Effect of Structure and Pore Size of Mesoporous Molecular Sieve Materials on the Growth of Carbon Nanotubes

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Abstract. Microporous and mesoporous molecular sieve materials with different channel structures and pore sizes were applied as supports for Fe-loaded catalysts to catalytically synthesize carbon nanotubes. The deposited carbon materials were characterized by the TEM technique. It was shown that the structures and pore sizes of supports greatly influence the forms and quality of the deposited carbon materials. The larger the pore size of the support used, the larger the diameter and pore size of the carbon nanotubes formed. It seems that the growth of carbon nanotubes can be orientated by the one-dimensional mesoporous structure of hexagonal mesoporous molecular sieve materials.

Key words: carbon nanotubes; mesoporous molecular sieve materials; pore size; growth direction

1. Introduction

The synthesis of the fullerene molecule ("buckyball") corresponding to a molecular-cage arrangement of sixty-carbon atoms (C_{60}) with the form of a "soccer ball" [1] intensely stimulated research on carbon-based and other materials with particular nanoscale shapes and forms and thus gave rise to a new chapter in carbon chemistry and a new branch of material science. Publications about C_{60} are so numerous that we can not enumerate them. An important milestone in development of this whole new class of carbon materials is the discovery by Iijima [2, 3] of tubular structures made of carbon, i.e., carbon nanotubes, at the beginning of the 1990s. Because carbon nanotubes appear perfectly graphitized, just like the fullerene molecules, and possess diameters in the range of 1–25 nanometers, they were speculated to fit well as components in submicrometer-scale devices and nanocomposite structures that are likely to be very important in emerging technologies [4]. Thus, a lot of progress has been made in the synthesis and purification of carbon nanotubes and in the investigation of their electronic, electric, transport, optical, magnetic and

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mechanical properties [5–15], as well as the introduction of guest atoms into tubules to form molecular wires [16–23], chemical conversion of carbon nanotubes into nanorods of other materials [24] and in possible technological applications [25–29].

Carbon nanotubes can be conventionally synthesized using several methods [30, 31], but these tubules always form together with significant amounts of other carbon products such as fibers and soot. Consequently, their purification is a very difficult problem and no simple chemical method is usually effective enough for their complete separation. Moreover, the length of carbon nanotubes produced by the arc-discharge method is normally shorter than 1 μm and the low yield of the process makes the product expensive [32]. Another more important problem is that the characterization and applications of nanotubes have been hampered because of their uncontrolled diameters and random growth patterns. Recently, a catalytic synthesis method, which formerly focused mainly on the prevention of "coke" formation on the surface of catalysts and the growth of carbon filaments [33–36], has been developed to prepare carbon nanotubes on Co/SiO$_2$ [32, 37]. The catalytic production method [38] enables the synthesis of carbon nanotubes to be conducted under relatively mild conditions. Zeolite materials are widely used as catalysts, absorbents and supports for catalysts. Hernadi *et al*. first reported the use of zeolites (NaY, HY and ZSM-5) as catalyst supports to synthesize carbon nanotubes and the chemical separation of the carbon nanotubes formed from the catalyst particles [39], but the growth directions and pore size still remained uncontrollable. Recently it has been reported that aligned carbon nanotubes can be synthesized by using iron or other metal nanoparticles embedded in mesoporous silica or porous alumna template as a catalyst [14, 15]. Since zeolites are porous materials with regular crystal structures and pore arrangements, they are speculated to act differently from other solid materials. However, many aspects of the catalytic production of carbon nanotubes using zeolite supports remain uninvestigated, especially the effect of the pore size of the zeolite support on the growth direction and diameter/pore size of the carbon nanotubes formed. Here we present our initial report of an investigation to adjust the diameter of the carbon nanotubes formed by tailoring the pore sizes of mesoporous molecular sieve materials and altering the pore sizes of microporous molecular sieve NaY.

2. Experimental

2.1. MATERIALS

A commercially available zeolite from the Petrochemical Institute of Fushun, China, with an atomic Si/Al ratio of 2.49 and unit cell parameter of 2.468 nm was used directly as the zeolite support. In order to investigate the effect of pore size of Y-type zeolite samples on the diameter and quality of the carbon nanotubes formed, a portion of NaY was steamed at 873 K for 4 h as described in ref. [40]. The product obtained was called SDY and was then divided into two portions. One portion of

SDY was used directly as a kind of support and the other was then treated with a solution of $(NH_4)_2SiF_6$ (0.5 M) at 363 K for 2.5 h, the procedure developed by Skeels and Breck [41], followed by filtration, washing and drying at 383 K in an oven for 2 h. The sample obtained in this manner was designated as FSY.

