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Synthesis of Porous Carbon Material and Its Use for Growing Carbon Nanotubes

Nazhipkyzy M.[1,2,*], Temirgaliyeva T.[1.2], Zhaparova A.A.[1.2], Nurgain A.[1.2], Lesbayev B.T.[1.2], Mansurov Z.A.[1,2], Prikhodko N.G.[1]

[1]Institute of Combustion Problems, The laboratory "Synthesis of carbon nanomaterials in flame", Bogenbay Batyr str., 172, 050012, Almaty, the Republic of Kazakhstan

[2]Al-Farabi Kazakh National University, Faculty of chemistry and chemical technology, Department of chemical physics and material science, al-Farabi avenue 71, 050038, Almaty,

The Republic of Kazakhstan

*meruert82@mail.ru

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Abstract. The scales of porous carbon materials usage are constrained by their considerably high cost. Therefore, development of new methods for production of porous carbon with the necessary complex of properties from cheap raw materials is actual. Also, porous carbon materials can be used for growth of carbon nanotubes as a matrices of catalyst particles. Herein, the method of fabrication porous carbon materials from waste of oil industry and their use as a matrices of catalyst particles to growth of CNT was developed. CNTs was synthesized by CVD using as hydrocarbon source - propan-butane gas mixture, as catalyst - Ni particles at 650 ℃, 700 ℃, 750 ℃, 800 ℃. Obtained carbon materials was investigated by Raman spectroscopy and by scanning electron microscope. Investigations on the properties of the obtained porous materials show soot particles sedimented in pores reduce well nanoparticles of metals from salts which act as nuclei for the growth of multiwall carbon nanotubes during pyrolysis of hydrocarbons by CVD method.

Introduction

At present, the total world production of porous carbon materials (PCM) makes up about one million tons a year and continues increasing. The main fields of using PCM are systems of adsorption purification and separation of gaseous and liquid media [1, 2]. In this paper methods for production of carbon porous material containing carbon nanotubes on the basis of soot having hydrophobic properties [3] and oil sludge are developed. It is known that only in oil production industry of the Republic of Kazakhstan more than 1.5 mln.t. of pollutants annually are intaken into the atmosphere, about 4 billion m^3 of oil gas burnt, tens of storehouses with sludge remain unliguidated. Therefore, the problem of utilization of oil wastes in our country is very actual now.

Different used oils, grounds containing residual oil, oil sludge and other materials refer to oil wastes. It is inexpedient and rather dangerous to store similar wastes during a long period of time. It is necessary to utilize them or subject to processing.

Oil and oil products used and contaminated with different harmful and toxic substances refer to oil sludges. Their composition may vary depending on the source of their origin. Also, all oil sludges contain water and different large and small admixtures with a solid consistency. In some cases, oil sludges are in the form of emulsion which is quite stable and its components cannot be separated [4].

Catalytic chemical deposition from vapour phase (CVD) has a number of advantages and that makes it the most widely used method for synthesis of carbon nanotubes (CNT). This method is decomposition of carbon containing molecules on catalytical particles of transition metals such as Fe, Ni and Co. Synthesis CVD is a multi-parametric process, however, the main effect on the structure, properties and yield of carbon material is exerted by a catalyst [5].

Preparation of catalysts supposes the use of carriers, as such, for example, oxides of aluminium, magnesium, silicon, barium, hydroxides and salts of metals, zeolites and so on can serve [6].

Among carriers, of great importance for preparation of catalysts are carbon materials. A well-developed catalytic chemistry of nickel as well as variety of carbon materials with a wide range of properties allowed to create a large set of metallic catalysts on carbon carriers [7]. In this paper we obtained MWCNT on the surfaces of PCM in various temperatures.

Experimental

A reaction mixture of oil sludge and hydrophobic soot was prepared for synthesis of porous carbon material and its use for growing carbon nanotubes. For this, oil sludge was mixed with soot during 15 minutes, then it was dissolved in toluene in the ratio 1:1 and mixed again during 40 minutes. After that, the reaction mixture was introduced into the reactor and heated in inert atmosphere to 700 ℃. Thermal treatment was carried out during 50 minutes, then the reactor was cooled to room temperature.

