

CARBON NANOTUBE SYNTHESIS BY PYROLYSIS OF CH₄ OVER SiO₂/Si₃N₄/Fe/Mo CATALYST

Fursikov P.V.^(a), Volodin A.A.^(a), Khodos I.I.^(b), Kasumov Yu.A.^(b), Tarasov B.P.^(a)

^(a) Institute of Problems of Chemical Physics of RAS, 142432 Chernogolovka, Russia

^(b) Institute of Microelectronics Technology and High Purity Materials of RAS, 142432 Chernogolovka, Russia

* Tel: +7-096-5221743; Fax: +7-096-5155420; E-mail: btarasov@icp.ac.ru

Introduction

For pyrolytic synthesis of well-structured carbon nanotubes located on a flat substrate surface 3d-metal catalysts such as supported nano-sized metal particles or photolithographically obtained thin metal films [1] are widely used. When grown on selected sites such objects are very promising for molecular electronic purposes. In our previous works we showed that prepared by means of electron lithography SiO₂/Si₃N₄ supported Co islanded films could also be employed to synthesize single wall (SWNT) as well as multi wall (MWNT) carbon nanotubes [2].

It is also well known that Mo additives to the metals enhance the catalytic performance of such catalysts [3]. The present work has aimed to synthesize CNT using SiO₂/Si₃N₄ supported island film Fe/Mo catalyst by pyrolysis of methane and to study the influence of hydrogen gas phase admixtures to the quantity and structure of grown carbon nanotubes.

Experimental

Carbon nanotubes were synthesized by pyrolysis of methane in a gas flow reactor at ambient pressure in the 800–1000°C range. A methane flow rate was constant and equal to 150 mL/min in all experiments. Hydrogen was added to a methane flow. The rate of hydrogen supply was varied from 10 up to 50 mL/min. Duration of the pyrolysis was 20 minutes in all experiments.

The SiO₂/Si₃N₄/Fe/Mo catalyst was prepared using rf-sputtering technique [2]. The average thickness of Fe and Mo layers was 1 nm and 0.2 nm respectively. A catalyst containing plate was placed in the central zone of the reactor, which was then evacuated and filled with hydrogen. This procedure was repeated to remove undesirable gas admixtures, mainly oxygen. The reactor was fed with a required hydrogen flow prior to furnace heating. As soon as the working temperature was attained, the reactor was fed with methane. After completion of the synthesis the reactor was cooled down in a hydrogen flow.

Carbonaceous products of the pyrolysis were characterized by means of transmission (TEM), and scanning (SEM) electron microscopy.

A special attention was given to the effect of hydrogen content in the gas mixture on quantity and structure of nanotubes formed.

Results and discussion

At the temperature of 800°C nanofibers were formed along with SWNT, while at 1000°C only very small amount of tubes was formed, obviously because of rapid carbonization of the work surface of the catalyst. In the course of methane pyrolysis under given conditions the optimal temperature for the effective SWNT growth was 900°C (Figs.1–3).

Little variation of the flow rate of feeded hydrogen essentially influence the quantity of synthesized carbon nanotubes. At the content of hydrogen of 25v/v.% in the mixture nanotubes were formed in very few cases (Fig.1).

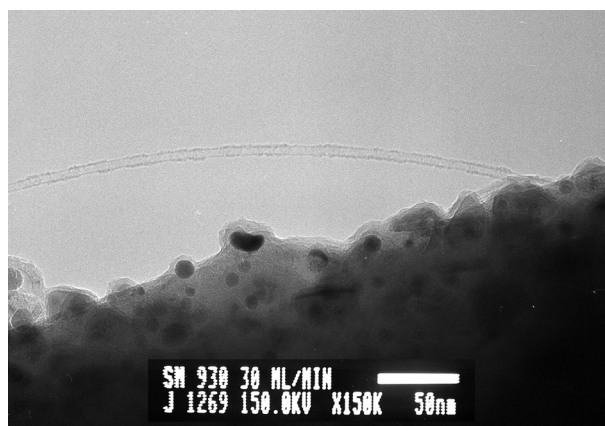


Fig.1. TEM micrograph of nanotubes in a sample prepared by pyrolysis of methane at 900°C, H₂ content is 25v/v.%.

This seems to be a result of that at such content of hydrogen, which reacts with almost all carbon formed on the catalytic surface, the equilibrium is strongly shifted to the formation of gas products. At lower hydrogen content (down to 21v/v.%) a greater number of SWNT is formed (Fig.2). However, with further decrease of the hydrogen content down to 17v/v.% MWNT and double-wall nanotubes were found in addition to SWNT (Figs.3, 4).