The synthesis of zeolite KL has been described previously [42]. By means of self-assembly of surfactants, pure hexagonal siliceous mesoporous molecular sieve materials, called SiMCM-41 and SiHMS respectively, were synthesized and post-treated to remove templates as described in Refs. [43–45].

2.2. PREPARATION OF CATALYSTS

Fe/SiHMS was prepared in the following manner: a known amount of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in a known amount of distilled water to prepare a solution of $Fe(NO_3)_3$, into this solution a known amount of acetic acid (HAc) was added until the ratio of Fe to HAc was 1:2 (mole). The pH was then adjusted to between 5.0–6.0 with stirring and a known amount of SiHMS was added with stirring to obtain a slurry with composition (in weight): $SiHMS : H_2O : Fe$ = 1 : 10 : 0.05. The prepared slurry was then immediately heated to 323 K and maintained at that temperature for 2 h with stirring, then the temperature was further increased to 353 K and maintained at that value under stirring until the slurry dried. Then the sample was further dried at 383 K in an oven for 2 h. In order to investigate the effect of zeolite molecular sieve materials with different structures and pore sizes on carbon nanotubes, Fe/SiMCM-41, Fe/NaY, Fe/USY, Fe/FSY and Fe/KL were also prepared using a similar procedure.

2.3. SYNTHESIS OF CARBON NANOTUBES

The catalytic decomposition of acetylene was carried out in a fixed bed flow reactor at atmospheric pressure. A ceramic boat containing 30 mg of catalyst was placed in a quartz tube (inner diameter 33 mm, length 70 cm) and the tube was placed in a tubular electric furnace. The catalyst was heated at a rate of 5 K/min from room temperature to 773 K in a nitrogen flow (60 mL/min) and then maintained at that temperature for 2 h. The temperature was then further increased to 973 K using a rate of 10 K/min. At this temperature the reaction mixture (10% C_2H_2 and 90% N_2) was introduced. Various reaction times and gas feeds were employed.

3. Characterization Methods

The nature of the carbon deposit on the catalysts was investigated by transmission electron microscopy (TEM) (JEOL 200 cx). The pore sizes of carbon nanotubules were also determined by the TEM technique. The SEM pictures of samples were taken with a Hitachi X-650.

Table I. The textural properties and composition of the catalysts used

Catalysts	Si/Al (mol)	Fe loaded (wt. %)	Pore size (nm)	S.A.[a] (m^2/g)
Fe/NaY-d-2	2.5	5.0	$\sim$0.7[b], $\sim$1.36[c]	697
Fe/SDY	3.8	5.0	$\sim$0.7[b], $\sim$2.64[d]	532
Fe/FSY	4.5	5.0	$\sim$0.7[b], $\sim$2.64[d]	442
Fe/KL	2.9	5.0	$\sim$0.7[b]	287
Fe/SiHMS(12)[e]	–	5.0	2.9[b]	1031
Fe/SiHMS(18)	–	5.0	3.6[b]	1029
Fe/SiMCM-41	–	5.0	3.3[b]	1042

[a] Surface area by N_2 adsorption.
[b] Diameter of window.
[c] Diameter of supracage pore measured by ^{129}Xe MAS NMR method.
[d] Diameter of secondary pore measured by ^{129}Xe MAS NMR method.
[e] The numbers in parentheses are the carbon numbers in the chain of the primary amines as template.

The porous properties of supports were investigated by a low temperature nitrogen sorption technique on a Micromeritics ASAP 2000 instrument. Before each measurement was conducted, the sample was calcined in a muffle stove at 673 K for 4 h, then introduced into the instrument and retreated under high vacuum (P<0.3 Pa) at 623 K for 4 h. The sorption data were analysed using the BJH method assuming of cylindrical pores [46]. For Y-type zeolites, which exhibit a tri-dimensional channel structure, the BJH model is less than ideal for investigating the inner supercage; for these samples an additional ^{129}Xe NMR measurement [47] was conducted. This latter method has been clearly demonstrated to be a powerful technique for the characterization of porous materials, especially zeolites.

