

INFLUENCE OF OXYGEN CONTAINING ADDITIVES TO ETHYLENE ON CATALYTIC SYNTHESIS OF CARBON NANOFIBERS

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Introduction

During the last years a set of carbonaceous compounds used for synthesis of carbon nanostructures (CNS) has noticeably grown. Feeding various additives in the reaction zone may lead to a change in both the yield of target product and structure of carbon filaments. For example, if sulfur is fed in the reaction zone double walled nanotubes may be mainly produced [1], a little amount (250 ppm) of phosphor gives carbon nanofibers (CNF) with the length of 6 cm [2], addition of CH_2Cl_2 to acetylene leads to the formation of bamboo-like nanotubes [3]. Helix-like nanotubes were synthesized by the pyrolysis of diethyl ether over zinc catalyst [4]. Feeding various additives changes not only the structure and the yield of carbon nanostructures but also their properties. For example, the paper [5] reported synthesis of nanotubes with big amount of SO_3H -groups, which reveal both the electron and proton conductivities. Thus the mere little feeding various additives in the reaction zone may influence the yield, structure and the properties of carbon nanostructures.

In the present work we studied the influence of gaseous oxygen containing additives to ethylene on the yield and the structure of the formed carbon nanofibers.

Experimental

MgO was used as a support for the catalysts. The catalysts were deposited on the surface of the support by precipitation of Ni from its aqueous solution $\text{Ni}(\text{NO}_3)_2$ followed by air drying at 150°C for half an hour and subsequent reduction to the metal just in the ethylene pyrolysis. Elemental analysis evidenced the contents of the deposited catalyst was 5% Ni/MgO.

The catalytic pyrolysis of ethylene was performed in a horizontal flow gas quartz reactor at atmosphere pressure and in the temperature range of $500\text{--}700^\circ\text{C}$. During the pyrolysis a gas mixture of the ratio $\text{C}_2\text{H}_4:\text{H}_2:\text{Ar} = 1.5:3:1$ was used. Gaseous additives were fed in the reaction zone by passing an argon flow through a bubbler filled with a liquid substance chosen from the set H_2O , $\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_2\text{SO}_4$, $(\text{CH}_3\text{O})_3\text{P}$ or $(\text{CH}_3\text{O})_3\text{B}$. Products of the synthesis were purified from MgO

and Ni by ultrasound treatment in the concentrated hydrochloric acid at 70°C for one hour and a half.

Results and discussion

Mass spectra of the initial gas mixture of the ratio $\text{C}_2\text{H}_4:\text{H}_2:\text{Ar} = 1.5:3:1$ revealed the peaks $m/z = 24, 25, 26, 27, 28, 29$ with the maximum at $m/z = 28$ ($[\text{C}_2\text{H}_4]^+$), as well as the peak at $m/z = 2$ ($[\text{H}_2]^+$). Gas reaction products have the peaks at $m/z = 12, 13, 14, 15, 16, 17$ with the maximum at $m/z = 16$ ($[\text{CH}_4]^+$). The peaks at $[\text{Ar}]^+$ and $[\text{Ar}]^{2+}$ corresponding to $m/z = 40$ and $m/z = 20$ are also present.

The data obtained allow one to make an assumption that the following reactions take place in the reaction zone:

- (1) $\text{H}_2\text{C}=\text{CH}_2 \rightarrow 2\text{C} + 2\text{H}_2$
- (2) $\text{H}_2\text{C}=\text{CH}_2 \rightarrow \text{C} + \text{CH}_4$
- (3) $\text{H}_2\text{C}=\text{CH}_2 + 2\text{H}_2 \rightarrow 2\text{CH}_4$
- (4) $\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2 \rightarrow \text{H}_3\text{C}-\text{CH}_3$

When ethanol vapors are fed in the reaction zone additional groups of peaks occur with the maxima at $m/z = 31$ and 45 , that is peculiar to the spectra of ethanol (Fig. 1). The mass spectra of the pyrolysis products had the peaks with the maximum at $m/z = 16$ corresponding to $[\text{CH}_4]^+$. In addition to that the peak at $m/z = 28$ occurred, which might correspond to the non-reacted $[\text{C}_2\text{H}_4]^+$ and the formed $[\text{CO}]^+$, as well as the peak at $m/z = 44$ corresponding to $[\text{CO}_2]^+$. The following additional reactions are feasible during the pyrolysis:

- (5) $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2$
- (6) $2\text{CO} \rightarrow \text{C} + \text{CO}_2$

When $(\text{CH}_3\text{O})_3\text{P}$ vapors are fed at 20°C the mass spectra of the products have only main peaks at $m/z = 40$ ($[\text{Ar}]^+$), $m/z = 28$ ($[\text{C}_2\text{H}_4]^+$), and $m/z = 2$ ($[\text{H}_2]^+$), while at 50°C – additional peak being present at $m/z = 79$, which corresponds to the $[\text{CH}_3\text{OPOH}]^+$ ion. Traces of $(\text{CH}_3\text{O})_3\text{P}$ were not found in the reaction products.

