ISSN 0023-1584, Kinetics and Catalysis, 2006, Vol. 47, No. 4, pp. 497–500. © MAIK "Nauka/Interperiodica" (Russia), 2006.
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Growth of Unusual Carbon Nanofilaments in Methane Pyrolysis

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Received December 29, 2004

Abstract—Two types of carbon nanofilaments (nanotubes) differing markedly in morphology and growth rate grow on substrate plates containing a supported catalyst in a methane atmosphere at ~1050°C. According to provisional estimates, nanofilaments of one of these types grow at a rate of 5–10 μm/s, which is 50–100 times as high as the growth rate observed for ordinary catalytic filaments (tubes). These filaments are as long as several millimeters, being 50 to 100 nm in diameter. A preliminary examination of their structure has demonstrated that there is no catalyst particle at the filament end and that the filament is likely a carbon-rich polymer. A possible mechanism of the growth of these carbon filaments is discussed.

DOI: 10.1134/S0023158406040045

At present, two mechanisms are distinguished for the growth of carbon filaments (tubes) resulting from heterogeneous catalytic pyrolysis in the presence of supported catalyst particles. A filament may grow either at its tip, with a catalyst particle at the growing end, or at its root, with a catalyst particle remaining on the substrate throughout the process [1, 2]. The tip growth is better studied and is considered in detail by Alstrup [3]. The location of the particle (at the tip or at the root of the growing carbon filament) is determined by the interaction between the metal catalyst and the substrate [1]. It is universally accepted that, in both cases, the catalyst plays an active role in the decomposition of carbon-containing molecules, liberating carbon atoms, and in the transport of carbon to the growing edge of the tube wall or filament [1, 4]. The growth rate of the carbon structure in this case is limited by carbon diffusion. According to experimental data, the linear rate (v) of the tip growth of a filament (tube) is inversely proportional to the square root of the diameter of the catalyst particle (d): $v \sim d^{-0.5}$. For particles greater than 50 nm in diameter, v is no higher than 0.2 μm/s [1]. The linear rate of root growth is no higher than ~0.1 μm/s and decreases rapidly as the tube length increases [4]. These data are in good agreement with the simple estimate according to which the growth rate of a catalytic particle with a diameter of 50–60 nm is 0.08–0.16 μm/s [2]. However, the model suggested by Chesnokov and Buyanov [2] predicts that the linear rate of tip growth as a function of particle diameter will obey another law, namely, $v \sim d^{-1}$.

Here, we present experimental data concerning the formation of unusual carbon nanofilaments. There must be a catalytic particle on the substrate for the nucleation of such a nanofilament, but the growing nanofilament has no catalytic particle at its tip. The linear growth rate of this filament is many times as high as the observed growth rate of an ordinary catalytic tube (filament) or the upper limit of the growth rate in the universally accepted model.

EXPERIMENTAL

Filamentous carbon was grown in an isothermal quartz tubular reactor with an inner diameter of 18 mm. The reactor was placed into an electric furnace with an isothermal zone length of 8 cm. A quartz boat containing a catalyst supported on a substrate plate was placed in the middle of the isothermal zone. In our experiments, the most active catalyst was iron oxalate microparticles obtained by spraying a solution or by evaporating a thin solution film on a hot surface. The resulting catalyst particles were characterized by a wide size distribution, ranging from a few hundredths of a micrometer to tens of micrometers. The substrate material was quartz, silicon, synthetic graphite, or sapphire. A substrate with a catalyst was placed into the reactor and was heated to 1050 ± 10°C in flowing argon. Next, an 80% CH_4 + 20% H_2 mixture was passed through the reactor at a rate of 0.6 l/min for 5–15 min. Thereafter, the mixture was displaced with argon, and the reactor was cooled to room temperature in a slow argon flow. The substrate was withdrawn from the reactor, and the products were examined by light microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Electron microscopic studies were carried with a Philips 515SEM instrument (accelerating