4. Results and Discussion

4.1. THE TEXTURAL PROPERTIES AND COMPOSITION OF THE CATALYSTS USED

The textural properties and compositions of used catalysts are shown in Table I. After steam treatment and chemical corrosion, some secondary pores were created. Because their size is nearly double those of the supercages, these secondary pores were believed to have developed via the connection of two adjacent supercages. Besides these secondary pores, there are larger pores with pore sizes of $\sim$4 nm (and $\sim$10.5 nm in SDY). For FSY, owing to the presence of additional corrosion due to F^-, the number of pores with diameters of $\sim$4 nm and $\sim$10.5 nm were decreased and pores with sizes in the range of 30–90 nm were present instead (see Figure 1).
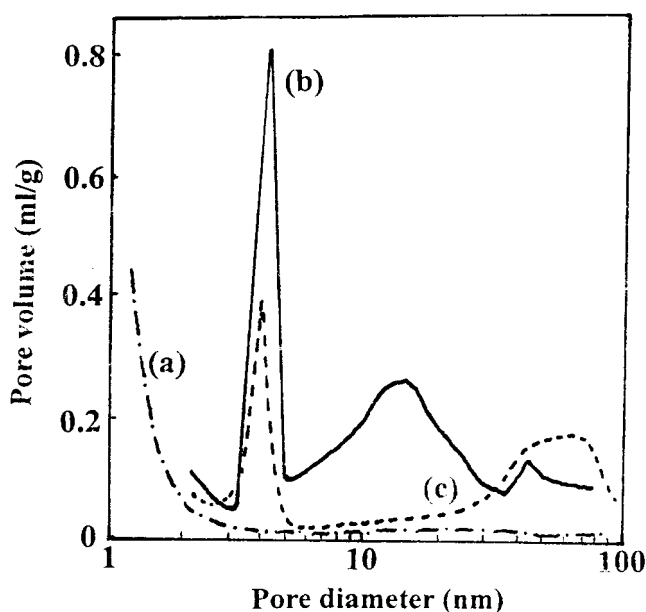
Figure 1. Pore size distribution of (a) NaY, (b) SDY and (c) FSY, obtained by low temperature nitrogen sorption with the BJH model.

The TEM pictures shown in Figure 2 clearly demonstrate the mesostructure of SiHMS and SiMCM-41. All three samples exhibit a one-dimensional hexagonal channel structure. From Table I and Figure 2, we can also see that the pore size of this kind of mesoporous materials can be tailored by changing the chain length of the surfactant used as the template.

4.2. FORMS OF DEPOSITED CARBON MATERIALS

Carbon materials produced by either arc discharge or thermal deposition of hydrocarbon are usually in the form of carbon nanotubes, carbon nanofibers and/or amorphous carbon. As shown in Figure 3, all three forms were found on Fe/NaY in our experiment (this is also true for other samples). Which kind of carbon predominates depends on the structure of the support, the preparation method of the catalyst and the synthesis conditions for carbon nanotubes. An obvious property of the carbon nanotubes formed on Fe/NaY catalysts is that almost all the tips of the tubes are open, indicating that the interaction between the catalyst particles and the supports is strong [36].
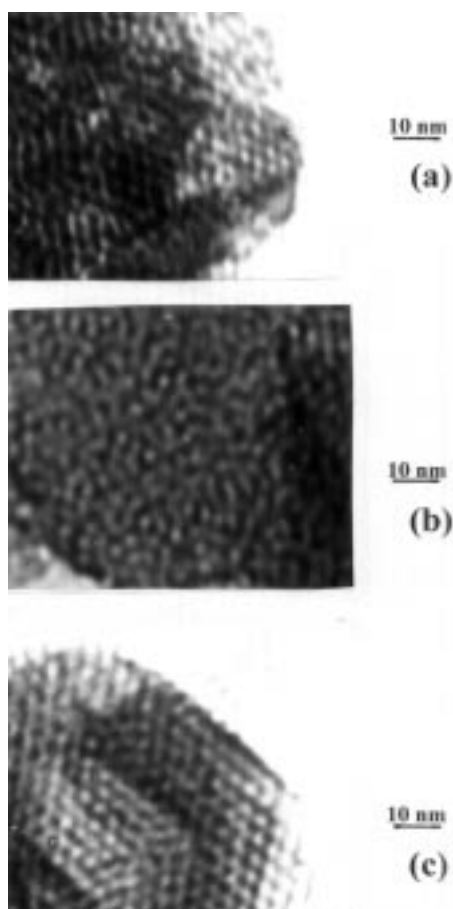
Figure 2. TEM pictures of (a) SiHMS(12), (b) SiHMS (18) and (c) SiMCM-41.

