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Preparation of carbon nanofibers over carbon nanotube-nickel catalyst in propylene decomposition

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Abstract A variety of structural and morphological forms of carbon nanofibers, which comprise perpendicularly and obliquely stacking graphite fibers and the two composite forms made of outer coaxial graphite tubes and inner perpendicularly or obliquely stacking fibers, were fabricated in catalytically decomposing propylene–hydrogen mixture over carbon nanotube-supported nickel catalysts. The growth mechanism for composite carbon nanofibers was proposed. The different types of carbon filaments are promising to be applied in catalyst support and capsules for drug delivery or nanoscale electrical devices.

Introduction

Carbon nanofibers (CNFs) have attracted attention as a unique form of carbon materials because of their particular properties, such as high resistance to strong acids and bases, high surface area, and high mechanical strength[1]. Catalyst plays a key role in the production of CNFs. Much research work has been devoted to the development of efficient catalysts for production of CNFs[2–4].

Carbon nanofibers are defined a kind of turbostratic graphic structure with 3–100 nm diameter and 0.1–1,000 μm length [5]. They involve three fundamentally different types, in which the basal planes of graphite are arranged along, across, and at an angle to the filament axis, that is, coaxially cylindrical, platelet, and coaxially conical carbon nanofibers [6]. The morphologies of carbon fibers are related to the size and morphology of transition metal (Fe, Co, or Ni) used as active phase in the hydrocarbon decomposing process. Here we report several types of carbon nanofibers synthesized by decomposition of propylene–hydrogen mixture on the aid of nickel-based catalysts supported by carbon nanotubes.

Experimental

Synthesis of carbon nanotube-supported nickel catalyst

Carbon nanotubes (CNTs) used as catalyst support were prepared by catalytically decomposition of propylene using diatomite-supported nickel as catalyst. As-prepared CNTs were immersed in concentrated hydrofluoric acid for 24 h to eliminate diatomite. Then they were refluxed in concentrated nitric acid and mild sulfuric acid (60 wt%) for 30 min to modify their surface properties [7].

The catalyst was prepared by a precipitation reaction. CNTs (1 g) were dispersed in 5 mL of the solution containing 0.7 g nickel nitrate, and ammonium carbonate (0.4 g) was dissolved in 4.5 mL distilled water. The solution of ammonium carbonate was added slowly with vigorous stirring, to the solution of nickel

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nitrate. The precipitate was washed several times with distilled water, then filtered and dried at 373 K overnight. Then the catalysts with 15 wt% of NiO loading were obtained by calcination of these dried precipitates at 873 K for 4 h.

Carbon nanofiber synthesis

The calcined catalysts were in situ reduced by hydrogen (200 mL/min) at 450 °C for 15 min, followed by pyrolyzing propylene (500 mL/min) and hydrogen (100 mL/min) mixture at different temperature from 600 to 800 °C for 30 min. Then carbon nanofibers were produced.

Characterization techniques

Transmission electronic microscopy (TEM) and high-resolution transmission electronic microscopy (HRTEM) were used to provide information about the microstructure of the carbon nanofibers. TEM was carried out using a JEOL-300CX, operating at 20 kV. HRTEM was carried out on a JEOL 2010F with an accelerating voltage of 200 kV. Suitable transmission specimens were prepared by ultrasonic dispersion of carbon nanofibers in alcohol from which a drop of the suspension was applied to a holey carbon support film. The NiO loading was analyzed by X-ray fluorescence spectroscopy using a XRF-1700.

Results and discussion

Carbon nanofibers were synthesized when the CNT-supported nickel catalysts was used. There were mainly herring-bone nanofibers and platelet nanofibers. In another case, the combined nanofibers were formed.

Herring-bone nanofibers and platelet nanofibers

As shown in Fig. 1, herring-bone carbon fibers were observed when the pyrolyzing temperature was higher than 750 °C using nickel catalysts supported on carbon nanotubes with NiO loading of 15 wt%. We designate them to CNF1. The diameter of CNF1 was in the range of 80–120 nm. CNF1 exhibited a relatively disordered structure, the orientation of graphite basal plane was at an angle to the fiber axis. TEM image of the samples confirmed that the method used for the formation of carbon fibers was highly selective, since little other forms of carbon were observed. The yield was very high, and the maximum yield reached to 36 g/g catalyst. CNF1 were also reported to be products of decomposition of ethane with CNT-supported nickel catalyst obtained by impregnation method by Pham-Huu and his co-workers [8].