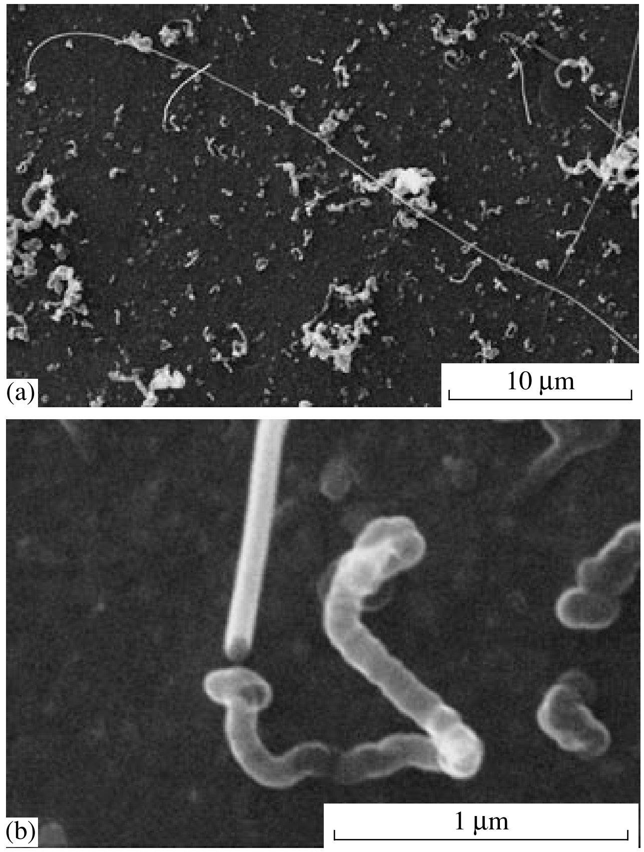

Fig. 1. SEM images: (a) general view of type 1 and 2 nanofilaments; (b) type 1 filaments (on bottom) and the end of a type 2 filament (above) at a higher magnification.

voltage 30 kV, secondary-electron mode) and a Philips 430ST instrument (accelerating voltage 200 kV).

Primary examination of pyrolysis products was performed by light microscopy. Carbon filaments whose length is several micrometers or more are well distinguishable under a light microscope even if their diameter is as small as 50–100 nm. Owing to a wide field of view and to the possibility of micrometer screw operation, the light microscope enabled us to estimate filament lengths between a few tens of micrometers and a few millimeters.

RESULTS

The reaction products contained two types of nanofilaments (nanotubes), which differed in morphology and growth rate and were called type 1 and type 2 nanofilaments.

Type 1 nanofilaments and microfilaments are comparatively short (from a few micrometers to several tens of micrometers in length) and vary widely in diameter (from ~0.1 to 2.0 μm). They are tortuous, and some of them are shaped as a loop or a helix (Fig. 1). The growing end of some filaments has a cap. As a rule, this is evidence of a catalyst particle present there. Typically, filaments grow as bundles on large, 5- to 10-μm, catalyst particles. Smaller particles originate individual filaments. The growth rate of this type of filament ranges between 0.02 and 0.2 μm/s.

Nanofilaments of the second type are as long as 2–5 mm. Their diameter is below 100 nm and varies noticeably from one filament to another. Generally, the surface of such a filament is smooth and the filament itself is straight (Figs. 2a, 2b). The filaments are parallel to the substrate plate and are 20–200 μm from its surface. When the lower end of the filament is observable, it is found to lie on the substrate surface (possibly on a submicron-sized catalyst particle) or to be butted against a type 1 filament or a large catalyst particle. The other end of the filament is free. From the length of a type 2 nanofilament and from the duration of the run, we estimated the filament growth rate at 5–10 μm/s.

The morphological difference between the types of nanofilaments is clearly seen in Fig. 1b. The nanofilaments shown in Fig. 1b have nearly equal diameters. We have examined a large number of specimens using a scanning electron microscope and have found no type 2 filaments smaller than 30–50 nm in diameter.

The structure of nanofilaments was determined by the TEM examination of specimens grown at the edge of a silicon wafer. This technique made it possible to study carbon nanostructures without separating them from the holder. Using this technique, we precisely determined where the filament originates from and where the growing end is located. We found that there are no catalyst particles at the ends of a type 2 nanofilament. Gaining such information involves difficulties in focusing the electron beam on the soaring or vibrating filament end. In order to circumvent these difficulties and obtain high-resolution images, the pyrolysis products were transferred from the substrate onto a copper grid covered with a holey carbon film. HREM studies have demonstrated that type 1 filaments are tapered nanotubes or microtubes, which were earlier observed in many experiments. Their structure has been described in detail [1, 2, 5].