4.3. EFFECT OF STRUCTURE AND PORE SIZE OF SUPPORTS ON THE OPTIMAL
     REACTION TIME

It was found that carbon nanotubes could be produced on a Fe/NaY catalyst over
a wide range of reaction times that ranged from 2 min to 1.5 h (see Figure 4). For
a reaction time of less than 2 min, the amount of carbon nanotubes produced was
very low. At reaction times over 1 h, as a result of the homogeneous decomposition
of acetylene, the amount of deposited amorphous carbon was increased rapidly. As
reported by Hernadi *et al.* [39], this effect is partly due to deactivation of catalyt-
ically active sites as a function of reaction time and to the increasing surface area,
which favours homogeneous decomposition of the reactant. However, the optimal
reaction time range in our experiments was found to be wider than that reported by
Hernadi *et al.* [39], probably due to the difference in reaction conditions employed
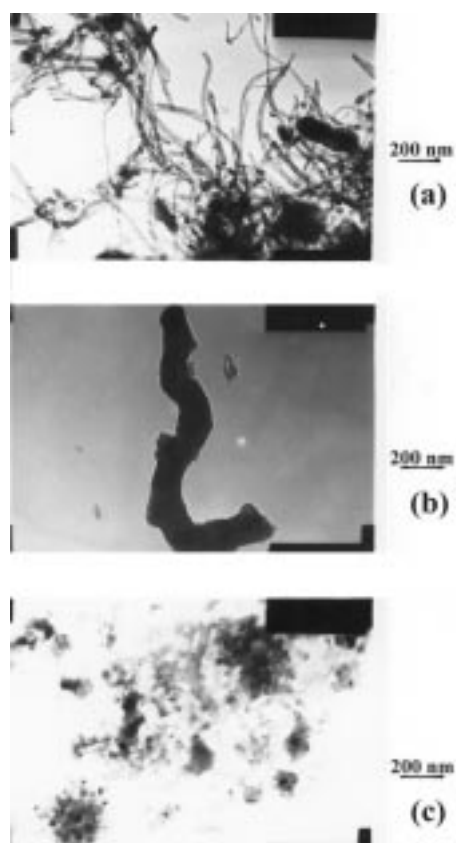(Fe content in catalysts, gas feed, etc.).

Figure 3. Forms of deposited carbon materials on Fe/NaY. (a) Carbon nanotubes, (b) carbon nanofiber, (c) amorphous carbon.

Very different from Fe/NaY, growth of carbon nanotubes on mesoporous molecular sieve materials was limited to a relatively narrow range of reaction time. For Fe/SiHMS(12), few carbon nanotubes were observed for a reaction time of 10 min (Figure 5a). Up to about 30 min, the amount of carbon nanotubes increased greatly as shown in Figure 5b. However, if the reaction time was too long, the deposited carbon materials were mainly carbon nanofiber and amorphous carbon (see Figure 5c). We believe that the difference between the preferable reaction times for Fe/NaY and Fe/SiHMS(12) reflects the different channel structures and surface areas of NaY and SiHMS(12). NaY shows a relatively small surface with a window of $\sim$0.7 nm, a portion of the channels will be blocked by deposited Fe(III) species and a Fe(III) species will be substantially precipitated on the outer surface. However, the channel structure for SiHMS is one-dimensional and its window (i.e., the pore size) and surface area are much larger than those of NaY, thus the Fe(III) species can be distributed widely on the inner surface of the SiHMS. This is indicated by the lighter color (yellow) of Fe/SiHMS(12) relative to that (brown)
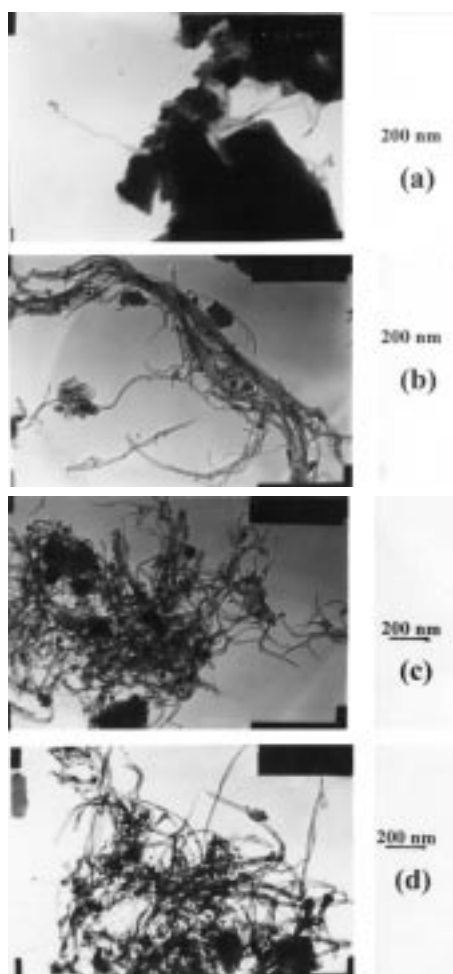
Figure 4. TEM pictures of carbon nanotubes formed on Fe/NaY after different reaction times. (a) 2 min, (b) 10 min, (c) 1 h and (d) 1.5 h.

of Fe/NaY. Based on the above phenomena, we speculate that the carbon nanotube growth on Fe/SiHMS(12) seems to initiate on the inner surface and takes more time to be observed than that for Fe/NaY, for which carbon nanotubes form on the outer surface. For this reason, carbon nanotube growth in Fe/SiHMS(18) is observed at an even longer time (1 h, see Figure 6) than that for Fe/SiHMS(12), because the pore size of SiHMS(18) is larger than that of SiHMS(12).

