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ROLE OF CATALYST SUPPORT (CS) IN THE GROWTH OF MULTI-WALLED CARBON NANOTUBES (MWCNTS)

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Since the first observation of carbon nanotubes in 1991, their synthesis by different techniques has been extensively investigated. Several production methods have been developed aiming at the production of carbon nanotubes (CNT). Main methods are laser vaporization, electric arc discharge and catalytic chemical deposition of hydrocarbons over metal catalysts (CCVD technique). This paper describes how to produce multiwalled carbon nanotubes (MWCNTs) in pilot plant by CCVD technique. The aim of this investigation was to decide the intervals of reaction parameters with the most effective catalyst support on a large scale. The products were analysed by transmission electron microscopy (TEM). Analysis has shown the diameter and length of carbon nanotubes.

Key words: multi-walled carbon nanotubes, synthesis, CCVD technique, large scale production

Introduction

Carbon nanotubes (CNTs) were discovered in the soot of arch discharge by Iijima in 1991 [1]. Carbon nanotubes are allotropes of carbon and members of the fullerene structural family. Nanotubes are categorized as single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs) (*Fig. 1*). MWCNTs consist in a variable number of graphene sheets rolled coaxially into a cylinder of nanometric diameter [2]. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 0,34 nm. Typical diameter of MWCNTs are 10…20 nm typical length is above 20 μm.

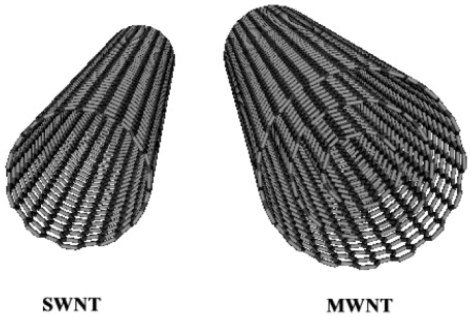

Figure 1: SWCNT and MWCNT

Nowadays carbon nanotubes are one of the most actively investigated materials. CNTs are the most promising of all nanomaterials due to their unique electronic and mechanical properties which ensure themselves to a variety of applications, such as field-emission displays [3], nanoscale sensors [4], nano-structured composite materials [5].

Several production methods have been developed aiming at the production of carbon nanotubes in large scale, such as laser vaporization [6], electric arc discharge [7] and catalytic chemical vapor deposition of hydrocarbons over metal catalysts (CCVD technique) [8]. The first two methods are high temperature processes and can produce high quality nanotubes. However, the yields are poor and hence not adaptable for large-scale production. In contrast CCVD technique is a very efficient method to produce multi-walled carbon nanotubes (MWCNTs) because this way could be a possibility to produce nanotubes at relatively low temperatures on a large scale at relatively low cost. This method is the most promising method to commercialize the carbon nanotubes growth.

In CCVD method transition metals (Fe, Co or Ni) supported on oxides, zeolite or silica are used as catalyst precursor [9]. The combinations of transition metals and supports can be changed depending on the characteristics required, for example the size of the tubes.

Bimetallic combinations of these transition metals are used for the synthesis of CNTs and the relatively high yield and quality have been explained by characteristic behaviour of this alloy phase [10]. A very effective catalyst is a binary mixture Co-Fe. Catalysts have been prepared by impregnation method using salts of Fe and Co.

Recently, several papers dealt with the mechanism of the formation of nanotubes. Particularly the role of the catalyst support and the particle size of the metal have been discussed. The most frequently used catalyst support are silica, zeolites and oxides. The role of the

catalyst support is a difficult problem. Reaction is influenced by interaction between the metal particle and the catalyst support [11]. If the interaction is strong, a metal particle does not budge from catalyst support. If the interaction is weak, a metal particle budge from catalyst support and growing of the tube starts from this point. Due to weak interaction high quality and yield can be obtained [12].

During our investigation MWCNTs were produced in a pilot scale equipment by CCVD technique. The aim of our investigation was to decide the intervals of the reaction parameters with the most effective catalyst support on a large scale.