After preparation of porous carbon material and creation of nuclei for the growth of carbon nanotubes, the material was impregnated with 0.5 M alcohol solution of crystallohydrate of nickel nitrate $Ni(NO_3)_2*6H_2O$. Then the prepared sample was dried at 100 ℃ during 15 minutes. Then, to obtain catalytically active centres on the carrier for growing carbon nanotubes, the porous carbon material impregnated with nickel catalyst was annealed at 400 ℃ during 1hour.

The main method for optimization of catalytically active centres of nickel catalyst is reduction of nickel by hydrogen atoms of the porous material at 400-500 ℃. The decomposition reaction of nickel nitrate followed by reduction to particles of nickel proceeds as follows:

$$2(Ni(NO_3)_2*6H_2O) \xrightarrow{300^0C} 2NiO + 2NO_2\uparrow + O_2\uparrow + 12H_2O$$

$$2Ni(NO_3)_2 \xrightarrow{500^0C} 2NiO + 4NO_2 + O_2\uparrow$$

$$2NiO + C \xrightarrow{200-400^0C} 2Ni + CO_2\uparrow$$

To grow carbon nanotubes on porous carbon material impregnated with nickel catalyst, the method of CVD was used. Propane-butane mixture was used as the raw material. Pyrolysis of hydrocarbon raw material was carried out at temperatures 650 ℃, 700 ℃, 750 ℃, 800 ℃. Porous carbon material in the amount of 0.5 g with nickel catalyst was loaded into a boat of 10 cm length and placed into the centre of a quartz tube. The temperature was increased to 650 ℃, 700 ℃, 750 ℃, 800 ℃ at inert atmosphere, then during 30 minutes at predetermined temperatures a propane-butane gaseous mixture was supplied. The rate of supply of argon was 80 cm^3/min, the rate of hydrocarbon supply was 80-100 cm^3/min. after completion of reaction, the reactor was cooled to room temperature.

Figure 1 presents a general scheme of the unit for synthesis of porous carbon material and CNT by the method of catalytic decomposition of hydrocarbon vapours (CVD). The body of the reactor is a tube with the length of 35 cm and diameter of 13 cm. A removable quartz tube is inserted into the space of the body. Inside the reactor there is a quartz tube with the length of 45 cm and diameter of 3.5 cm.

Results and discussion

It is known [5] that the properties of catalysts depend much on the nature of precursor and the character of its interaction with the carrier. At the same time, preparation of heterogeneous catalysts includes the following basic stages:

1) preparation of the carrier, in this case preparation of porous carbon material;

2) coating the precursor onto the surface of catalyst, impregnation with alcohol solution of nickel nitrate;

3) transformation of the initial compound of catalyst into the active form [5, 7], thermal processing at 400 ℃ during 1 hour. Deposition of metallic precursor is realized in two main ways [8].

The first way is interaction of metal compounds in solution with the surface of the carrier: this is either physical adsorption or chemical binding with the surface functional groups or ion exchange, etc. Catalysts obtained in this way are often called adsorption catalysts. Conventionally, in such catalysts, as a rule, metal is present in the form of high catalytic activity.

The second way is impregnation of the carrier with solution of the precursor leading to billing of pores of the carrier, but in this case, interaction between compounds of metal with carbon is quite weak [9]. Such catalyst are called impregnation catalysts. Nickel catalyst on the carrier from porous carbon material obtained from oil sludge is an impregnation catalyst. According to the mechanism proposed in [10], carbon from the gaseous phase interact with metal, dissolving in the volume of a catalytic particle. The gradient of carbon concentration on different surfaces of a catalytic nanoparticle results in diffusion of carbon, and upon reaching supersaturation, in formation of tubular structures in a solid phase.

Figure 1 presents Raman spectra (RS) of the obtained samples. For multiwall carbon nanotubes (MCNT) in RS one can observe two characteristics modes: G (1500…1600 $см^{-1}$), due to vibrations of hydrogen atoms in the plane of graphene layer and D (1330-1370 $см^{-1}$), due to the break of symmetry of an ideal graphite layer. However, sometimes side surfaces of carbon nanotubes may contain a layer of amorphous carbon which also contributes to the intensity D-peak on Raman spectra.