By contrast, type 2 nanofilaments have an unusual structure. They may be either true filaments (without a channel inside) or tubes with a narrow channel. The diameter of such a channel does not exceed 1/5 of the outer diameter of the tube (Fig. 2b). Focusing the electron beam on some area of a nanofilament without a channel (i.e., heating the filament) caused the filament skin to strain and bend (these areas are pointed with arrows in Fig. 2a). In a few seconds, the filament skin flaked off, resulting in discontinuities in the body of the filament (Fig. 2c). Later, the area exposed to electron radiation and heating showed no observable changes. It is interesting that no pattern due to graphitic planes is observed at the nanofilament tip (Fig. 2d), while this pattern is usually seen in an HREM image of a nanotube. The filament tip is tapered and bears no catalyst particle.

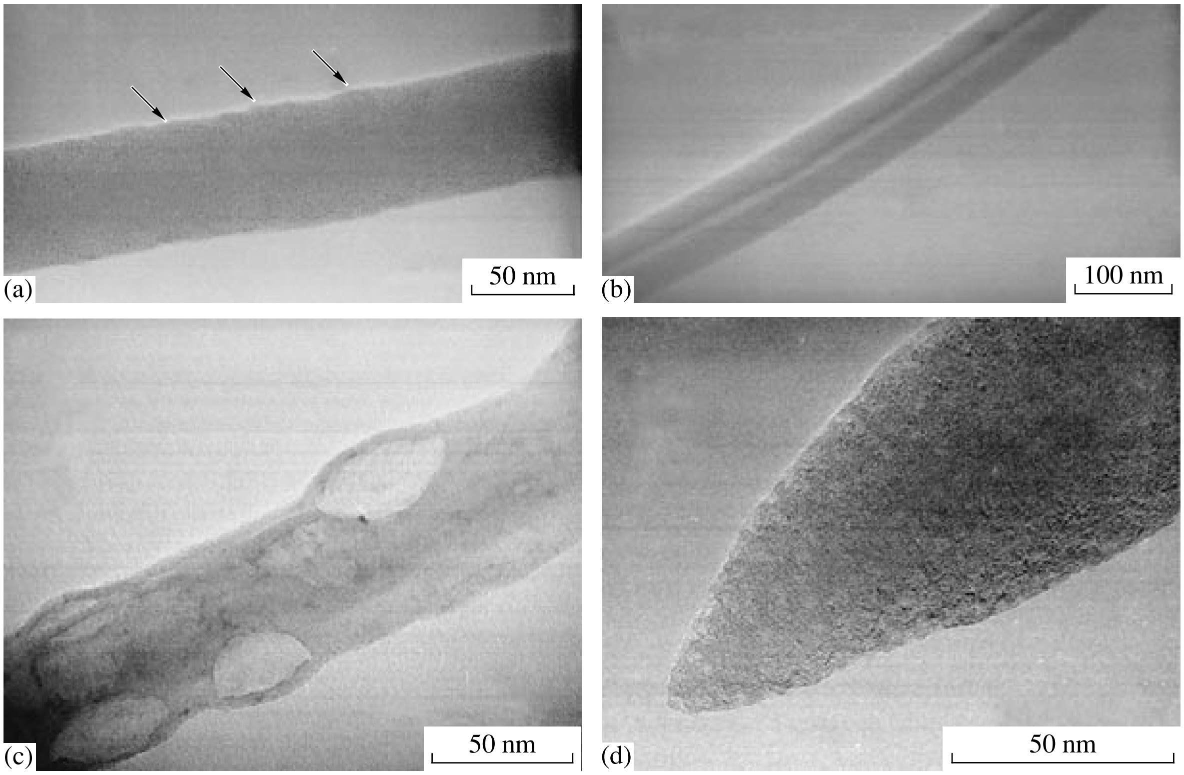

Fig. 2. TEM images of type 2 carbon nanofilaments: (a) filament having no internal channel, (b) filament with an internal cavity (nanotube), (c) nanofilament skin flaking off under the action of a focused electron beam, and (d) growing end of a nanofilament (no catalyst particle present).