Experimental

Catalyst and chemicals

Catalysts have been prepared by University of Szeged, Department of Applied and Enviromental Chemistry. Bimetallic catalysts (Fe and Co) were used with different supports (oxides, silicates). Co-acetate and Fe-acetate were impregnated in 2-5 w/w % on different supports. Salts of Fe and Co were obtained from Sigma-Aldrich. Reaction conditions were reductive in this way Co- and Fe-acetat can reduce.

As for the carbon source, a simple hydrocarbon (ethylene) was used. Ethylene and nitrogen (as carrier gas) were obtained from Messer.

Synthesis of carbon nanotubes

Simple hydrocarbons were decomposed in a catalytic reaction.

$$C_nH_k \rightarrow n\,C + k/2\,H_2$$

The scheme of pilot plant can be seen on *Fig. 2*.

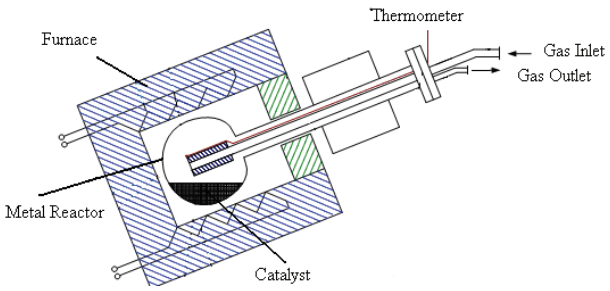

Figure 2: Scheme of pilot plant

After placing the catalyst (5-10 g) in metal reactor (5 dm^3), the temperature was increased to 700 °C. During rising of temperature, carrier gas (nitrogen) flow was maintained through the reactor at the rate of 50 l/h. After reaching desired temperature hydrocarbon (ethylene) was introduced into the reactor at the rates of 10…40 l/h for 60…120 min. Reaction parameters can be found on *Table 1*.

Table 1: Reaction parameters

Reaction temperature	700 °C
Reaction time	60…120 min
Amount of catalyst	5…10 g
Flow rate of hydrocarbon	10…40 l/h
Flow rate of carrier gas	10…40 l/h

In our experiments the support material of catalyst, flow rates of ethylene and flow rates of carrier gas are the variable parameters for the controlled production of MWCNTs because the morphology and the quality of carbon nanotubes depend on these parameters. The main parameters (reaction temperature, amount of catalyst, type of catalyst, type of hydrocarbons) were constant because these parameters were optimized in the course of preliminary research.

The aim of our investigation was to decide the intervals of the reaction parameters with the most effective catalyst support on a large-scale.

Analysis

The products were analysed by transmission electron microscopy (TEM). Analysis has shown the diameter and length of carbon nanotubes.

Outlet gas were analysed by gas chromatography system (GC). We followed up the hydrogen content of the outlet gas by GC therefore the end of the reaction and amount of formed hydrogen can be determined.

Results and discussion

Ethylene was decomposed in a catalytic reaction. Formed carbon was analysed by TEM and amount of formed hydrogen was analysed by GC.

Different experimental conditions (catalyst supports, C_2H_4 flow rate, N_2 flow rate, reaction time) and results (diameter and length of tubes, density, conversion) are given on *Table 2*. Reaction temperature, type of catalyst, type of hydrocarbon were constant because these parameters were optimized in the course of preliminary research. The reaction temperature was 700 °C, bimetallic catalyst (Fe and Co) were used, source of carbon was ethylene. Two different catalist support (A and B) were used in our experiments.

Conversion was calculated from amount of formed carbon and amount of formed hydrogen. These are equal. When support „A" was used, conversion was usually more than 70% in comparison with if support „B" was used conversion was fewer than 35%.

Density is a good indicator of quality of tubes and selectivity. Carbon nanotubes have a very low density (~20 kg/m^3) in contrast to other modifications of carbon (e.g. graphite: ~2200 kg/m^3, active carbon 300…600 kg/m^3). Density was about 17 kg/m^3 in presence of support „A" and about 80 kg/m^3 in presence of support „B". When support „B" was used a lot of amorphus carbon was formed (it can be seen from TEM analysis).

