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The study of carbon nanotubules produced by catalytic method

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Abstract

Catalytic methods for the production of carbon nanotubules have been developed based on the decomposition of acetylene on well-dispersed metal particles strongly adsorbed on a support. Cobalt on silica was found to be the best catalyst–support combination for the production of graphitic tubules. The method for the catalyst preparation and the reaction conditions were optimized. Straight and coiled carbon tubules were obtained with inner and outer diameter of 3–7 and 15–20 nm, respectively, and up to 30 μm in length. These nanotubules were not coated by amorphous carbon. Traces of amorphous carbon could be removed by hydrogen. High resolution electron microscopy images and electron diffraction patterns of the straight nanotubules were similar to those obtained by the arc-discharge method. Coiled nanotubules were revealed by TEM to be regular polygonized helices where the bends are caused by pairs of pentagon–heptagon carbon rings among the hexagonal network.

1. Introduction

Tubular derivatives of fullerenes grown by the arc-discharge method [1] exhibit properties which are different from those of the closed cage fullerenes such as C_{60}, C_{70}, C_{76} ... . Their high mechanical strength [2], capillary properties [3] and remarkable electronic structure [4–6] allow envisagement of a wide range of potential uses. They may, for instance, find applications as quantum wires, molecular sieves or as a support for finely dispersed matter [7]. The main limitation of the arc-discharge tubules is their relatively small length (< 1 μm). Furthermore, the low yield of the process makes the product expensive. The catalytic production method [8] avoids these difficulties. The nanotubes produced by this method may have lengths up to 50 μm. Moreover, the process is simpler and more reproducible than the arc-discharge method. Unfortunately, there are also drawbacks. The catalytically fabricated tubules are usually thicker than those obtained by the arc-discharge process and often covered by a thick layer of amorphous carbon.

The growth of hollow carbon filaments during the pyrolysis of hydrocarbons in the presence of metal particles was described earlier [9–12]. The growth mechanism was assumed to involve two phenomena. The first consists of catalytic decomposition including the formation of the metal carbide, the diffusion of carbon through the metal and the formation of graphite on the opposite end of the particle. The second phenomenon is the formation of amorphous carbon by pyrolysis covering the surface [13–16].

The objective of our research was to optimize the catalytic process for the production of long carbon fibres free of an amorphous carbon coating.

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2. Experimental

The catalytic decomposition of acetylene was carried out in a flow reactor at atmospheric pressure. A ceramic boat containing 20–50 mg of the catalyst was placed in a quartz tube (inner diameter 4 mm, length 60 cm). The reaction mixture of 2.5%–10% C_2H_2 (Alphagaz, 99.6%) in N_2 (Alphagaz, 99.99%) was passed over the catalyst bed at a rate of 0.15–0.59 mol $C_2H_2\,g^{-1}\,h^{-1}$ over several hours at temperatures in the range 773–1073 K.

The catalysts were prepared by the following methods. Graphite supported samples containing 0.5–10 mass% of metal were prepared by impregnation of natural graphite flakes (Johnson-Matthey, 99.5%) with the solutions of the metal salts in the appropriate concentrations: Fe or Co oxalate (Johnson-Matthey), Ni or Cu acetate (Merck). Catalysts based on SiO_2 were obtained by volume impregnation of silica gel (with pores of 9 nm – Janssen Chimica) with aqueous solutions of Fe(III) or Co(II) nitrates in the appropriate amounts to obtain 2.5 wt% of metal or by ion-exchange-precipitation of the same silica gel with 0.015 M solution of Co(II) nitrate (Merck) following a procedure described in Ref. [17]. The catalyst prepared by the latter method had 2.1 wt% of Co. All samples were dried overnight at 403 K and then calcined 2 h at 773 K in flowing nitrogen and reduced in a flow of 10% H_2 in N_2 at 773 K during 8 h.

The samples were examined before and after catalysis by SEM (Philips XL 20) and TEM in both a JEOL 200 CX operating at 200 kV and a JEOL 4000 EX operating at 400 kV. The specimens for TEM were either directly glued on copper grids or dispersed in acetone by ultrasound then dropped on the holey carbon grids.