4.4. EFFECT OF STRUCTURE AND PORE SIZE OF SUPPORTS ON GROWTH OF CARBON NANOTUBES

Although it was very recently reported that the growth directions or sizes can be controlled by catalytic synthesis of carbon nanotubules in the pores of a Fe/silica
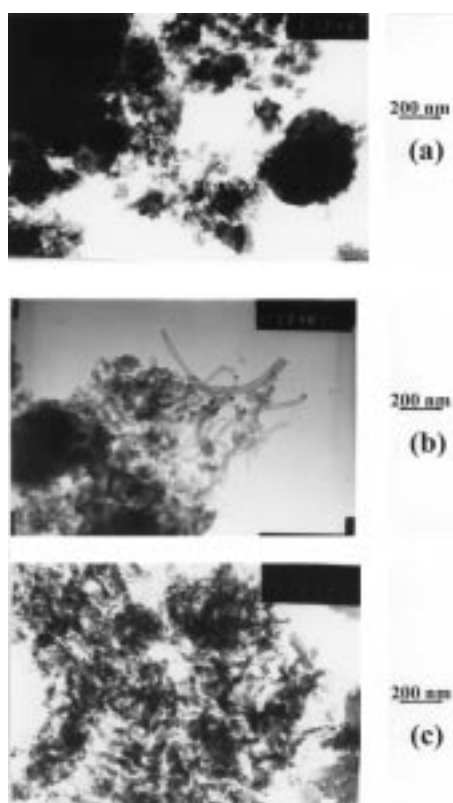
Figure 5. TEM pictures of carbon nanotubes formed on Fe/SiHMS(12) after different reaction times. (a) 10 min, (b) 30 min and (c) 1 h.

substrate [14], it is not easy to control the arrangement and pore size in an amorphous porous silica substrate. Another promising method to obtain an aligned growth of the carbon nanotubules with given pore size is chemical vapour deposition based synthesis of carbon nanotubes using an alumina membrane [15]. Unlike amorphous porous materials, the pore sizes of crystalline zeolite materials can be tailored by various treatment methods, such as chemical corrosion, steaming, change of the components in samples, use of different templates, etc. For this reason, we attempted to adjust the pore size of carbon nanotubes by adjusting the pore size of the zeolite supports.

Table II shows that, although the loaded Fe content is same for all the Fe/Y-type zeolite catalysts, the pore size of carbon nanotubes formed on them varies with the supports. The pore size of carbon nanotubes formed on Fe/NaY is only ∼10 nm. However, after adjusting the pore size of the support, the pore size of the carbon nanotubes formed is changed. From Table II it is evident that after the steaming treatment, not only were secondary pores (2.64 nm in diameter, see Tables I and II) created by connecting two adjacent supercages (1.34 nm in diameter), but also
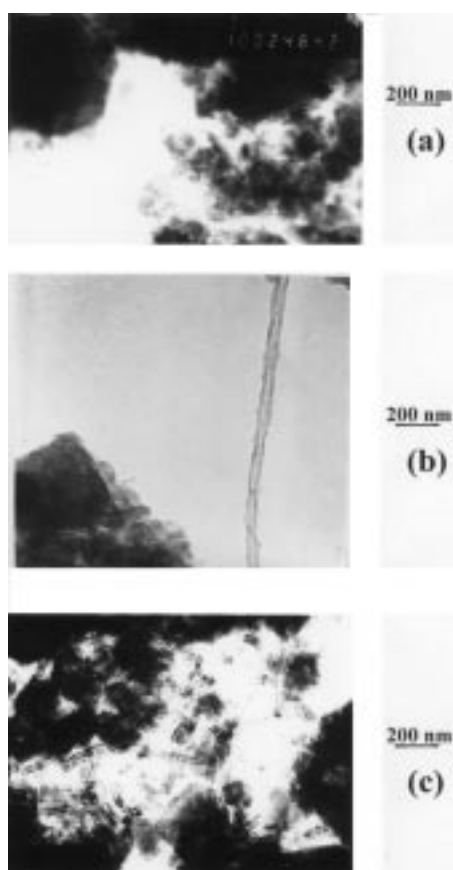
Figure 6. TEM pictures of carbon nanotubes formed on Fe/SiHMS(18) after different reaction times. (a) 10 min, (b) 30 min and (c) 1 h.

some pores with larger size were formed in support SDY (see Figure 1b, obtained by the BJH model). The diameter and pore size of the carbon nanotubes formed on Fe/SDY correspondingly increase to ~23 and ~14 nm, respectively. When SDY was further treated with a $(NH_4)_2SiF_6$ solution, as a result of the removal of partial framework aluminum species, some pores with a larger size than that before the treatment were formed (see Figure 1c and data for FSY in Table II). It is interesting that the diameter (~27 nm) and pore size (~17 nm) of carbon nanotubes formed on FSY were again observed to be larger than those of carbon nanotubes formed on Fe/SDY, respectively.