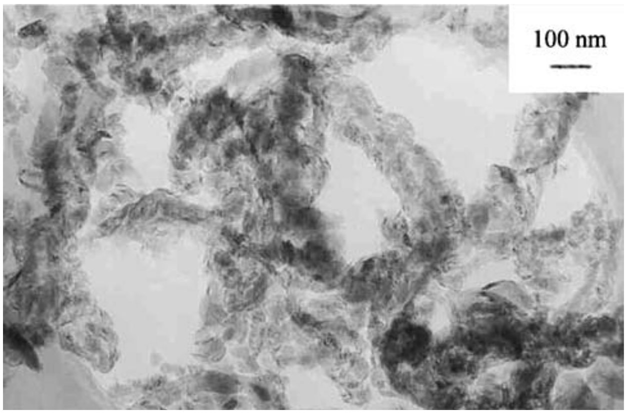

Fig. 1 TEM image of herring-bone carbon fibers synthesized at 750 °C over nickel catalysts supported on carbon nanotubes with NiO loading of 15 wt%

When the reaction temperature was lower than 650 °C, platelet stacking carbon fibers shown in Fig. 2 were produced, which is named CNF2 hereafter. CNF2 were made of perpendicularly stacked graphite sheets with low graphitization. There was no regular interlayer space. The stacking of graphite sheets changed from loosely to closely, and the carbon layer orientation deflected at minor angle.

The microstructure of carbon fibers depended significantly on the synthesis temperature. This result might be attributed to the variation of orientation of nickel basal plane when the reaction temperature increased from 650 to 750 °C.

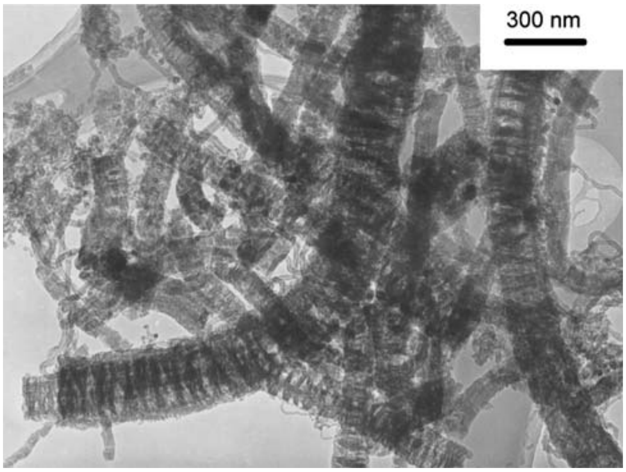

Fig. 2 TEM image of platelet stacking carbon fibers synthesized at 650 °C over nickel catalysts supported on carbon nanotubes with NiO loading of 15 wt%

The surfaces of CNF1 and CNF2 are composed exclusively of graphite edges, which provide more accessible sites for metallic particles after chemical modification, therefore they are expected to be attractive catalyst support materials.

Composite nanofibers

When we improved the NiO loading of catalyst to about 53 wt% by increasing the amount of nickel nitrate (2.5 g) and ammonium carbonate (1.4 g) in the process of catalyst preparation, new types of carbon nanofibers—the composite fibers with two different graphite stacking orientation shown in Figs. 3 and 4 were obtained at 650 °C, which are called CNF3 and CNF4 respectively. The outer part of the composite was tubular graphite structure, and the inner part was made of either cone-shaped or platelet stacking graphite sheets. CNF3 and CNF4 were prepared in one experiment, CNF3 took most portion of the sample, and only several CNF4 were observed.

The outer and inner diameters of CNF3 was 60–80 and 30–50 nm, the diameter of interface was 40–60 nm. The interplanar spacing of the outer and inner layers determined by measuring the high-resolution transmission electron microscopy (HRTEM) image were 0.34–0.35 nm. They were open at least on one end, as was observed in Fig. 3. The conical stacking carbon lattices linked up with the cylindrical stacking lattice at the interface, but for the inner surfaces composed of exposed edge layers, either near-neighbor layers linked up to form steps and terraces, or deformed fragments of the graphite basal planes form closed-layer structures, although it could not be excluded that minor portion of the inner surfaces still remained open.

The outer diameters of CNF4 was about 90–100 nm, the irregular outer diameter of core was in the range of 60–70 nm. The interlayer spacing of outer was close to 0.34 nm, while that of core planes was about 0.355 nm. It seemed that the core part contained spaces from low magnification image, but the HRTEM image clearly showed the presence of graphite layers at the spaces. At the interface most of the neighbor or near-neighbor graphite layers closed up each other, only minor portion of surfaces were open.

The exposed ends of inner conical stacking sheets for CNF3 are more reactive than the basal planes [9], and they are hydrophilic[8]. So this type of filament can be promising for nanofluidic application such as capsules for drug delivery. The orientation of graphite sheets between outer part and core for CNF4 is vertical, resulting in prominent distinctions of heat and electric properties, thus they are expected to be useful in molecular-scale devices.

