PLASMA CATALYSIS OF CARBON NANOPARTICLES SYNTHESIS IN THE PYROLYTIC CHAMBER

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For experimental studies the generation of carbon nanoparticles with continuous removal of material was used plasma-liquid system with discharge in reverse vortex flow of "tornado" type. As a model of hydrocarbon has been used 96% ethanol. To generate reverse vortex flow used inert gas argon. The possibility of continuous transport of carbon nanomaterials from the synthesis area of solid-phase chemically passive microparticles revealed. Analysis of gas samples was carried out on gas chromatograph 6890N Agilen. Purified carbon samples investigated by Fourier spectrometer "Infralyum FT-801"

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INTRODUCTION

One of the main tasks of the process of generation of nanomaterials is to create a continuous cycle of the system. In previous experiments have been conclusively proved that the substrate temperature has a decisive influence on the size and morphology of the final product [1]. So you need ensured process with the continuous formation and removal of formed carbon material from the reaction volume on the chemically passive particles with controlled temperature of surface.

1. EXPERIMENTAL

For experimental studies the generation of carbon nanoparticles in plasma-liquid system with continuous removal of material was used plasma discharge in the reverse vortex flow of "tornado" type [2], whose scheme is shown in Fig.1.

It consists of a cylindrical glass vessel by diameter of 90 mm and height of 70 mm, sealed by the flanges at the top and at the bottom (1). The vessel was filled by the work liquid (2) through the inlet pipe and the level of liquid was controlled by the spray pump. The basic cylindrical T-shaped stainless steel water-cooled electrode on the lower flange is fully immersed in the liquid. The electrode on the upper flange made from duralumin had a special conic hub with the axial nozzle by diameter 2 mm and length of 10 mm. The gas was injected into the vessel through the orifice (9) in the upper flange tangentially to the cylinder wall and created a reverse vortex flow of tornado type, so the rotating gas went down to the liquid surface and moved to the central axis where flowed out through the nozzle in the form of jet (5) into the pyrolytic chamber (3). Since the area of minimal static pressure above the liquid surface during the vortex gas flow is located near the central axis, it creates the column of liquid at the gas-liquid interface in the form of the cone

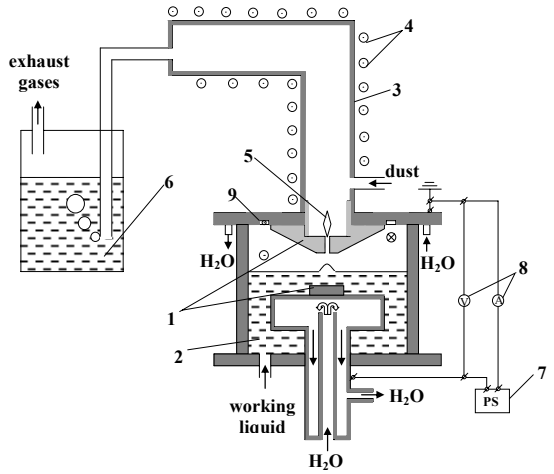

Fig. 1. Schematic setup: 1 - electrodes, 2 - working liquid, 3 - pyrolytic chamber, 4 - heater, 5 - plasma torch, 6 - flask of distillate, 7 - PSU, 8 - instrumentation

with the height of ~ 5 - 7 mm above the liquid surface (without electric discharge).

The voltage was supplied between the upper and the lower electrodes (1) in the liquid by the DC power source (7) powered up to 10 kV. The conditions of breakdown in the discharge chamber were regulated by three parameters: by the level of the work liquid; by the gas flow rate and by the value of voltage. The range of discharge currents varied within 25-100 mA. The pressure in the discharge chamber during the discharge operation was ~ 1.2 bar; the static pressure outside the reactor was ~ 1 bar.

Fine dust that provides removal and formation of carbon particles uniformly fed into a heated reaction metal chamber (3), where it is rapidly heated to required temperature. Thermal heating chamber is provided a heating coil (4), the set temperature is the temperature substrates for the formation of carbon nanomaterials. It should be noted that the contribution to the temperature of the reaction chamber also allows plasma torch (5) and the gas flow, which transports dust particles in chamber, so you need to take into account the amendments to the final

temperature of dust. Temperatures recorded system thermocouple located at the inlet and outlet pyrolytic chamber. For substrate temperature for the formation of carbon nanomaterials is temperature, which is set at the entrance of the reaction chamber in the dust to mix activated materials.