3. Results and discussion

Fe, Co, Ni and Cu supported on graphite were used as catalysts for the acetylene decomposition at 700°C. All catalysts showed high reactivity and the structure of the resulting carbon deposits was strongly dependent on the nature of the metal. Four structural forms of carbon were observed: amorphous carbon layers on the surface of the catalyst, filaments of amorphous carbon, graphite layers covering metal particles and tubules made from well-crystallized graphite layers usually covered with amorphous carbon on their outer layers.

On the Fe and Co catalysts most of the filaments were graphitic, showing typical diffraction patterns. The smallest inner diameter of these filaments was about 10 nm. Their outer diameters varied from 25 to 30 nm for tubes not covered with amorphous carbon to about 130 nm for tubes which were covered. Amorphous filaments were also found. The relative amount of well-graphitized tubes was higher on the Co sample than on the Fe catalyst. On Ni–graphite most of the carbon filaments were amorphous. Sometimes well-crystallized graphite layers were identified as covering metal particles.

On the Cu catalyst all the carbon precipitated in the amorphous form. Often the formation of graphitic layers around the metal particles was observed similar to those reported in Ref. [18] for the metal-catalyzed production of fullerene tubules in the arc-discharge process. The structure of these metal particles was not well identified. However, some of them gave spots in the diffraction patterns showing crystallinity.

As previously reported [11,13], the outer diameter of the fibres depends on the size of the metal particles. We also noticed a dependence of the thickness of the filaments on the diameter of the metal crystallites. The graphite support does not insure the stability of the metal particles. Some aggregates up to 500 nm in diameter were found. Also the thickness of the produced filaments was not controlled and varied from 30 to 150 nm (Fig. 1). The increase in the metal content from 2.5 to 10 wt% in the graphite catalysts leads to the growth of the metal particles. A smaller amount of supported metal (0.5 wt%) shows about the same dispersion as the 2.5% sample leading to similar results in catalysis.

The use of silica with a regular pore structure as a support favours in many cases the formation of stable and well-dispersed metal catalysts. As the amount of metal of about 2–2.5 wt% was estimated to be much less than that needed for the formation of a monolayer on the surface of the silica gel, we prepared metal catalysts both by volume impregnation and by ion-exchange.

Fe- and Co-silica catalysts prepared by the vol-

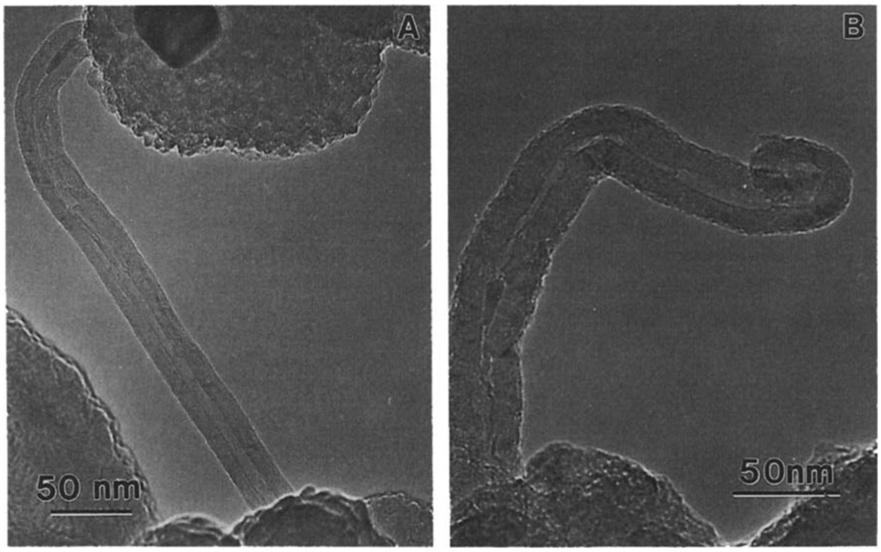

Fig. 1. HREM images of carbon filaments obtained after 5 h of acetylene cracking at 973 K on (a) Co–graphite catalyst; (b) Fe–graphite catalyst.

ume impregnation method had metal crystallites with sizes varying from 4 to 100 nm. The filaments obtained on these catalysts are thinner than those obtained on graphite-supported samples. Graphitic tubules were covered by amorphous carbon which also covered the surface of the metal catalyst possibly decreasing its activity. The method used enabled us to obtain graphitic nanotubules with inner diameters of ≈ 10 nm and outer diameters of 20–25 nm. Similar to graphite-supported catalysts, the percentage of uniform graphitic tubules obtained on Co–silica was higher than that obtained on Fe–silica.