The above phenomena clearly demonstrate the effect of the pore size of supports on the diameter and pore size of the carbon nanotubes formed. This effect can also be demonstrated by comparing the data for Fe/SiHMS or Fe/SiMCM-41 with those for Fe/KL As mentioned above, Fe/SiHMS or Fe/SiMCM-41 possesses a one-dimensional channel structure and large pore sizes, thus they are active catalysts for the synthesis of carbon nanotubes. However, although KL also has a one-

Table II. Effect of pore size of supports on the size of carbon nanotubes

Catalysts	Si/Al (mol)	Fe loaded (wt.%)	Pore size (nm)	Carbon/cat. (wt.%)	Diameter of nanotubes (nm) Outer	Inner
Fe/NaY-d-2	2.5	5.0	~0.7,[b] ~1.36[c]	20.2	~17	~10
Fe/SDY	3.8	5.0	~0.7,[b] ~2.64[d]	25.1	~23	~14
Fe/FSY	4.5	5.0	~0.7,[b] ~2.64[d]	30.2	~27	~17
Fe/KL	2.9	5.0	~0.7[b]	14.5	Very few carbon nanotubes	
Fe/SiHMS(12)[e]	–	5.0	2.9[b]	35.3	~45	~13
Fe/SiHMS(18)	–	5.0	3.6[b]	36.7	~50	~17
Fe/SiMCM-41	–	5.0	3.3[b]	54.2	~44	~15

[a] Surface area by N_2 adsorption.
[b] Diameter of window.
[c] Diameter of supracage pore measured by ^{129}Xe MAS NMR method.
[d] Diameter of secondary pore measured by ^{129}Xe MAS NMR method.
[e] The numbers in parentheses are the carbon numbers in the chain of the primary amines as template.

dimensional channel structure, Fe/KL shows very low activity for the catalytic synthesis of carbon nanotubes. This can be attributed to the fact that KL has no supercages like those in NaY and also because of its small window of ~0.7 nm. Moreover, from the data for Fe/SiHMS(12), Fe/SiHMS(18) and Fe/SiMCM-41 listed in Table II, we also see that the larger the pore size of the support, the larger the diameter and pore size of the carbon nanotubes produced.

From all the above, we come to the conclusion that it is possible to adjust the diameter and pore size of carbon nanotubes by tailoring the pore size of the zeolite supports employed.