The ratio I(D)/I(G) in RS of the sample obtained at 650 ^{0}C makes up 1.03, 700 ^{0}C – 1.18, 750 ^{0}C – 1.18, 800 ^{0}C – 0.69. Thus, defectness of carbon nanotubes the degree of which is evaluated indirectly by the relation of peaks D and G in spectra of combination scattering is conditioned by the sum total of two factors: 1) break of the symmetry of surface grapheme layers of nanotubes due to the presence of hydrogen atoms in the state of sp^3-hybridization (in the composition, for example, of alkyl groups); 2) the content of a layer of amorphous carbon on side surfaces of carbon nanotubes.

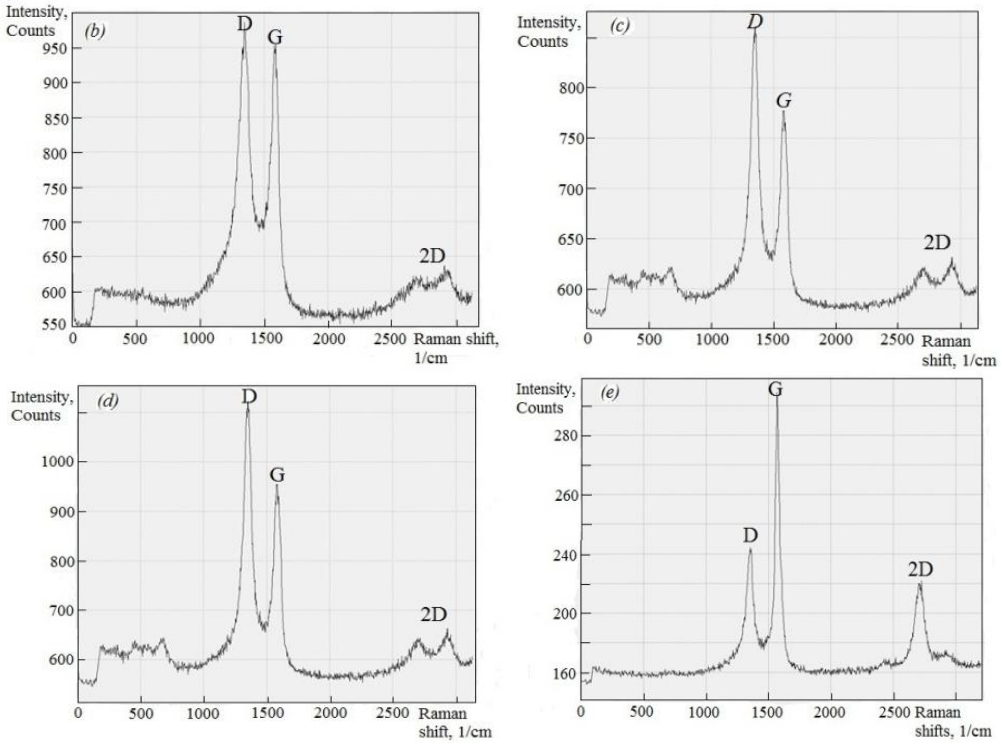

Fig. 1. Raman spectra of the initial porous carbon material (a) and CNT obtained by CVD method at 650 ^{0}C (b), 700 ^{0}C (c), 750 ^{0}C (d), 800 ^{0}C (e)

With the increase in the relation of I(D)/I(G) the defectiveness of the structure of the obtained carbon nanotubes increases. As the results of RS spectroscopy show, carbon nanotubes obtained at 800 ^{0}C by CCVD method contain the less amount of defects.

Figure 2 presents the scanning electron microscopic (SEM) images of MWCNT obtained by CVD method in various temperatures. The morphology of MWCNT shows that CNT obtained under above mentioned conditions have a curved, tubular form.