The method of precipitation-ion-exchange provides a better dispersion of metals on SiO_2; this was carefully shown for $Cu-SiO_2$ [17]. The application of this method allowed us to obtain Co–silica cata-

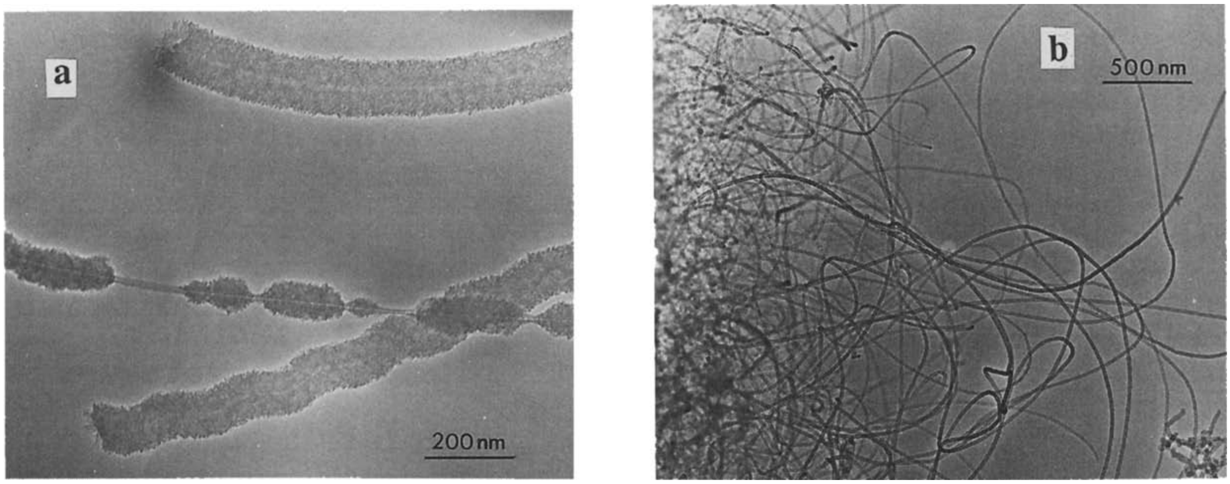

Fig. 2. (a) Carbon fibres covered with amorphous carbon after 5 h of acetylene cracking at 973 K on $Co-SiO_2$ catalyst. (b) Nanotubules not coated with amorphous carbon obtained on the same $Co-SiO_2$ catalyst at 873 K after 5 h reaction.

lysts with metal clusters of 4–15 nm. The temperature of acetylene decomposition as well as the flow rate were varied on these catalysts in order to obtain optimal conditions. We have found that a decrease in the temperature from 973 to 873 K leads to a strong decrease in the amorphous carbon production (Figs. 2a and 2b). However, it also has an influence on the process of graphitization. High resolution images and diffraction patterns of tubules prepared at various temperatures showed that the degree of crystallinity