4.5. EFFECT OF STRUCTURE OF SUPPORTS ON GROWTH DIRECTION OF CARBON NANOTUBES

Control of the pore size and growth direction of carbon nanotubes is of great significance. Although Fe/NaY is a very active catalyst for the growth of carbon nanotubes, the carbon nanotubes still grow at random. This is because the channel structure of NaY is tri-dimensional, that is, its channels are not aligned in one direction. Moreover, its small windows, as mentioned above, do not favour the aligned growth of carbon nanotubes. Careful observation of the TEM pictures of carbon nanotubes formed on Fe/HMS or Fe/SiMCM-41, indicated that, although on the edge of these two catalysts the growth direction of carbon nanotubes is random, nanotubes were observed to grow almost in the same direction in the central part of each catalyst. Figure 7 shows carbon nanotubes grown on Fe/SiHMS(12) and Fe/SiMCM-41 (both pictures were taken in the respective central regions). Many black rings or white spots are present in both pictures. Assuming the catalyst
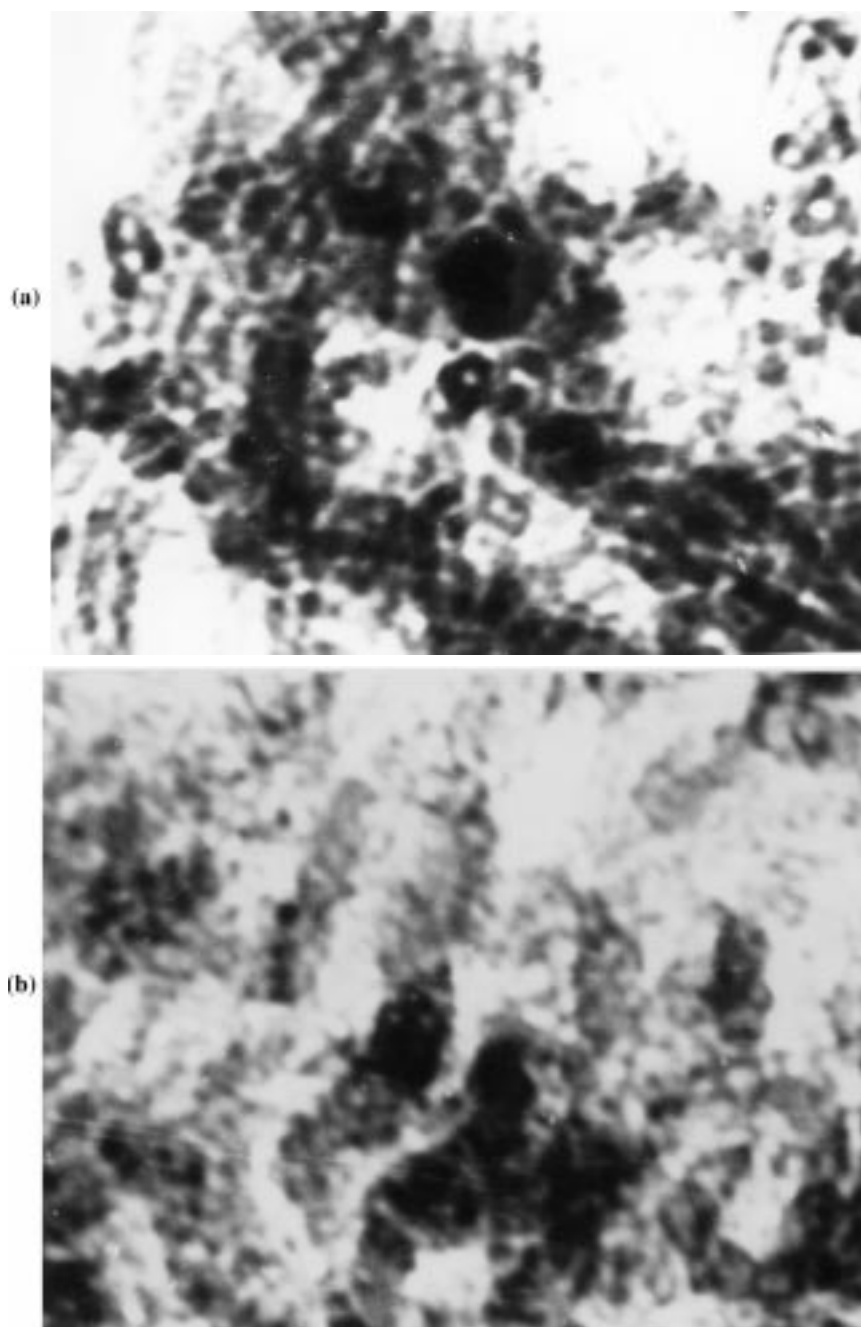
Figure 7. TEM pictures of carbon nanotubes formed on (a) Fe/SiHMS(12) and (b) Fe/SiMCM-41.

particle is laid parallel to the plane of the paper, we believe that these black rings and white spots are images of the pores of carbon nanotubes which have grown vertically from the catalyst. No similar phenomenon was observed for Fe/NaY, Fe/SDY and Fe/FSY. Based on the above observations, we suggest that a one-dimensional mesoporous structure can be employed to orient the growth of carbon nanotubes to a certain degree.

