CARBON NANOTUBES PREPARED USING Fe/MCM-41 AS CATALYST TEMPLATE

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Introduction

Due to their extraordinary structural characteristics, carbon nanotubes (CNTs) are finding their applications in many fields, such as field emission electron sources, scanning probes, chemical sensors, field-effect transistors, and nano-electronic devices [1]. Among various preparation methods, chemical vapor deposition (CVD) has many advantages owing to its simplicity, low cost, and easily controlled growth factors. The mesoporous molecular sieves (such as MCM-41, SBA-15) can be used as good carriers of catalysts for the growth of CNTs prepared by CVD because they have excellent characteristics of strong metal-support interactions, high specific surface area, large pore volume, uniform pore structure, and tunable pore size [2-4]. But there are few researches on ABW as catalyst templates to synthesize CNTs. In this paper, CNTs were prepared by CVD at 600 and 700 ℃ in H_2 and Ar atmosphere using iron catalyst supported on MCM-41 or ABW molecular sieves (Fe/MCM-41 or Fe/ABW) as catalytic template and acetylene as carbon source. The effects of reaction temperatures and molecular sieves on the formation of CNTs were investigated.

Experimental

Preparation of Fe/MCM-41: The Fe-loading catalyst was prepared by wet impregnation method. First, 2 g of $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved in 20 ml of distilled water. Subsequently, 0.2 g of MCM-41or ABW molecular sieve was added into the iron nitrate aqueous solution. After stirring for 2 h, the resulting suspension was statically placed at ambient temperature for 12 h. After evaporating the solvent, the residual solid was dried at 80 ℃ for 24 h to obtain the Fe-loading MCM-41 or ABW molecular sieve catalyst, designated as Fe/MCM-41 or Fe/ABW.

Synthesis of CNTs: CNTs were synthesized in a quartz tube (32 mm i.d. and 1000 mm long), which was mounted in a horizontal tube furnace. An 18 mm-long quartz boat with about 0.1 g of catalyst was placed at the isothermal zone in a horizontal quartz tube reactor. Initially, the tube was heated up to 700 ℃ in 50 ml min^{-1} of steady Ar flow. In order to reduce the iron oxides to elemental iron, the catalyst was reduced at 700 ℃ in H_2 atmosphere for 1 h. Then synthesis reactions were carried out for 30 min by introducing a mixture of C_2H_2 and Ar into the reactor at a flow rate of 30 and 300 ml min^{-1}. After the growth process, the furnace was cooled to room temperature in 60 ml min^{-1} of Ar flow. To separate molecular sieve, the product collected was dissolved in 40% NaOH solution for 2 h, filtered, washed with distilled water and dried at 80 ℃ for 24 h. For comparison, the products were also prepared using the Fe-loading molecular sieve as catalysts unreduced by H_2.

Characterization: The morphology and structure of the products were characterized by high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD).

Results and Discussion

Fig. 1 shows the HRTEM images of the products prepared at 600 and 700 ℃ using Fe/MCM-41 as catalyst. It can be seen that the products prepared at 600 ℃ consist of the curly CNTs with about 20 nm in outer diameter (Fig. 1a) and poor crystallinity (Fig. 1b). As shown in Fig. 1c, the products prepared at 700 ℃ consist of the curly CNTs with about 30 nm in outer diameter and better crystallinity (Fig. 1d). This indicates that the temperature played an important role in CNTs formation.

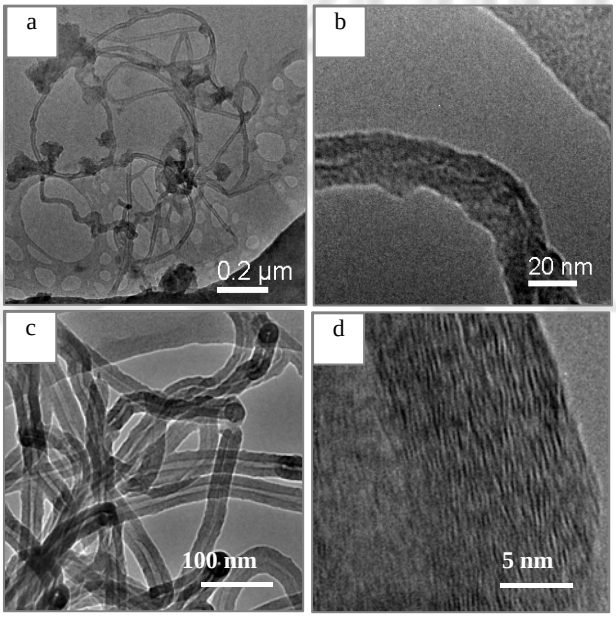

Fig. 1 HRTEM images of the products prepared at different reaction temperatures using Fe/MCM-41 catalyst. (a) 600℃; (b) enlarged image of (a); (c) 700℃; (d) enlarged image of (c)

