The growth of carbon nanotubes at the channel ends of the SAPO₄-5 zeolite structures


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Available online 23 September 2005

Abstract

The growth of carbon nanotubes (CNTs) were evidently observed, at the channel ends of the mesoporous SAPO₄-5 zeolites. The Fe-catalyst SAPO₄-5 crystallites prepared by the sol–gel method were employed to the thermal CVD process, at a temperature ~650 °C for 30 min, using the mixture of acetylene and ammonia gases. The recorded SEM images show the formation of well aligned MWNTs at the channel ends of the crystallites. The analysis of HRTEM shows that, the outer diameter of CNTs varies in the range of 25–27 nm, whereas, the inner diameter varies in the range of 14–17 nm. The diameter of the CNTs was found to be varied marginally as compared to that of the channel diameter of the SAPO₄-5 crystallite. Furthermore, the observed formation of CNTs, along the ab-plane, could either be originated at a depth from the channels or at the channel ends of the crystallites. Although the former is attributed to the precipitation of the Fe-catalyst in the channels, the later is thought to be due to the out diffusion and clustering of Fe-atoms near the channel ends of the crystallites. The recorded micro-Raman spectrum showed the small ratio of, I(D)/I(G), which suggest that, the synthesized tubes are of high quality with less amount of defects.

Keywords: CVD; Carbon nanotubes; Mesoporous materials; Selective growth

1. Introduction

Ever since the discovery in 1991 [1], carbon nanotubes have captured the attention of researchers worldwide. The CNTs have many potential applications due to high degree of thermo-chemical stability, high mechanical strength, electron emission properties [2–4] and easy synthesis methods [5–9]. However, the pace of this nanotechnology watershed has been halted by efforts to synthesize CNTs at industrial standards, such as, selective growth, control diameter, high degree of orientation, etc.

Among various parameters in the synthesis of CNTs, template architecturing of the catalytic-nanoparticle is an important class of issue, in order to control the diameter of the CNTs. A considerable amount of work has been carried out in controlling the diameter of CNTs by regulating the particle size of the catalytic-nanoparticles. However, it was found that, during synthesis process, agglomeration of the catalytic-nanoparticles takes place, which retards the control of the diameter of the thin MWNTs or SWNTs.

The growth of CNTs is also possible in various nano-structured templates. Xie et al. has produced CNTs using iron nanoparticles in mesoporous materials [10], Iwasaki et al. has synthesized CNTs by embedding cobalt nanoparticles in the alumina [11,12] nano-holes (~50 nm). The clay carbon templates [13] were prepared by Barata-Rodrigues for the diameter controlled synthesis of CNTs, whereas, Fonseca et al. has used the micro-mesh [14] supported transition metal catalyst for the production of CNTs. However, each finding has its own limitations.

An alternative approach to the selective synthesis of monosized and well aligned CNTs is the zeolites, used as the hosts to encapsulate the catalytic transition metal. Zeolites being molecular sieve materials have had a significant impact due to high reactive surface area, structural homogeneity, and could be used in potential applications, such as petrochemical research [15] and micro reactor technology [16–19]. Furthermore, zeolites are well suited host candidates for the different
kinds of adsorbing molecules [20] and hence could be used as supporters for the catalyst particles. Recently, Tang et al. [28] have reported the synthesis of the CNTs in the channels of AlPO₄ crystallites.

In the present work, we have used SAPO₄-5 (silicoaluminophosphate) zeolite, for obtaining the growth of the CNTs. The SAPO₄-5 has excellent thermal and hydrothermal stabilities as compared to other zeolite crystallites, such as MeAPO-5 [21], pure-silica molecular sieves, AlPO₄ [22–27]. They have an unusual surface selectivity and could be operated at a higher temperature range from 600–1000 °C with insignificant degradation of the structure. The Fe-catalyst embedded SAPO₄-5 was prepared by a sol–gel method and the CNTs were grown using the thermal CVD method at a temperature ~650 °C. The study reveals that, the well-aligned and controlled diameter CNTs were observed at the channel ends and on the selective surface areas of the SAPO₄-5 crystallites.

2. Experimental

Initially, the ammonium chloride (NH₄Cl, powder form) was added to the de-ionized water along with the Fe (II) acetate (molecular formula-(C₂H₃O₂)₂ Fe) powder (pH ~5.5). The SAPO₄-5 (zeolites) crystallites (length ~20 μm and width ~5 μm, typical crystallite shown in Fig. 1(a)) were used as support materials to grow CNTs. The SAPO₄-5 crystallites were dehydrated at a temperature ~150 °C for 12 h. After the dehydration process, the crystallites were immersed in the Fe-solution and the solution was employed to the magnetic starring for 24 h at a constant temperature ~50 °C and later dried in a furnace at ~80 °C.