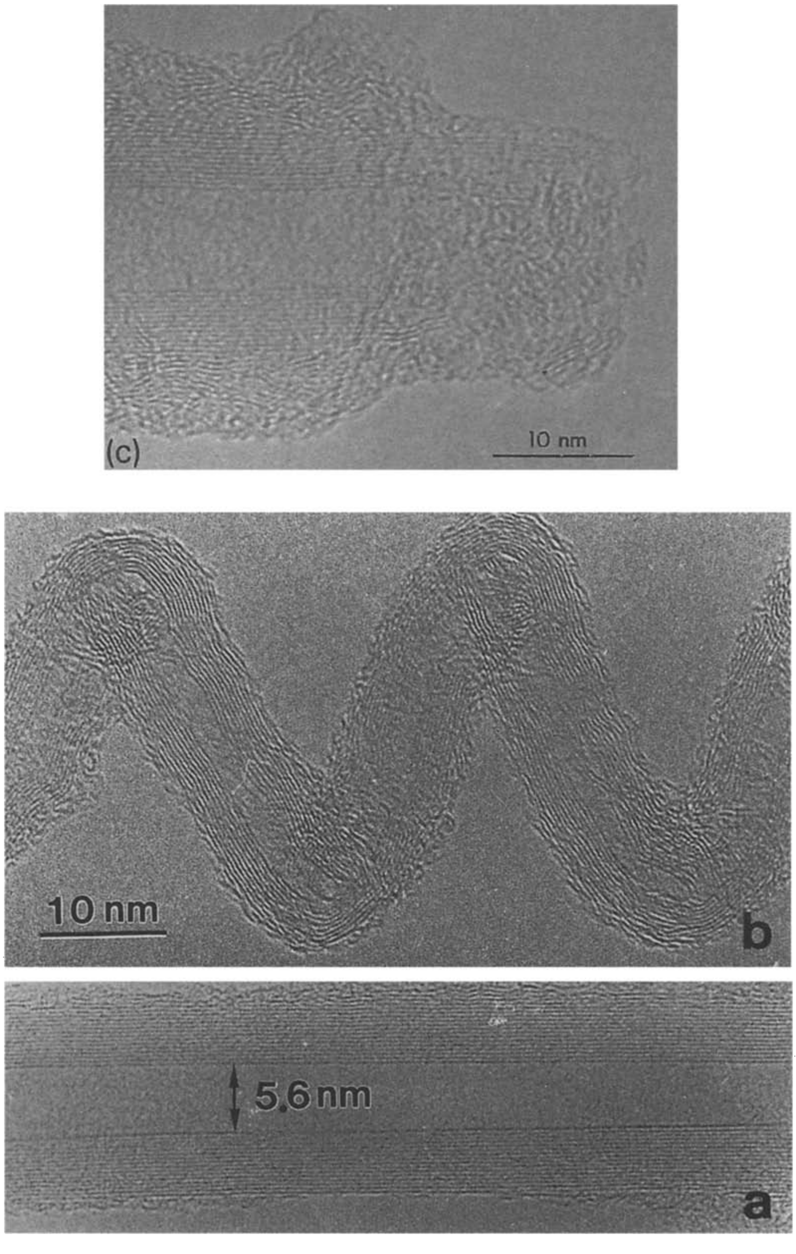

Fig. 3. High resolution TEM images of the well-graphitized nanotubules obtained on Co–SiO_2 catalyst at a reduced C_2H_2 flow rate at 973 K (3.5 h). (a) A cylindrical nanotubule with inner diameter about 6 nm; (b) a helix-shaped nanotubule with radius of about 18 nm, pitch about 30 nm, consisting of 10 graphitic tubes (diameter of the innermost tube is about 2.5 nm); (c) the end of a nanotubule showing the amorphous carbon cap at the end.

increases with temperature and it is the highest at 973 K (for the latter crystallinity only the graphitic tubules were taken into account). The flow rate of C_2H_2, or reaction contact time, also has a strong influence on the process. A decrease in the contact time at constant temperature leads to the predominance of graphitizing over pyrolysis. The tubules produced under optimal conditions were as thin as fullerene tubules and almost free from amorphous carbon (Fig. 3).

Note that coiled nanotubules were also formed on the Co–silica catalyst (Figs. 3 and 4). They were recently examined by TEM and electron diffraction [19]. It was suggested that the coiled tubules consist of regularly polygonized helices where the bends are related to pairs of pentagon–heptagon carbon rings in the hexagonal network (Fig. 5).

Graphitic tubules obtained under the described conditions have lengths ranging from a few 0.1 μm to a few tens of μm. In accordance with Ref. [8] we can conclude that the length depends on the duration of the catalytic process. However, the conditions for the production of long and well-graphitized tubules have still to be optimized.

Some data show the role of hydrogen in the mechanism of the formation of graphitic layers on Fe catalysts [10]. We have investigated the influence of H_2 on the production of graphite tubules over Co–silica both during the reaction and after acetylene decomposition. In the first case we have introduced hydrogen into the reaction mixture (in a proportion 1:4 with respect to C_2H_2) at 973 K. The results obtained after this treatment were similar to those obtained with C_2H_2 alone. Heating of the catalyst after the C_2H_2 reaction in the mixture of hydrogen with nitrogen at 873 K resulted in gassification of the amorphous carbon leading to the cleaning of the graphitic tubules. The possible gassification of the graphitic carbon was not investigated. It is nevertheless interesting to note that it could be a useful technique for thinning carbon nanotubules 'layer-by-layer' and maybe for their opening in softer conditions than those used in oxidation [20–22].