Fig. 2 shows XRD patterns of the products prepared at 700 ℃ using Fe/MCM-41 as catalyst. The peaks at about 26.0° can be attributed to the diffraction of (002) plane of carbon. The broadened peak at 26.0° suggests the poor crystallinity of the products, in good accordance with HRTEM observation. The most of other peaks can be ascribed to the diffraction of Fe catalyst, suggesting that the metal nanoparticles play a key role of catalyst in the growth of CNTs.

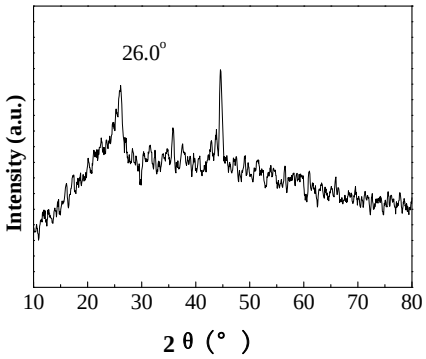

Fig. 2 XRD patterns of the products prepared at 700℃using Fe/MCM-41 catalyst.

Fig. 3 shows the HRTEM images of the products prepared at 700 ℃ using untreated Fe/MCM-41 as catalyst. As shown in Fig. 3a, the products are also composed of the curly and pure CNTs with about 25 nm in outer diameter. But the CNTs had poor crystallinity than that prepared using H_2-reduced Fe/MCM-41 as catalyst (Fig. 3b). This indicates that catalyst reduction by H_2 promoted the crystallization and growth of CNTs.

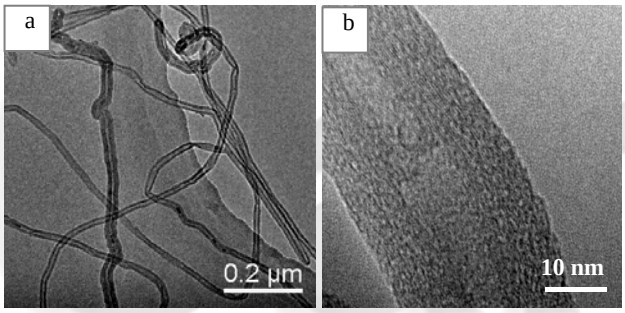

Fig. 3 HRTEM images of the products prepared at 700℃using Fe/MCM-41 as catalyst without reduction of H_2. (a) low magnification image; (b) high magnification image

To investigate the influence of the kind of molecular sieve on the formation of CNTs, the products were also prepared by CVD using Fe/ABW as catalyst. Fig. 4 is the HRTEM images of the products prepared at 600 and 700 ℃. It can be seen that the products prepared at 600 ℃ were composed of the curly solid carbon fibers with about 200 nm in outer diameter (Fig. 4a). As shown in Fig. 4b, the products prepared at 700 ℃ consist of the curly CNTs with about 30 nm in outer diameter and poor crystallinity (Fig. 4b). This indicates that the kind of molecular sieve also put effect on the growth of CNTs.

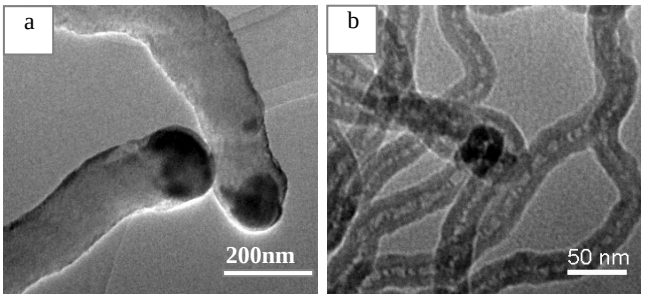

Fig. 4 HRTEM images of the products prepared at different reaction temperatures using reduced Fe/ABW catalyst by H_2 (a) 600℃; (b) 700℃

Conclusions

CNTs with 20-30 nm in diameters were prepared by CVD at 600 and 700 ℃ in H_2 and Ar atmosphere using Fe/MCM-41 and Fe/ABW molecular sieves as catalytic template and acetylene as carbon source. The effects of reaction temperatures and molecular sieve on the formation of CNTs were investigated. The diameters and graphitization degree of CNTs became larger and better with increasing temperature, H_2 reduction promoted the crystallization and growth of CNTs in preparation process, and the kind of molecular sieve also influenced the growth of CNTs.

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