Transmission electron microscopy (TEM) data evidence that the mere little amounts of gaseous additives fed in the reaction zone leads to significant change of the structure of the formed CNF. For example, during the synthesis without additives we produced nanofibers with the

diameters varied within the large (10–40 nm) range.

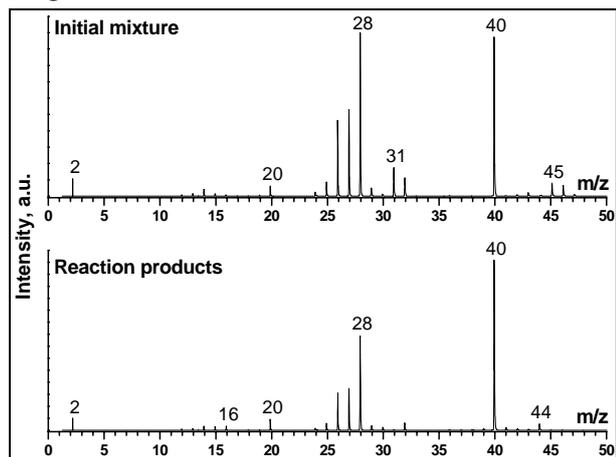


Fig. 1. Mass spectra of the initial gas mixture at with C_2H_5OH vapors and the pyrolysis products.

The thinnest nanofibers having narrow distribution in the diameters (10–15 nm) were synthesized when the vapors $(CH_3)_2SO_4$ and $(CH_3O)_3P$ were fed in the reaction zone (рис. 2). At this feeding the vapors of $(CH_3)_2SO_4$ led to overall decrease in the yield of carbonaceous products. The presence of sulfur is apparently to favor quick carbonization of the working surface of the catalyst.

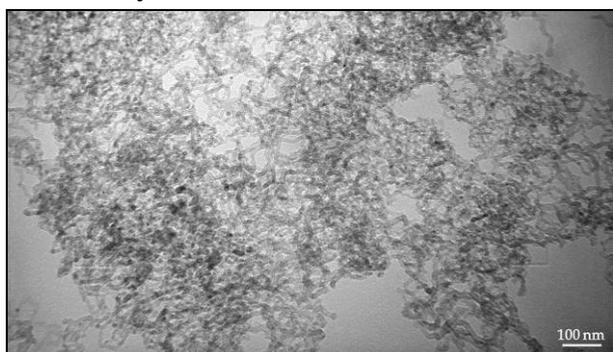


Fig. 2. TEM image of the pyrolysis products at feeding $(CH_3O)_3P$ vapors.

The presence of the vapors of water and ethanol in the gas mixture had the similar effect on the yield and composition of the solid carbonaceous products. The synthesized fibers had highly defected structure of the walls. The diameter of these fibers varied within the range of 10–20 nm, and the channel diameter was within the range of 3–5 nm. Sometimes the inner channel was absent.

Feeding the vapors of $(CH_3O)_3B$ in the system led to the formation of thicker fibers with diameters of 15–30 nm and inner channel diameters of 5–15 nm (Fig. 3). Along with the nanofibers very big structures were formed with the outer diameter up to 250 nm the inner channel – up to 150 nm.

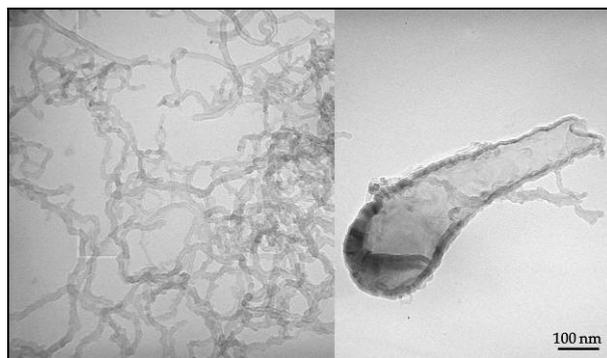


Fig. 3. TEM image of the pyrolysis products at feeding $(CH_3O)_3B$ vapors.

The data of elemental analysis evidenced that the contents of sulfur in the carbonaceous products of the pyrolysis conducted at the feeding of $(CH_3)_2SO_4$ was 5.3 mass. %, and the hydrogen content was the largest in the fibers synthesized when the vapor additives (1.5%) of water and ethanol were fed. In the other cases the hydrogen contents was less than one per cent.

Conclusions

Feeding oxygen containing additives to the process of catalytic pyrolysis of ethylene allows one to vary the structure of CNF that is of importance for organizing direct synthesis of various types of carbon nanostructures.

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