The TEM micrograph of the calcined catalysts was shown in Fig. 5. The NiO loading examined by X-ray fluorescence spectroscopy (XRF-1700) was 52.76 wt%.

The NiO particles were dense and had diameters of 10–50 nm, some of which agglomerated. CNTs were almost completely covered with NiO particles.

It is now recognized that metal catalysts have a tremendous impact on the growth characteristics of carbon nanofibers. Here we pay more attentions to the formation of CNF3 and CNF4 and suppose a mechanism in Fig. 6. It is well-known from surface science studies that the interaction of a given gas molecule with a metal surface is frequently limited to certain crystal faces of the solid. This phenomenon is governed mainly by geometric arrangements of the metal atoms. When catalyst particles are undergoing reaction, some of crystallographic faces are capable of chemically dissociating the carbon-containing gases, but they are unable to precipitate dissolved carbon atoms, and another set of faces exhibit the reverse properties [10]. The latter faces control the geometric alignment of the graphite platelets. The schematic representations given in Fig. 6a, b corresponds to the type of nanofibers shown in the TEM micrograph, Figs. 3 and 4, respectively. Here, there is only a single face of the particle involved in the interaction with the hydrocarbon

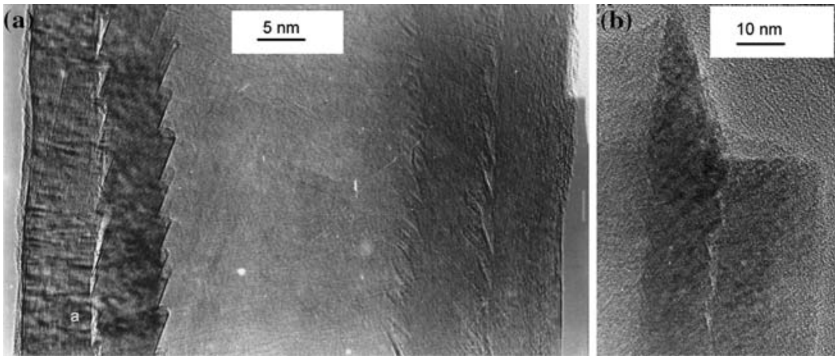

Fig. 3 HRTEM image of combined carbon nanofibers with conical graphite stacking form for the inner structure (**a**) and the morphology of (**a**) at one end (**b**)

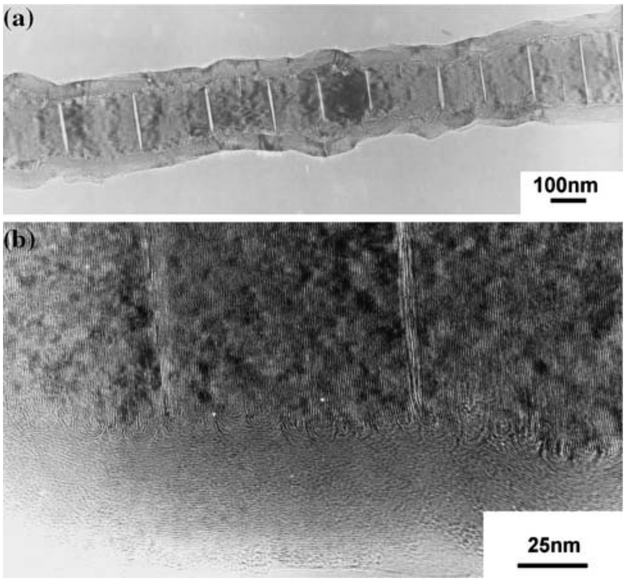

Fig. 4 TEM image of combined nanofibers with flat graphite stacking form for the core structure (**a**) and HRTEM image of (**b**)

reactant molecule and several faces where precipitation of carbon can occur. The agglomeration of metal particles with different size is responsible for the formation of the composite fibers with two different graphite stacking orientation.