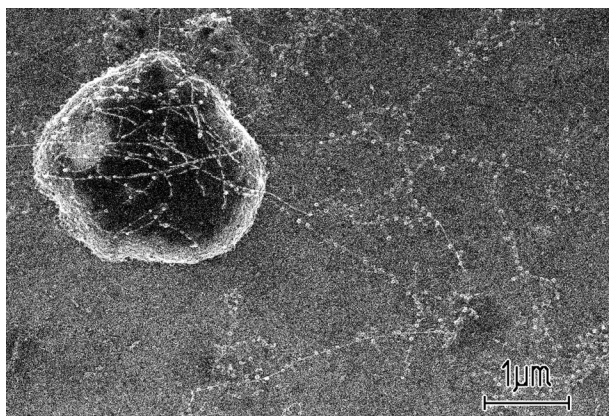


Fig.2. SEM micrograph of nanotubes in a sample prepared by pyrolysis of methane at 900°C, H₂ content is 21v/v.%.

The analysis of the temperature effect and the hydrogen content in the gas mixture on properties of formed carbon nanostructures allowed one to conclude that their nucleation and growth on the Fe/Mo catalyst followed the decomposition-diffusion-precipitation mechanism [4]. An initial hydrocarbon molecule undergoes decomposition on one of the surfaces of a Fe particle when H atoms are subsequently detached from chemisorbed CH_m species. Then carbon atoms diffuse toward another surface where carbon precipitates and carbon nanotubes grow. The following condition is to be fulfilled for their efficient growth: the rate of carbon precipitation (v_{prec}) is to be higher than that of carbon supply from the gas phase (v_{sup}). If $v_{\text{prec}} < v_{\text{sup}}$, the catalytic surface will be coked that leads to terminating the growth of carbon nanotubes.

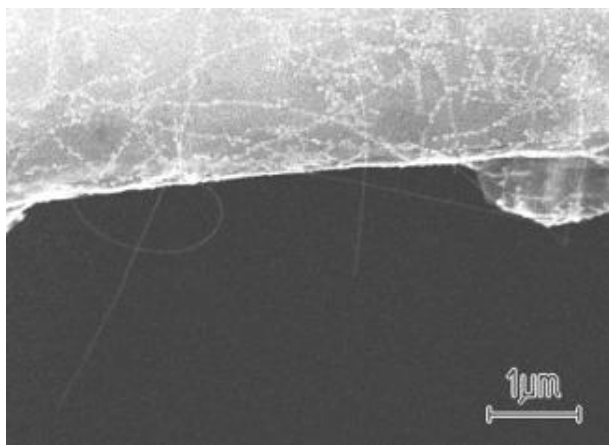


Fig.3. SEM micrograph of nanotubes in a sample prepared by pyrolysis of methane at 900°C, H₂ content is 17v/v.%.

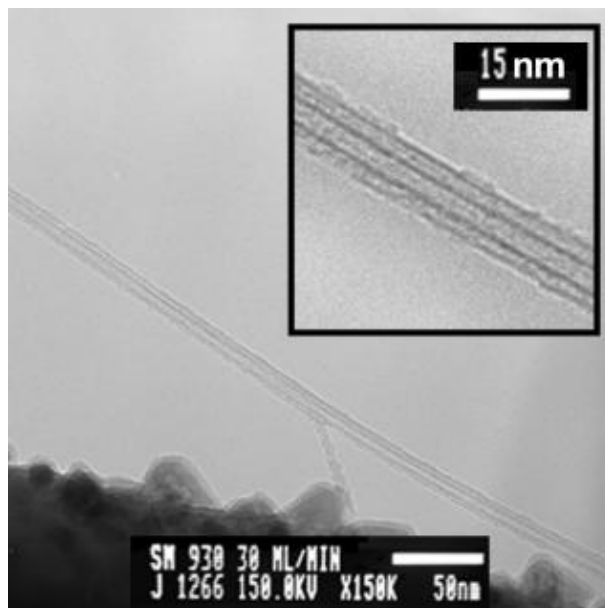


Fig.4. TEM image of a nanotube in the sample prepared by pyrolysis of methane at 900°C, H₂ content is 17v/v.%.

To summarize, the presence of Mo in a bimetallic catalyst allows the reaction of hydrocarbon decomposition to be realized at lower temperatures, and the use of hydrogen to lower the coking rate of catalytic surface becomes more efficient.

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