Dust particles and the synthesized nanomaterials, which were removed by gas flow, are collected into the flask with distillate (6) for the further decantation and evaporation.

Use of chemically inert dust particles makes it possible not only to provide centers of formation of carbon nanomaterials and make the resulting products outside the system, but also greatly simplify the process of purification.

As a model hydrocarbon used 96% ethanol C_2H_5OH. Inert gas argon used to form reverse vortex flow for eliminate the burning of ethanol. The thickness of the gas layer between the liquid surface and the top flange was 8 mm. Since alcohol is very volatile substance has been selected polarity "solid cathode", which provides a lower flow rate of fluid.

2. METHODS AND RESULTS

Emission spectra were measured with system that was made up of optical fiber, spectrum device with CCD-line and PC. The spectrometer worked in range 200 – 1100 nm with resolution 0.6 nm. PC was used as a control device for measuring and data processing. The main component in the spectra of radiation is the molecule C_2, also present CN, CH.

The main component of the plasma is C_2 molecules are also present radicals CN, CH, and atoms H, C. Presence atoms and molecules of carbon is a favorable factor for the formation of carbon structures.

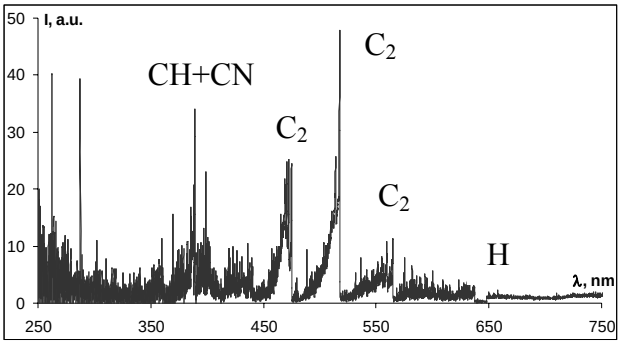

Fig. 2. Typical emission spectrum of argon/alcohol plasma in the reactor type TORNADO-LE

Analysis of gas samples was carried out on gas chromatograph 6890N Agilen. Conditions of analysis on gas chromatograph: detector - katharometer; detectors temperature 200 °C; carrier gas - argon; analysis of the light gases carried through the column MOLSIV, 15 m long; analysis of hydrocarbons - PLOTQ on column 15 m long; samples were injected directly into the chromatograph dispenser.

Samples of gas were collected directly at the output of the pyrolytic chamber (without water filtration) and outlet flask of distillate (with water filtration). Mode of the following: voltage 5.2 kV, current 50 mA, temperature in the pyrolytic chamber 275…300 ° C. Gas collected at the outlet of the reaction chamber has the following composition (in decreasing order): H_2, CO, CH_4, C_2H_2, C_2H_4, H_2O, C_2H_5OH, C_2H_6, CO_2, nC_4H_{10}, iC_4H_{10}, C_3H_6.

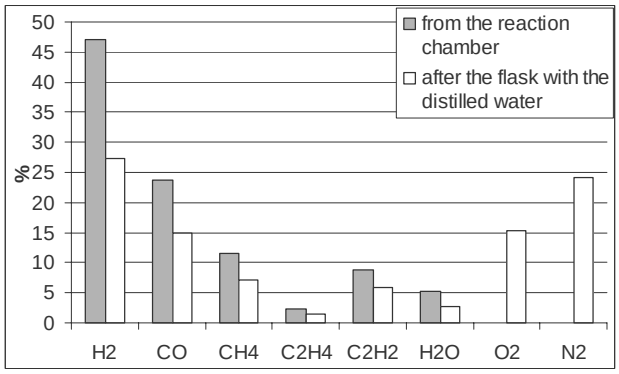

Fig. 3. The main components of exhaust gas

Gas changes its chemical composition with the passage of through the water. Hydrogen displaces the nitrogen and oxygen dissolved into water. The composition in the ratio of carbon-obtained molecules does not change, it means that chemical reactions occur mainly in the pyrolytic chamber and finished before exit of it.

To study the absorption spectra of solid samples was used FTIR spectrometer "Infralyum FT-801". Samples were prepared on glass BaF_2 thickness of 4 mm, absorption band in the range 2300…2400 cm^{-1} corresponds to the spurious band of air (fig.4). Spectra have the slope of the baseline caused by dispersion and scattering [3]. The tables of characteristic frequencies, the bands of the IR spectrum can be associated with certain functional groups that make up molecules, such as: CH, CH_2, CH_3, CO, C-C bond in aromatic rings [4].

