CATALYTIC SYNTHESIS OF CARBON NANOMATERIALS FROM ETHANOL VAPOR

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Introduction

A number of recent scientific papers consider ethanol as promising reagent for synthesis of carbon nanotubes [1-4]. 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. At present work we investigated particularities of catalytic pyrolysis of the ethanol vapor and characteristics of the process of carbon fibrous nanomaterials synthesis.

Results and discussion

Tubular quartz reactor with system of alcohol control supply was used. Reaction mixture was heated by external electric furnace. Liquid ethanol flow was 1- 0,25 ml/min. Argon served as transport gas. Ar flow was 10 – 100 ml/min in different experiments. Experiments were carried out at normal and at low (0,1 bar) pressure. Nickel was used as catalyst.

Catalytic material was prepared by own developed method. Base of catalyst was ashless filter paper treated by tetraethoxysilane and water vapor. Further species were heated on air at 700^0C for 2 h. Obtained "paper" consisted on thin walls silica microtubes. It was soaked by the nickel nitrate solution and annealed at 600^0C for 1 h. Prepared catalytic material has high specific area and good gas permeability. Samples with 10 and 25 mass % of NiO were explored in our experiments. Composition of gas mixture was controlled by IR spectroscopy during pyrolisis. Arbitrary deposition rate of carbon nanomaterials was valued as an increase in catalyst substrate mass per time unit.

Obtained results demonstrated a number of unusual features of the process of CNT catalytic synthesis from ethanol vapor. It was found that carbon nanofibrous material starts to grow at temperature higher than 400^0C. Rate of deposition increases sharply with temperature rise and achieves maximum at 550^0C.

At this temperature 70-times (7000%) products output (for catalyst mass) can be obtained at normal pressure for 30 min. Further temperature growth leads to the products output reduction (for 5–10 times at 750^0C). Below 750^0C process goes strictly selectively. No carbon deposition occurs on the reactor walls and on the control substrate without catalyst. At the temperature higher 750^0C deposition rate of the carbon nanomaterial slightly increases. But side nonselective process of pyrolysis takes place.

Another feature of CNT synthesis from ethanol is unusual dependency of the product deposition rate on substrate place inside the reactor. When the flows of alcohol and argon are small maximum output of the product is on the substrate near the reactor entry. Mass of the deposits gradually decreases on the substrates located deeper. Such behavior can be connected with exhaustion of gaseous reaction mixture. Nevertheless the products output on substrates at the beginning part of the reactor became smaller when alcohol flow rises. Maximum outputs of the product are on the substrates located in the center and the end of reactor. The same phenomenon is observed when argon flow rises.

At low pressure (0,1 bar) the process keeps described features but the rate of deposition decreases greatly.

To explain results obtained we analyzed IR spectra of the reactor's exhaust gases at the conditions provided maximum product output. Flow rate of the ethanol as well as quantity and location of the catalytic material in the reactor was varied. It was found that ethanol vapor practically don't change when pass through reactor without catalyst. If the catalyst locate near the reactor entry and flows of the ethanol and argon are high IR spectrum of exhaust gases except absorption bands of ethanol has the band at 1725 cm^{-1} refering to aldehydes, double band at 2140 cm^{-1} belonging to carbon monoxide and very sharp picks at 3020 and 1305 cm^{-1} of methane [5]. When the alcohol flow is small and the reactor fill with catalyst for full length intensive additional absorption band of carbon dioxide at 2350 cm^{-1} appears in the spectrum.

Obtained results demonstrate that ethanol molecules in the course of catalytic pyrolysis have a number of conversions in accordance with chemical reactions (1-5).

$$C_2H_5OH = CH_2O + CH_4 \quad (1)$$
$$C_2H_5OH = C_2H_4O + H_2 \quad (2)$$
$$CH_2O = CO + H_2 \quad (3)$$
$$C_2H_4O = CO + CH_4 \quad (4)$$
$$2CO = C + CO_2 \quad (5)$$

Probably methane doesn't participate in the process of carbon nanomaterial deposition at temperature below 750^0C. On the other hand presence of carbon dioxide in exhaust gases is solid sign of the reaction of CO disproportionation (5). It is known that nickel is effective catalyst of this reaction.

So, the reaction of carbon monoxide disproportionation (5) probably determines characteristics of the process of carbon nanomaterials synthesis from ethanol vapor, such as low temperature of the process, high selectivity and other.

Products of synthesis were tested by methods of electron microscopy, Raman spectroscopy, DTA etc. It was demonstrated that carbon nanofibers with diameter 50 – 80 nm and narrower and nanotubes can be synthesized. General trend is following: more perfect structure forms at low pressure and growth rate. Methods of catalyst preparation and preliminary treatment play essential role also.

Conclusions

It was found that ethanol molecules in the course of catalytic pyrolysis decomposed with formation a number of more simple substances. At the temperature below 750^0C reaction of carbon disproportionation is responsible for the carbon nanomaterials formation. Products of synthesis depending on conditions are carbon nanofibers with various diameter and nanotubes.

References

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