As opposed to the data reported earlier on the filament formation on transition metals [10,11] we did not find metal particles on the top of the carbon tubules. The filaments growing in our conditions are terminated by a thin cap of amorphous carbon (Fig. 3c).

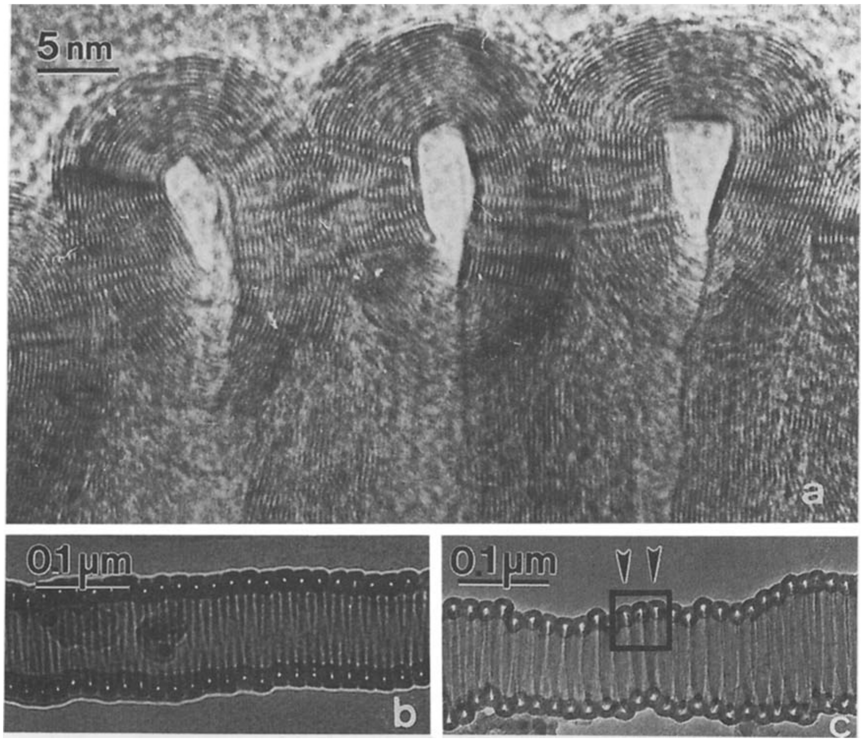

Fig. 4. HREM image of a tightly wound helix-shaped carbon nanotubule; insets show two such tubules at lower magnification.

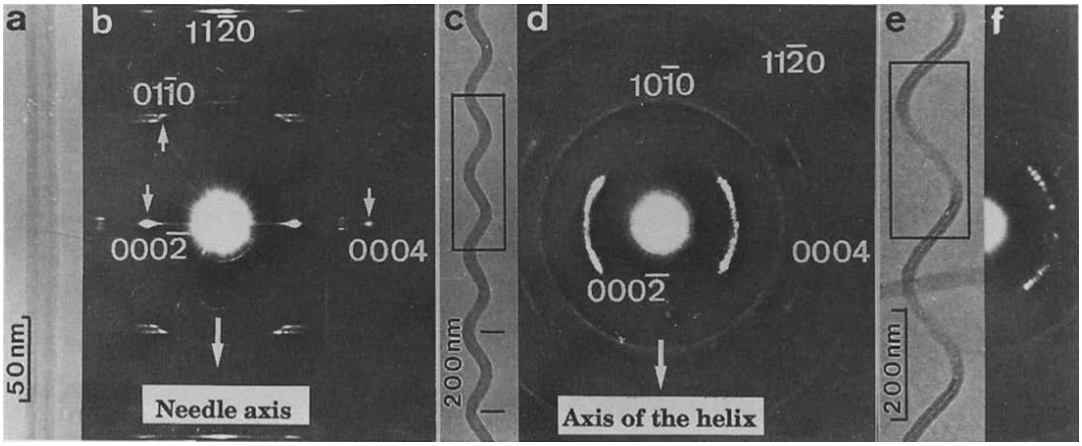

Fig. 5. Electron diffraction patterns (EDP) of two different kinds of well-graphitized carbon nanotubules obtained by the optimized Co–SiO_2 catalyst method. (a), (b) A cylindrical carbon nanotubule and its EDP showing the similarity to that of arc-discharge-produced nanotubules; (c), (d) a helix-shaped nanotubule and its EDP; (e), (f) the diffraction pattern shows a spotty intensity distribution when only one pitch of helices is selected, which indicates that the helices are polygonized.