Acknowledgements

References

1. H. R. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and, R. E. Smalley: *Nature* **318**, 162 (1985).
2. S. Iijima: *Nature* **354**, 56 (1991).
3. S. Iijima and T. Ichihashi: *Nature* **363**, 603 (1993).
4. A. Rubio: *Condensed Matter News* **6**, 6 (1997).
5. P. M. Ajayan: *Condensed Matter News* **3**, 9 (1995).
6. T. W. Ebbesen: *Physics Today* **49**, 26 (1996).
7. R. Tenne: *Adv. Mater.* **7**, 965 (1995).
8. H. Dai *et al.*: *Science* **272**, 523 (1996).
9. M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson: *Nature* **381**, 678 (1996).
10. N. Hamada, S. Sawada, and A. Oshiyama: *Phys. Rev. Lett.* **68**, 1597 (1992).
11. J. P. Lu: *Phys. Rev. Lett.* **74**, 1123 (1995).
12. T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio: *Nature* **382**, 54 (1996).
13. S. Frank, P. Poncharal, Z. L. Wang, and de W. A. Heer: *Science* **280**, 1744 (1998).
14. W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, R. A. Zhao, and G. Wang: *Science* **274**, 1701 (1996).
15. G. Che, B. B. Lakshmi, C. R. Martin, E. R. Fisher, and R. R. Ruoff: *Chem. Mater.* **10**, 260 (1998).
16. C. Guerret-Plecourt, Y. Le Bouar, A. Loiseau, and H. Pascard: *Nature* **372**, 761 (1994).
17. N. Zabala, M. J. Puska *et al.*,: *Phys. Rev. Lett.* **80**, 3336 (1998).
18. A. Rubio, J. L. Corkill, and M. L. Cohen: *Phys. Rev. B.* **49**, 5081 (1994).
19. N. G. Chopra *et al.*: *Science* **269**, 966 (1995).
20. A. Rubio, Y. Miyamoto, X. Blase, M. L. Cohen, and S. G. Louie: *Phys. Rev. B.* **53**, 4023 (1996).
21. G. Fasol: *Science* **280**, 545 (1998).
22. P. M. Ajayan and S. Iijima: *Nature* **361**, 333 (1993).
23. Y. Miyamoto, A. Rubio, X. Blase, M. L. Cohen, and S. G. Louie: *Phys. Rev. Lett.* **74**, 2993 (1995).
24. W. Han, S. Fan, Q. Li, and Y. Hu: *Science* **277**, 1287 (1997).
25. J. C. Charlier: *Phys. Rev. B.* **53**, 11108 (1996).
26. Y. Miyamoto, A. Rubio, S. G. Louie, and M. L. Cohen: *Phys. Rev. B.* **50**, 4976 (1994).
27. Y. Miyamoto, A. Rubio, S. G. Louie, and M. L. Cohen: *Phys. Rev. Lett.* **76**, 2121 (1996).
28. W. A. De Heer *et al.*: *Science* **270**, 1179 (1995).
29. J. J. Davis, H. A. O. Hill, M. L. H. Green, J. Sloan, and S. C. Tsang: *Absract Book of the Second International Interdisciplinary Colloquium on the Science and Technology of the Fullerenes,* pp. 173 (1996).

30. V. P. Dravid, X. Lin, Y. Wang, A. Yee, J. B. Ketterson, and R. P. H. Chang: *Science* **259**, 1601 (1993).
31. N. Hatta and K. Murata: *Chem. Phys. Lett.* **217**, 398 (1994).
32. V. Ivanov, J. B. Nagy, Ph. Lambin, A. Lucas, X. B. Zhang, X. F. Zhang D. Bernaerts, G. Van Tendeloo, S. Amelinckx, and J. Van Landuyt: *Chemical Physics Letters* **223**, 329 (1994).
33. P. C. M. Van Stiphout, D. E. Stobbe, F. Th. V. D. Scheur, and J. W. Geus: *Appl. Catal.* **40**, 219 (1988).
34. A. I. La Cava, C. A. Bernardo, and D. L. Trimm: *Carbon* **20**, 219 (1982).
35. P. Magnoux and M. Guisnet: *Zeolites* **9**, 329 (1989).
36. R. T. K. Baker: *Carbon* **27**(3), 315 (1989).
37. V. Ivanov, A. Fonseca, J. B. Nagy, A. Lucas, P. Lambin, D. Bernaerts, and X. B. Zhang: *Carbon* **33**, 1727 (1995).
38. K. Hernadi, A. Fonseca, J. B. Nagy, D. Bernaerts, J. Riga, and A. A. Lucas: S*ynthetic Metals* **77**, 31 (1996).
39. K. Hernadi, A. Fonseca, J. B. Nagy, D. Bernaerts, A. Fudala, and A. A. Lucas: Z*eolites* **17**, 4 6 (1996).
40. G. T. Keer: *J. Phys.Chem.* **71**, 4155 (1967).
41. G. M. Skeels and D. M. Breck: *Proc. 6th Int. Zeolite Conf.,* (Ed. D. Olsen and A. Bisio) pp. 87–93, UK, Butterworths (1984).
42. N. He, S. Bao, and Q. Xu: *Chin. J. Chem.* **15**, 42 (1997).
43. N. He, S. Bao, and Q. Xu: *Stud. Surf. Sci. Catal.* **105**, 85 (1997).
44. C. T. Cresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S.: *Nature* **359**, 710 (1992).
45. P. T. Tanev and T. J. Pinnavaia: *Science* **267**, 865 (1995).
46. E. P. Barrett, L. G. Joyner, and P. P. Halenda: *J. Am. Chem. Soc.* **73**, 373 (1951).
47. T. Demarquay and J. Fraissard: *J. Chem. Phys. Lett.* **136**, 314 (1987).