Almost all organic compounds show peak or group of peaks of absorption near 3000 cm^{-1}. Absorption in this area caused by the stretching vibrations of C-H bonds. Absorption in 1460, 1380 cm^{-1} caused by the different deformation vibrations of C-H bonds.

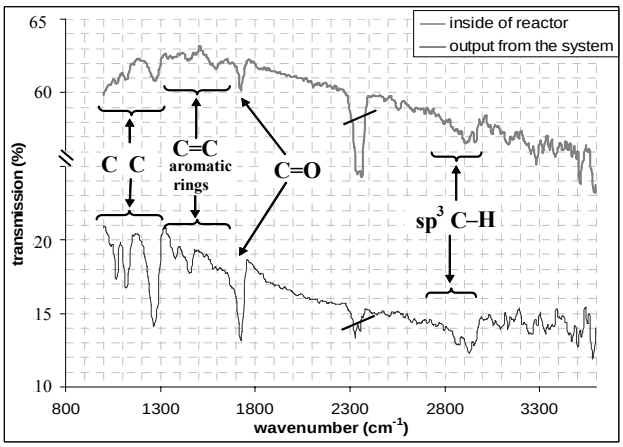

Fig. 4. FTIR spectra of samples: obtained in a plasma reactor and sampled output from the system

Stretching vibrations of the double bond C=O are intense signal in the range of 1800…1650 cm^{-1}. Carbonyl group belongs to the most easily noticeable structural fragments of molecules detected by IR-spectroscopy. The provisions of carbonyl absorption bands in the spectrum depends on the nature of substituent at the carbonyl group C=O.

Aromatic rings found in the IR spectrum of moderate stretching vibration peak of C-H in the area 3030 cm^{-1}. Another characteristic feature - stretching vibrations of aromatic carbon-carbon bonds are usually observed at 1600 and 1475 cm^{-1}.

For alcohol characteristic absorption bands: a broad band of intense vibrations of associated OH groups at ~ 3300 cm^{-1}, an intense band of valence vibrations of C-O in the 1200-1000 cm^{-1}. In the transmission spectra can see faint traces of ethanol absorption bands (1050, 1250, 1400 and 2950 cm^{-1}).

CONCLUSIONS

• The possibility of generating carbon nanostructures in plasma-liquid system type "TORNADO" was investigated.

• The possibility of working in continuous mode was found.

• The possibility of continuous transport of nanomaterials chemically passive microparticles from the zone of formation was discovered.

• It is shown that the main chemical reactions occurring in the reaction chamber.

• Formed carbon materials are structured, with carbon-carbon bonds mainly sp^2 and sp^3 hybridization.

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ПЛАЗМЕННЫЙ КАТАЛИЗ СИНТЕЗА УГЛЕРОДНЫХ НАНОЧАСТИЦ В ПИРОЛИТИЧЕСКОЙ КАМЕРЕ

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Для исследования генерации наночастиц углерода с непрерывным удалением материала была использована плазменно-жидкостная система с обратновихревым потоком типа "торнадо". В качестве модельного углеводорода был использован 96% этанол. Для создания обратновихревого потока использовали инертный газ аргон. Выявлена возможность непрерывного удаления углеродных наноматериалов из области синтеза с помощью твердофазных химически пассивных микрочастиц. Анализ проб газа проводился на газовом хроматографе 6890N Agilen. Очищенные образцы углерода исследовали с помощью фурье-спектрометра "Инфралюм ФТ-801".

ПЛАЗМОВИЙ КАТАЛІЗ СИНТЕЗУ ВУГЛЕЦЕВИХ НАНОЧАСТИНОК У ПІРОЛІТИЧНІЙ КАМЕРІ

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Для дослідження генерації наночастинок вуглецю з безперервним видаленням матеріалу була використана плазмово-рідинна система зі зворотньовихровим потоком типу "торнадо". В якості модельного вуглеводню був використаний 96% етанол. Для створення зворотньовихрового потоку використовували інертний газ аргон. Виявлено можливість безперервного видалення вуглецевих наноматеріалів з області синтезу за допомогою твердофазних хімічно пасивних мікрочастинок. Аналіз проб газу проводився на газовому хроматографі 6890N Agilen. Очищені зразки вуглецю досліджували за допомогою фур'є-спектрометра "Інфралюм ФТ-801".