This indicates a difference in growth mechanism compared with the one previously postulated, where the metal particle plays the role of carbon transporter and graphite layers form on the back of the crystallite. In our case graphitization appears to proceed on the same metal surface as carbon adsorption. In the presence of H_2, which is produced by the decomposition of hydrocarbon, free carbon valences on the ends of graphite chains can be stabilized by the formation of C–H bonds. The growth mechanism of carbon nanotubules on Co–silica needs to be carefully studied since SiO_2 was shown to be an inhibitor of filament formation [23]. A study is in progress to show the possible influence of exposed crystal planes in directing the formation of carbon nanotubes [24].

4. Conclusion

A Co–silica catalyst for the large scale production of carbon nanotubules by the decomposition of acetylene was proposed and the reaction conditions were optimized. Since the diameter of the tubules depends on the size of the metal cluster, we prepared catalysts having regular and well-dispersed metal particles. The thickness and structure of the carbon nanotubules are found to be similar to those obtained by the arc-discharge method but they are much longer and free from an amorphous carbon coating.

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References

[1] S. Iijima, Nature 354 (1991) 56.
[2] R.E. Smalley, in: Proceedings of the Robert A. Welch Foundation Conference on Chemical Research XXXVI "Regulation of Proteins by Ligands", Houston, October 26–27, 1992, p. 161.
[3] M.R. Pederson and J.Q. Broughton, Phys. Rev. Letters 69 (1992) 2689.
[4] J.W. Mintmire, B.I. Dunlap and C.T. White, Phys. Rev. Letters 68 (1992) 631.
[5] N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Letters 68 (1992) 1579.
[6] K. Harigaya and M. Fujita, Phys. Rev. B 47 (1993) 16563.
[7] T. Fujimoto, A. Fukuoka, S. Iijima and M. Ichikawa, J. Phys. Chem. 97 (1993) 279.
[8] M. José-Yacamàn, M. Miki-Yoshida, L. Rendon and J.G. Santiesteban, Appl. Phys. Letters 62 (1993) 657.
[9] W.R. Davis, R.J. Slawson and G.R. Rigby, Nature 171 (1953) 756.

[10] A. Sacco, P. Thacker, T.N. Chang and A.T.S. Chiang, J. Catal. 85 (1984) 224.
[11] J.S. Speck, M. Endo and M.S. Dresselhaus, J. Cryst. Growth 94 (1989) 834.
[12] N.M. Rodriguez, M.S. Kim and R.T.K. Baker, J. Catal. 144 (1993) 93.
[13] G.G. Tibbets, J. Cryst. Growth 66 (1984) 632.
[14] L.S. Lobo and M.D. Franco, Catal. Today 7 (1990) 247.
[15] M.S. Kim, N.M. Rodriguez and R.T.K. Baker, J. Catal. 131 (1991) 60.
[16] R.T.K. Baker, Carbon 27 (1989) 315.
[17] J.C. Lee, D.L. Trimm, M.A. Kohler, M.S. Wainwright and N.W. Cant, Catal. Today 2 (1988) 643.
[18] P.M. Ajayan, J.M. Lambert, P. Bernier, L. Barbedette, C. Colliex and J.M. Planeix, Chem. Phys. Letters 215 (1993) 509.
[19] X.B. Zhang, X.F. Zhang, D. Bernaerts, G. Van Tendeloo, S. Amelinckx, J. Van Landuyt, V. Ivanov, J.B. Nagy, Ph. Lambin and A.A. Lucas, Nature, submitted for publication.
[20] P.M. Ajayan and S. Iijima, Nature 361 (1993) 333.
[21] S.C. Tsang, P.J.F. Harris and M.L.H. Green, Nature 362 (1993) 520.
[22] P.M. Ajayan, T.W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki and H. Hiura, Nature 362 (1993) 522.
[23] R.T.K. Baker and J.J. Chludzinski Jr., J. Catal. 64 (1980) 464.
[24] M. Kawaguchi, K. Nozaki, S. Motojima and H. Iwanaga, J. Cryst. Growth 118 (1992) 309.