Hydrogen content of the outlet gas was followed up. It could be seen from *Fig. 3*, *Fig. 4* and *Fig. 5* higher hydrogen contents were achieved when support „A" was used. When support „B" was used the reactions were finished sooner and hydrogen contents were lower than in presence of support „A".

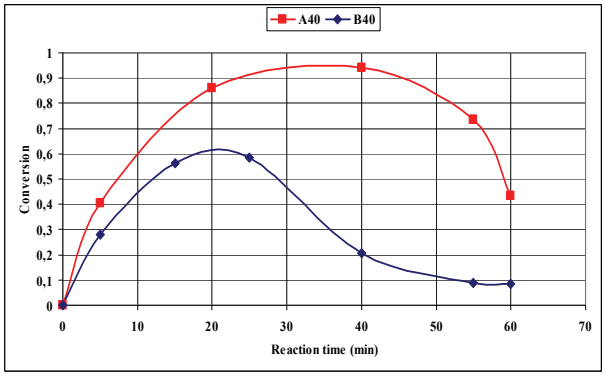

Figure 3: Hydrogen content of the outlet gas (A40: support „A", C_2H_4 flow rate 40 l/h; B40: support „B", C_2H_4 flow rate 40 l/h)

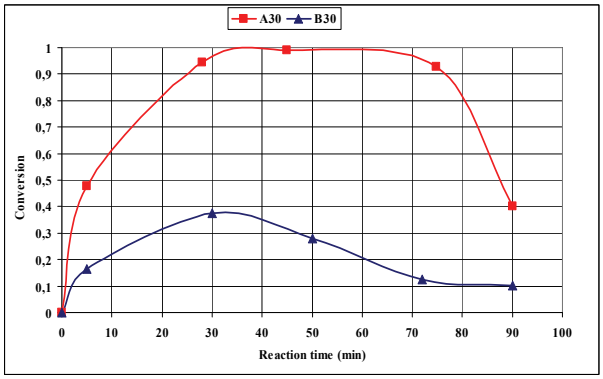

Figure 4: Hydrogen content of the outlet gas (A30: support „A", C_2H_4 flow rate 30 l/h; B30: support „B", C_2H_4 flow rate 30 l/h)

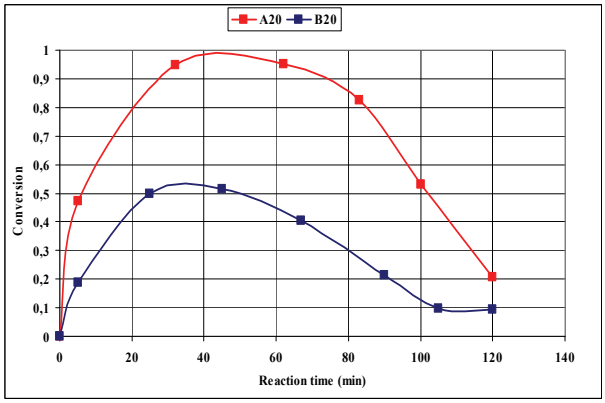

Figure 5: Hydrogen content of the outlet gas (A20: support „A", C_2H_4 flow rate 20 l/h; B20: support „B", C_2H_4 flow rate 20 l/h)

The best results were recieved in presence of „A" catalyst support. The main parameters were optimized in the course of preliminary research. Change of C_2H_4 flow rate and reaction time does not influence significantly quality of the formed MWCNTs but conversion is influenced by them. Highest conversion has been obtained when C_2H_4 flow rate was 30 l/h and reaction time was 90 min. As long as these determined parameters are used high quality MWCNTs can be produced and high conversion (85%) can be reached.

Diameter and length of tubes were determined from TEM analysis *(Fig. 6* and *Fig. 7)*. Similar results were achieved in all reactions in presence of support „A" as far as the quality of the tubes is concerned. The formed carbon nanotubes can be seen on Fig. 6. The quality of the formed tubes in a batch was more uniform. Diameter of tubes changed from 10 nm to 20 nm. Length of tubes was usually longer than 30 µm. In contrast, when support „B" was used (Fig. 7) diameter and length of tubes were variable. Diameter of tubes changed from 10 nm to 100 nm and length of tubes was shorter than 10 µm.