The outer cylindrical stacking sheets and the inner conical or platelet stacking sheets precipitate contemporarily at the neighbor rear crystallite planes of metallic particle, as seen in Fig. 6. On one hand, carbon atoms diffuse through the bulk particle to the rear plane and precipitate in conical or platelet stacking form. On the other hand, carbon atoms diffuse along the surface to the neighbor-rear crystallite plane and precipitate in cylindrical stacking form. The graphite layers with different orientation grow all together. When they meet at the interface, the graphite planes with different orientations connect each other if they match, if the orientation is normal like that of CNF4, the graphite layers link up between near layers, as is also the case for the inner surface with exposed graphite edges. The graphite sheets reconstruct spontaneously to remove the dangling bonds because the surface energy of open edges is almost 40-fold higher than that of basal planes [11]. It is early observed, when bulk graphites are oriented at some angles to the filament axis, the surface tends to be covered by steps and terraces formed by fragments of the basal planes; when bulk graphites are oriented normally to the filament axis, the closed-like structures are formed on the surface when the neighbor or next-neighbor graphite layers are linked like a kind of "nano-caps" [12–14]. Similar morphology with CNF4 is ever found except the presence of spaces between core graphite sheets by Ci and co-workers, which originates from transformation of worm-like carbon filament under laser irradiation [15]. It also indicates that this morphology provides minimal surface energy. Hence, the composite nanofibers adopt the same morphology at the exposed edge sites.

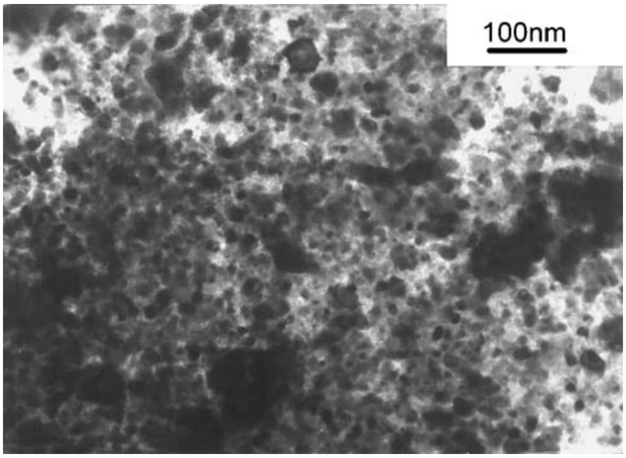

Fig. 5 TEM micrograph of the calcined catalysts

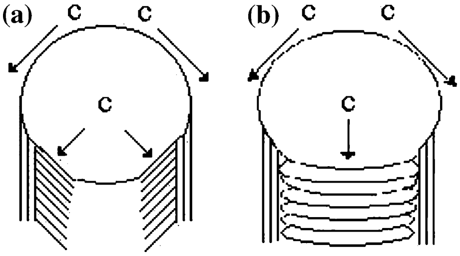

Fig. 6 Schematic representations of the formation mechanisms of CNF3 (**a**) and CNF4 (**b**)

Role of the carbon nanotube support

Various types of carbon nanofibers were formed by decomposition of propylene on CNT-supported nickel catalyst. We can thus understand the function of the carbon nanotubes as a new catalyst support and the interaction between carbon nanotubes and metal. The shape and crystalline orientation of the catalyst particles are responsible for the microstructure of carbon nanofibers [10]. The state of the metal is affected by the metal–support interaction. In turn, this interaction depends on the surface structure of support. Carbon nanotubes are hydrophobic in nature because they only exhibit basal planes. However functional groups such as hydroxyl or carboxyl can be introduced onto their surface by oxidized treatment using concentrated nitric acid and mild sulfuric acid, leading to the improvement of their hydrophilic character. Therefore the interactions between metallic particles and oxidized carbon nanotubes can be enhanced. When NiO loading is lower (15 wt%), the stronger interactions between metallic particles and oxidized carbon nanotubes limit the shape and crystalline orientation of the catalyst Ni particles. Carbon nanofibers produce from the interaction of Ni with propylene/H_2 mixture at 650 °C, graphite platelets are stacked in a direction parallel to the base of the particle and perpendicular to the fiber axis. The functional groups on the surface of the carbon nanotubes decompose when they are heated to relatively high temperature [16] e.g. 750 °C, accordingly the interaction between the metallic particles and oxidized carbon nanotubes is weakened. So the morphology and crystalline orientation of nickel particles change, leading to the formation of herring-bone carbon nanofibers. When NiO loading is higher (53 wt%), the interaction between some metallic particles and oxidized carbon nanotubes is lower due to the limited functional groups on the surface of the carbon nanotubes. Thus the agglomeration of Ni particles with different size occurs, resulting in the formation of the composite fibers with two different graphite stacking orientation.

Conclusions

A variety of carbon nanofibers were fabricated by pyrolysis of propylene–hydrogen mixture with carbon nanotube-nickel as catalyst. The morphologies of these fibers were related to that of nickel particles and the support–metal interaction. CNF1 and CNF2 can be applied as catalyst support due to the more accessible sites for active phase particles. CNF3 can be promising for nanofluidic application capsules for drug delivery because of the more reactive inner surface. CNF4 may be useful in molecular-scale devices owing to the notable distinction of their heat or electric properties between inner and outer part.

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