, *Catal. Today* 37 (1997) 295.
- [6] R. Andrews, D. Jacques, A.M. Rao, F. Derbyshire, D. Qian, X. Fan, E.C. Dickey, J. Chen, *Chem. Phys. Lett.* 303 (1999) 467.
- [7] A. Peigney, Ch. Laurent, F. Dobigeon, A. Rousset, *J. Mater. Res.* 12 (1997) 613.
- [8] J. Kong, A.M. Cassell, H. Dai, *Chem. Phys. Lett.* 292 (1998) 567.
- [9] H.M. Cheng, F. Li, G. Su, H.Y. Pan, L.L. He, X. Sun, M.S. Dresselhaus, *Appl. Phys. Lett.* 72 (1998) 3282.
- [10] H. Dai, A.G. Rinzler, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, *Chem. Phys. Lett.* 260 (1996) 471.
- [11] J.H. Hafner, M.J. Bronikowski, B.R. Azamian, P. Nikolaev, A.G. Rinzler, D.T. Colbert, K.A. Smith, R.E. Smalley, *Chem. Phys. Lett.* 296 (1998) 195.
- [12] A. Thess, R. Lee, P. Nikolaev, H.J. Dai, P. Petit, J. Robert, C.H. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fischer, R.E. Smalley, *Science* 273 (1996) 483.
- [13] V. Brotons, B. Coq, J.M. Planeix, *J. Mol. Catal. A* 116 (1997) 397.
- [14] A.M. Rao, E. Richter, S. Bandow, B. Chase, P.C. Eklund, K.A. Williams, S. Fang, K.R. Subbaswamy, M. Menon, A. Thess, R.E. Smalley, G. Dresselhaus, M.S. Dresselhaus, *Science* 275 (1997) 187.
- [15] D.E. Resasco, B.K. Marcus, C.S. Huang, V.A. Durante, *J. Catal.* 146 (1994) 40.
- [16] S.M. Stagg, C.A. Querini, W.E. Alvarez, D.E. Resasco, *J. Catal.* 168 (1997) 75.
- [17] Z. Shi, Y. Lian, F. Liao, X. Zhou, Z. Gu, Y. Zhang, S. Iijima, *Solid State Commun.* 112 (1999) 35.
- [18] B. Kitiyanan, W.E. Alvarez, D.E. Resasco, submitted.
- [19] J.F. Colomer, G. Bister, I. Willems, Z. Konya, A. Fonseca, G. Van Tendeloo, J.B. Nagy, *Chem. Commun.* (1999) 1343.