For the thermal CVD process, the Fe-catalyst-SAPO₄-5 crystallites were placed in the tube furnace and the mixture of gases C₂H₂/ NH₃ (61/500 sccm) was passed for 30 min at 650 °C to pyrolyze the acetylene to form CNTs. In another experiment, a few Fe-catalyst-SAPO₄-5 crystallites were employed to the DC (direct current)-PECVD process in order to study and compare the growth nature of CNTs on the SAPO₄-5 crystallites.

The fabricated crystallites and carbon nanotubes were analyzed by using scanning electron microscopy (SEM; Philips FEG XL 30 kV), a high resolution field emission transmission electron microscope (FETEM; JEOL JEM-3000F, 300 kV) and the micro-Raman spectroscopy (20 mW, 514.5 nm, RM1000-InVia).

3. Results and discussions

Fig. 1(a) shows the aggregate texture and morphology of the SAPO₄-5 crystallites. Fig. 1(b) shows the hexagonal P6 cc structure with axis of symmetry (i.e. c-axis) along [100] direction, perpendicular to the a–b plane. The surface morphology of the SAPO₄-5 crystallites after treating with the Fe-catalytic solution is shown in Fig. 1(c). The presence of elemental Fe, on the hexagonal surface of the SAPO₄-5 crystallites, was confirmed by using the EDX technique and the result is shown in Fig. 1(d).

After the CVD treatment, the SEM measurements were carried out and the results are shown in Fig. 2. The surface morphology (side view) of the SAPO₄-5 crystallite, after thermal CVD treatment, is shown in Fig. 2(a). The morphological details of the ab-plane are recorded in Fig. 2(b)–(d).

![Fig. 1. Recorded SEM images for: (a) texture and geometry of SAPO₄-5 crystallites (l ~20 μm and w ~5 μm); (b) details of the geometry of the crystallites, six-fold c-axis ⊥ to the a–b plane; (c) surface morphology of crystallites after Fe-catalyst solution processing; (d) recorded EDX spectrum of the surface of the Fe-catalyst-SAPO₄-5 crystallite.](image-url)
For comparison the surface morphology of the DC-PECVD treated SAPO₄-5 crystallite is shown in Fig. 2(e).

FETEM studies give further information about the morphology and microstructure of the synthesized CNTs. The results are shown in Fig. 3(a)–(c). In addition to FETEM, micro-Raman spectroscopy was carried out (beam diameter ≈1 μm) to characterize the quality of the synthesized CNTs on SAPO₄₋⁵ crystallites. The recorded spectrum is shown in Fig. 3(d). Fig. 4 shows the details of the growth of CNTs at the channel ends of the crystallites, along the \( ab \)-plane.

One can see from Fig. 1(b) and (c) that, the surface morphology of the SAPO₄₋⁵ crystallite is almost similar before and after the Fe-catalytic impregnation treatment. The EDX results showed the negligible amount of Fe (≈1%–2%) was present in the surface region of the crystallites. This phenomenon is attributed to the weak electro-chemical interaction [28] between the Fe atoms and the surface region of the SAPO₄₋⁵ crystallite. Furthermore, the electro-chemical nature of the surface region of the crystallite was found to be distinctly different [28], with very small local dipole moment, as compared to that of the channel walls. As a result, the affinity of the crystallite to precipitate the Fe atoms in the surface region of crystallites was found to be negligibly small.

Fig. 2(a) confirms the formation of a large amount of CNTs selectively grown along the \( ab \)-plane, of the crystallites. However, the growth of CNTs on the hexagonal surface region of the crystallite was found to be marginal and is consistent with the obtained EDX results. Furthermore, Fig. 2(b)–(d) shows the details of the growth and the surface morphology of the \( ab \)-plane. These results reveal the emergence of two possibilities, either the growth could be originated at a depth from the channels or at the channel ends of the SAPO₄₋⁵ crystallites.

In order to explore the growth mechanism of CNTs at a depth from the channels of the crystallites we have shaded the light on the structure, chemistry and the polarization mechanism of molecules in the channels of the SAPO₄₋⁵ crystallites. The crystallites of SAPO₄₋⁵ are hexagonal rods and have one-dimensional channels, along the \( c \)-axis, open from both sides. Moreover, the degree of molecular adsorption inside the channels is an order of magnitude higher than that on the outer surface [30] of the crystallites. After immersing the crystallites in the solution [31,32], the Fe-catalyst molecules might have diffused-in from both sides of the open channels, along the \( c \)-axis, rather than precipitating in surface region of the crystallites. And during the drying process (carried out at a temperature 80 °C) the various
volatile components of the Fe-solution, such as, C, O, and H may get evolved and diffused out from the channel pores of the crystallites. As a result, the precipitation (or trapping) of the elemental Fe takes place in the channel pores of the crystallites. Thus, it is thought that, during the impregnation treatment the Fe atoms might have interacted more effectively with the channels of the crystallites instead of precipitating in the surface region of SAPO$_4$-5.

