CATALYST NATURE INFLUENCE ON THE CARBON NANOTUBES PROPERTIES AND CHARACTER OF SYNTHESIS FROM ETHANOL VAPOR

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Introduction

Applicability of ethanol for the catalytic synthesis of carbon single- double- and multiwalls nanotubes and nanofibers was demonstrated in number of publications [1-5]. Several advantages of catalytic CVD process with ethanol vapor were noted. These are high selectivity, the possibility of obtaining of the single wall nanotubes without impurities of another carbon forms, relatively low synthesis temperature. However information about catalyst nature influence both on character of the process of CNT synthesis from ethanol vapor and properties of products obtained is practically absent in literature. At the same time these data are needed for practical application of carbon nanomaterials and selection of optimal conditions of its production. In this connection the purpose of this work was investigations in details of process of the catalytic pyrolisis of ethanol vapor with various Fe-group catalysts and examination of synthesis products.

Results and discussion

Experiments were carried out in a flow-type quartz reactor fitted with an ethanol flow controller. The reaction mixture was heated by an external electric tubular furnace. Ethanol (96%) and ethanol-water mixtures of various concentrations were used as reactants. Experiments were carried out at atmospheric pressure. The catalytic pyrolisis was carried out without transport gas. Ethanol was introduced in the reactor through thin ceramic tube. The flow rate of liquid reagent was varied from 1 to 30 ml/h. Catalytic support material was prepared by procedure devised in our laboratory [5]. The silica "paper" thus produced consisted of thin walls silica microtubes. It was impregnated with nickel, cobalt or iron nitrate solution and dried on air. These materials were used as the pro-catalyst. The nitrates decomposition took place in the reactor just before CNT catalytic deposition or earlier.

Obtained results demonstrated the nature of catalyst influence on both kinetic character of the process of ethanol vapor pyrolisis and properties of the CNT produced.

Fig. 1 shows relations which characterizes catalytic activity of nickel, cobalt and iron catalysts in the process of ethanol vapor pyrolisis. In this case catalytic activity was estimated as ability of the smallest mass of catalyst to converse into the product the biggest amount of reagent per time unit. Relations between extent of ethanol transformation into solid carbon product and ethanol flow divided on the catalyst mass are shown in fig.1.

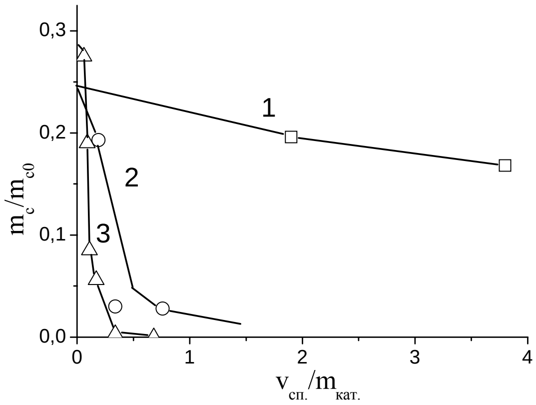

Fig.1. Relations between yield of CNTs and ethanol flow divided on the catalyst mass (ml/h*mg).

Catalyst: 1 – Ni; 2 – Co; 3 – Fe.T = 530^{0}C

Evidently that nickel has maximum catalytic activity. Increase of ethanol flow rate leads to slight decrease of extent of ethanol transformation into CNT. But the process rate increases also.

In the case of cobalt and iron situations have principal difference. In both cases the increase of ethanol flow rate brings to depression of the catalysis process rate. And higher definite flow rate process of solid carbon product deposition is stopped completely. Hereby processes of CNT deposition on cobalt and iron catalysts can be carried out with very small ethanol flow rate only.

Due to this fact we considered for a long time that it is impossible to produce CNTs from ethanol on Co and Fe catalysts with good output. However, keeping definite conditions these catalysts may be used successfully for CNTs large amount synthesis from ethanol vapor.

Fig. 1. shows that the limit of yield of carbon nanomaterial on the nickel catalyst approaches to 0,25. This fact agrees with step-like mechanism of ethanol pyrolisis which was proposed earlier [5]:

$C_2H_5OH = C_2H_4O + H_2,$ (1)
$C_2H_4O = CO + CH_4,$ (2)
$2CO = C + CO_2.$ (3)

In agreement with this scheme only quarter of carbon containing in ethanol may be released as solid product. At the same time if iron catalyst is used this value can achieve 0,3. Thus character of process with iron catalyst is changed. This fact is confirmed by IR spectra of exhaust gas mixture.

Another feature of iron catalyst is absence of phenomenon of catalytic activity loss during pyrolisis process. As result, in contrast with process on nickel and cobalt catalysts, process of CNTs deposition can be in progress for long time (tens of hours) with constant rate (fig. 2).

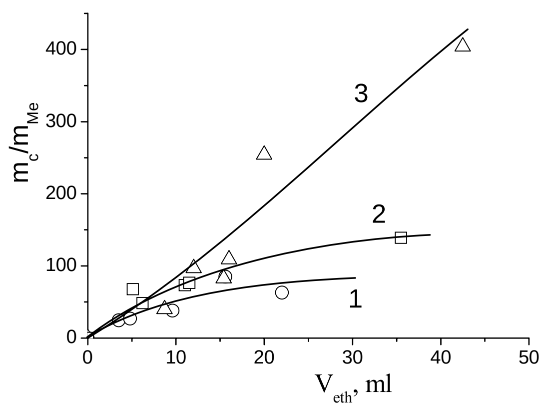

Fig.2. Kinetics of carbon nanomaterial deposition. Dependence of relative mass growth on the ethanol consumption.

Catalyst: 1 –Co; 2 – Ni; 3 – Fe. T = 530^{0}C

Samples of CNTs obtained from ethanol vapor with employment of different catalysts were characterized with methods of electron microscopy, IR- and Raman spectroscopy, thermogravimetry. The specific surfaces of the materials were determined. Investigation of oxidative modification of surface of the materials by high temperature treatment in concentrated nitric acid was carried out. Sorption characteristics of modified materials were examined against heavy metals cations.

It was established that properties of CNTs synthesized with different catalyst differ in great extent. This fact also confirms conclusion about great influence of catalyst nature on the ethanol pyrolisis character and properties of synthesized CNTs.

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