Table. 2: Experimental conditions and results

catalyst support	C_2H_4 flow rate (l/h)	N_2 flow rate (l/h)	reaction time (min)	diameter of tubes (nm)	length of tubes (µm)	density (kg/m^3)	conversion (%)
A	20	40	120	10…20	10…40	17	72
A	30	30	90	10…20	10…40	16	85
A	40	20	60	10…20	10…40	18	77
B	20	40	120	10…100	1…20	74	33
B	30	30	90	10…100	1…20	83	28
B	40	20	60	10…100	1…20	75	31

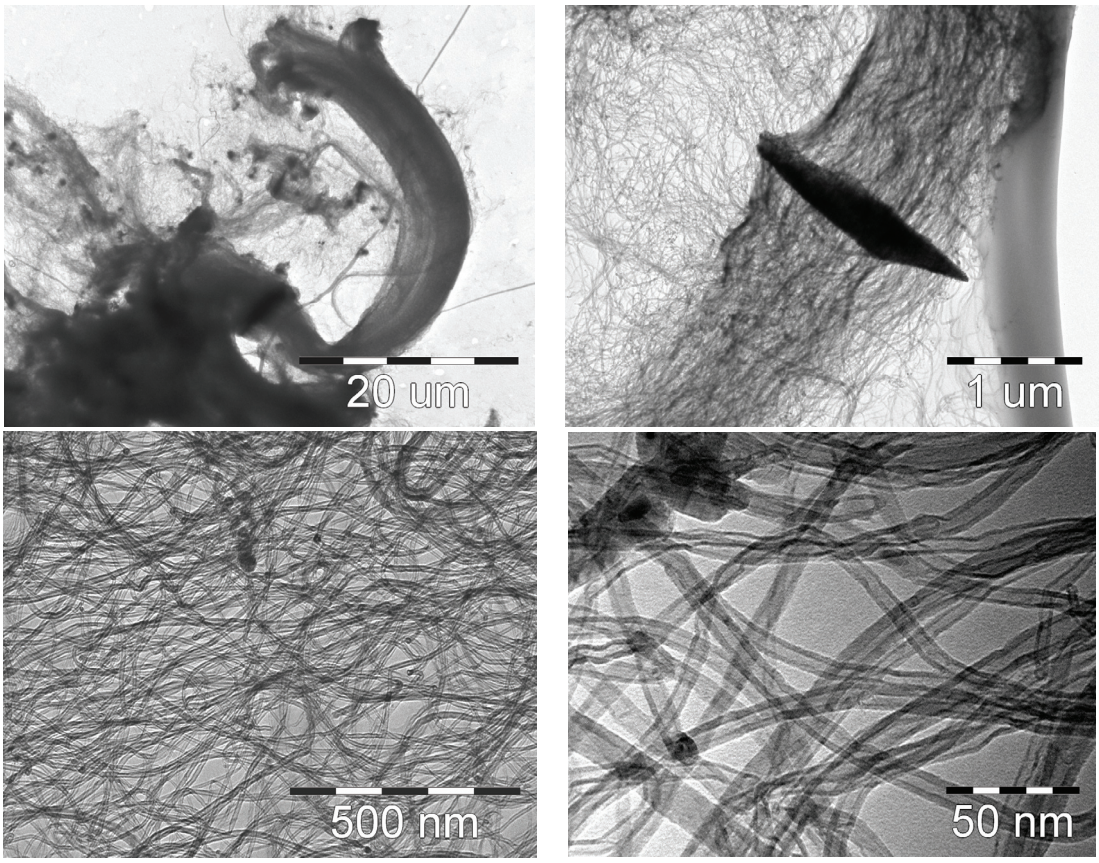

Figure 6: TEM images of MWCNTs produced by support „A”