Note that there is no clear knowledge of the conditions necessary for the formation of type 2 filaments, even though the pyrolysis process is described in sufficient detail (see EXPERIMENTAL). As a consequence, two successive pyrolysis runs carried out at strictly equal controlled parameters often resulted in essentially different yields of type 2 nanofilaments. In some cases, these filaments were not observed at all.

Pyrolysis under the same conditions and on the same substrates without a catalyst never resulted in filamentous carbon of type 1 or 2.

DISCUSSION

As is noted above, TEM studies have demonstrated that type 1 filaments are nanotubes or microtubes well known from the literature. Coaxially stacked graphitic cones forming the tube walls, a catalyst particle at the tip of the tube, and the observed growth rate—all these data suggest that type 1 filaments originate and grow by the familiar catalytic pyrolysis mechanism [1, 2]. According to this mechanism, the catalytic decomposition of hydrocarbons takes place on the exposed face of a particle. The resulting carbon atoms diffuse through the particle bulk or on the particle surface to the lateral faces of the catalyst particle, which are the place where graphitic layers nucleate and then grow to form the wall of a nanotube or the body of a filament. The growth rate of a carbon structure in this case is limited by the carbon diffusion rate. According to the literature, it does not exceed 0.1–0.2 μm/s [1, 2, 4]. The highest growth rate of type 1 tubes in our experiments is the same.

A radically different situation is observed in the formation of type 2 nanofilaments. They grow much more rapidly, their growth rate being almost two orders of magnitude higher than the theoretical growth rate for filaments (tubes) produced by catalytic pyrolysis. The filament is like a polymer, as judged from its behavior under the action of an electron beam. There is no catalyst particle at its tip. Therefore, the mechanism by which the type 2 filaments grow differs from the familiar catalytic growth mechanism.

Here, the following question arises: Can the noncatalytic growth of a carbon filament be so rapid? This question can be reformulated as follows: Can a solid phase grow so rapidly in the atmosphere of hydrocarbon pyrolysis products? Among the condensed carbon materials, soot is known to grow at the highest rate. This rate was most accurately measured in shock tubes. The mean diameter of soot particles was determined by TEM examination of the pyrolysis products. The duration of a run in a shock tube is no longer than 1–3 ms and is strictly limited by the arrival of an unloading wave, which abruptly terminates the particle growth. For a run duration of ~1.5 ms, the mean particle radius is 10–15 nm [6], from which the mean particle growth rate is estimated to be 7–10 μm/s. For a run duration of 3.2 ms, the mean particle radius is 8–20 nm [7], implying that the growth rate is 3–6 μm/s. Calculations in terms of the polyine model have demonstrated that the growth rate of a soot particle at the nucleation stage is 5–7 μm/s [8, 9]. This value is close to the highest growth rate that we measured for type 2 nanofilaments. Therefore, during the gas-phase pyrolysis of hydrocarbons near the soot formation threshold, such conditions are established that the formation of type 2 carbon filaments can be caused by the growth of coke deposits. For this to be the case, not only the gas-phase condition should be close to the soot formation threshold, but also the growth of the end of the carbon filament should be kinetically controlled, as in the case of a growing soot particle; that is, there must be know diffusion limitations. If diffusion is the limiting factor in the heterogeneous reaction, the growth rate of a coke film on the surface will be well below the growth rate of the soot particle [10] and, accordingly, well below the observed growth rate of a type 2 filament. Regarding the polymeric structure of such nanofilaments, note that it has been reliably established that the initial structure of the soot particles is also polymeric, with a low degree of aromaticity [11–13]. However, the soot turns rapidly into carbon containing traces of hydrogen.

If the high growth rate of type 2 filaments in hydrocarbon pyrolysis is explained by the special composition of the gas phase, then the following question will arise: Is it possible that the gas phase near the solid surface assumes such a structure that the coke film cannot grow uniformly throughout the solid/gas interface and forms individual filaments? This question is still open and requires further investigation.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 02-03-33335) and by MNTTs (grant no. 1024.2).

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