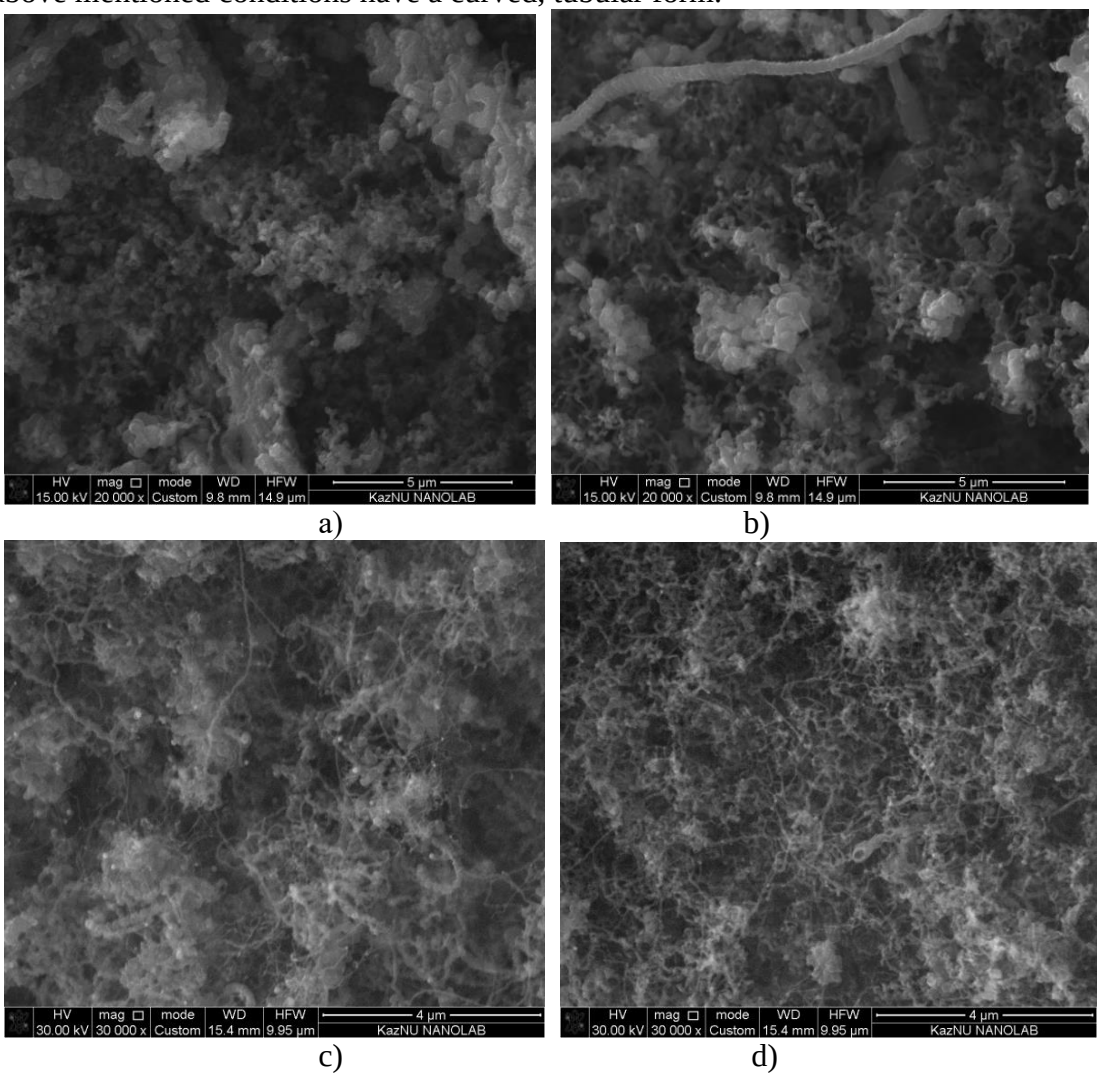

Fig. 2. SEM images of MWCNT obtained by CVD method at 650 ^{0}C (a), 700 ^{0}C (b), 750 ^{0}C (c), 800 ^{0}C (d)

The obtained images show formation of MWCNT on the surface of porous carbon material on the basis of oil sludge and hydrophobic soot in the presence of Ni particles which has the external diameter of 28-54 nm. The diameter of the internal channel makes up 10-15 нм, the thickness walls – 18.4 нм and more. Separate nanotubes are interlaced between each other in the volume of the material.

Conclusions

We developed the method of production low cost porous carbon materials based on hydrophobic soot and waste of oil industry. Obtained carbon porous material was used as a matrix for synthesis of multiwalled carbon nanotubes. Multiwalled carbon nanotubes have diameter range from 28 nm to 54 nm.

The developed technique by authors of work for producing a porous material based on hydrophobic soot and oil sludge can be used for recycling technology of waste petroleum refining industry to produce desired products and for synthesis of MWCNT.

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