Moreover, the Brønsted sites [29] (bridging hydroxyl) formed due to the substitution of silicon by the aluminum or phosphorous in the structure of AlPO$_4$-5 (SAPO$_4$-5) molecular sieves play a vital role in the growth process of CNTs. The Brønsted sites were found to be chemically active, moderately acidic in nature [33] and induce the localized charge on the channel walls of the SAPO$_4$-5 crystallites. In addition, these sites have high reactivity for dehydration of acetylene, for C–C bonding, for hydrogen transfer and aromatic cyclization [33]. During thermal CVD process, due to the pyrolysis [34,35], the dissociation of the acetylene takes place with the release of the carbon atoms. These carbon atoms could enter, diffuse and interact with the Fe-catalyst atoms and Brønsted sites present in the channel pores of the SAPO$_4$-5 crystallites which lead to the formation of CNTs. Thus, the presence of precipitated Fe-catalyst atoms and the Brønsted sites generates a favorable basis for the growth of the CNTs in the channels of the SAPO$_4$-5 crystallites.

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Furthermore, the growth of CNTs carried out by the DC-PECVD process (Fig. 2(e)) on the SAPO$_4$-5 crystallites, was found to be highly non-selective, and un-controllable in nature. In addition, a large amount of amorphous carbon was formed with wide range of diameter distribution of the grown CNTs.
This result clearly indicates that, thermal CVD is a well suited candidate for the diameter controlled, well aligned and selective growth of CNTs using the SAPO-5 crystallites.

The HRTEM (Fig. 3(a)) analysis reveals that, the outer diameter of the CNTs varies in the range of ~25–27 nm, whereas, the inner diameter was found to be in the range of 14–17 nm, which is inconsistent with the coordinate diameter of each channel [29], found to be ~1 nm (inner diameter ~0.8 nm). The observed variation in the diameter of CNTs emerges the possibility of the formation of CNTs at the channel ends of the SAPO-5 crystallites. During the pyrolysis process, the Fe-catalyst atoms in the channels of the crystallites could get thermally desorbed and diffused out from the channels of the crystallites. Due to the higher value of the cohesive energy [36,37] of the Fe-atoms, the clustering takes place near the crystallites. Due to the higher value of the cohesive energy of the Fe-atoms, the clustering takes place near the crystallites. Furthermore, the Fe-clusters formed near the channel ends of the crystallites could dissociate acetylene gas, during the pyrolysis process, and produce carbon atoms, which get dissolved into these Fe-clusters. Following the process, the supersaturated carbon atoms precipitate on the surface of the Fe-clusters, which results into the nucleation of the CNTs at the channel ends of the crystallites. Fig. 4 schematically shows the formation of CNTs at the channel ends of the SAPO-5 crystallites.

In the present work, we have seldom evidenced for the growth of CNTs at a depth from the channels of the SAPO-5 crystallite, moreover, the results suggest that the growth of CNTs could be originated from near the channel ends of the crystallite, along the ab-plane. Fig. 3(b) shows that, the synthesized CNTs had a bamboo-like structure covered with a very small amount of amorphous carbon deposit. The Fe catalytic particle was found to be at the middle of CNTs as shown in Fig. 3(c).

The recorded micro-Raman spectrum (Fig. 3(d)) indicates a strong G-band and relatively weaker D-band at a wavelength ~1595 cm⁻¹ and ~1348 cm⁻¹, respectively. In general, the ratio I(D)/I(G) can be used as the indicator [38] of the degree of disorder within the nanotubes. The estimated ratio I(D)/I(G), in our study, was found to be small, which reveals that, high-quality CNTs are produced by this method with low defect level. The present study reveals that, the SAPO-5 plays a vital role as a catalytic material in the growth process of CNTs selectively along the ab-plane of the crystallite.

4. Conclusions

Thus, zeolite-based catalyst system could be well positioned to meet some of the challenges in the growth process of CNTs. It is clear that SAPO-5 crystallite is moving further into the areas of selective, diameter controlled growth of CNTs. The thermal CVD process was used to obtain the diameter controlled, well aligned and selective growth of CNTs at the channel ends, of the SAPO-5 crystallites. The HRTEM analysis reveals that, the outer diameter of the MWNWs varies in the range 25–27 nm, whereas, the inner diameter varies in the range of 14–17 nm. The observed formation of CNTs, along the ab-plane, could either be originated at a depth from the channels, due to the precipitation of the Fe-catalyst and the Brønsted sites, or from the channel ends of the crystallites, due to the clustering of thermally desorbed Fe-atoms. Although the former is more chemistry oriented, the later is more speculative and convenient from the stand point of physical observation. The small ratio of the I(D)/I(G), estimated by the micro-Raman analysis, indicates the formation of high-quality CNTs with low concentration of defects.

Acknowledgements

Authors are grateful to Prof. K. B. Yoon and Dr. Y. J. Lee, Center for Microcrystal Assembly, Sogang University. The research work supported by the Ministry of Industry and Energy of Korean Government through Center for Nanotubes and Nanostructure Composites (CNNC) at Sungkyunkwan University is gratefully acknowledged. One of the authors (PSA) is thankful to the CSIR, New Delhi, for awarding the Research Associate ship.

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