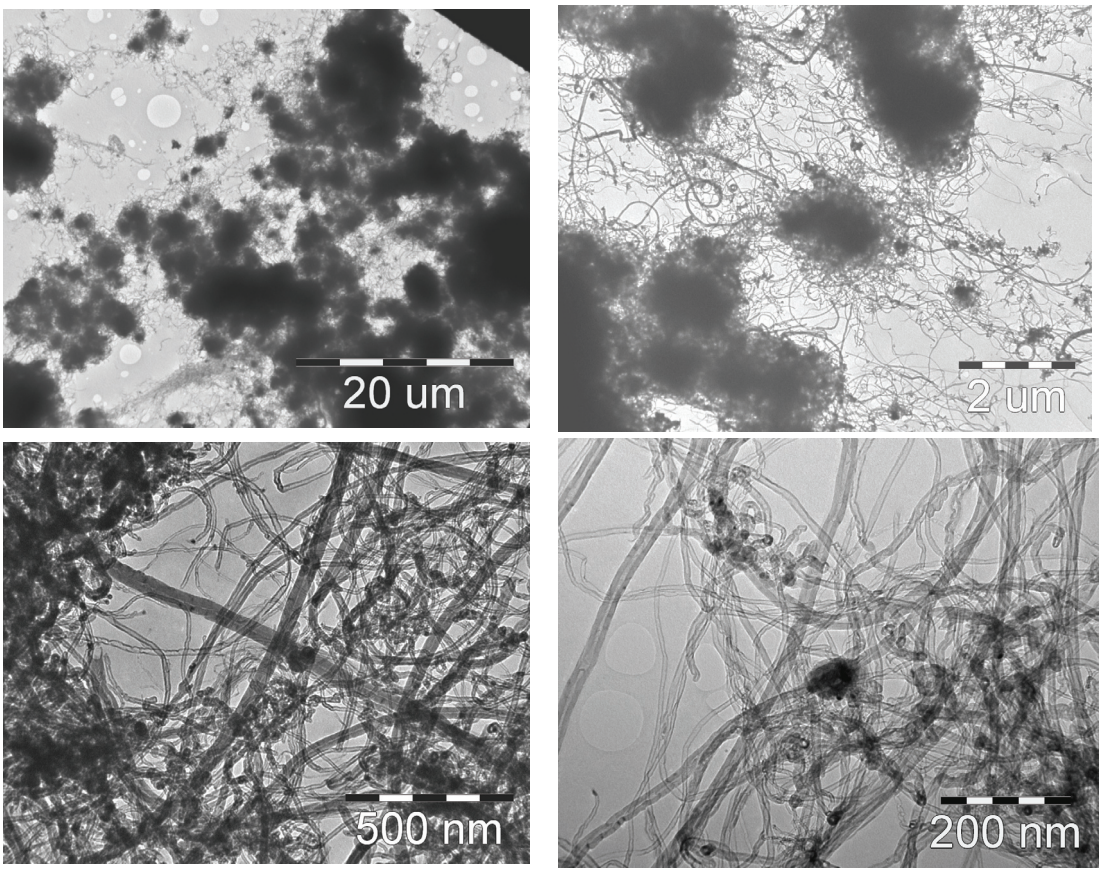

Figure 7: TEM images of MWCNTs produced by support „B”

The best results were recieved in presence of „A" catalyst support. The main parameters were optimized in the course of preliminary research. Change of C_2H_4 flow rate and reaction time does not influence significantly quality of the formed MWCNTs but conversion is influenced by them. Highest conversion has been obtained when C_2H_4 flow rate was 30 l/h and reaction time was 90 min. As long as these determined parameters are used high quality MWCNTs can be produced and high conversion (85%) can be reached.

In one batch 50 g multi-walled carbon nanotubes can be produced in pilot plant. Density of this product is 16 kg/m^3, diameter and lenght of tubes are almost uniform, diameter of tubes are between 10 and 20 nm and length of tubes are more than 30 μm.

Conclusion

Using the parameters determined in this study high quality MWCNTs can be produced and high conversion (85%) can be reached. In one batch 50 g multi-walled carbon nanotubes can be produced in the pilot plant. Density of this product is 16 kg/m^3, diameter and lenght of tubes are constant, diameter of tubes are between 10 and 20 nm and length of tubes are more than 30 μm.

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