Scientific bases and principles of obtaining carbon-metallic material by catalytic pyrolysis of ethanol

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Scientific bases and principles of obtaining carbon-metallic material by catalytic pyrolysis of ethanol

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Abstract. The method of producing of carbon-metal material in the form of mixture of carbon fibers and encapsulated in unstructured carbon particles of nickel in diameter from 10 to 150 nanometers catalytic pyrolysis of ethanol comprising the catalyst in the form of nickel oxide and magnesium applied on the surface of inert substrate and placed in theclosed sealed volume maintained at constant temperature is fed through the inlet manifoldethanol vapor andis removed through outlet manifold gaseous pyrolysis products, wherein ethanol vapor diluted with inert gas in a ratio ethanol: inert gas of 1:4 ...5. The inert gas dilution use ethanol vapor argon. The catalyst is used in the form of alloy of nickel oxide (II) and magnesium in a weight ratio of NiO: MgO 4:1. The temperature is maintained constantly during synthesis of the form in the range of 600 to 750 °C. Synthesis was carried out under atmospheric pressure. The catalyst applied on the surface of inert substrate in the form of graphite foil is used in pulverized or granular state.

Introduction. Nowadays the technology of producing carbon-metallic material by catalytic pyrolysis of ethanol is used in the chemical industry. Scientific production experience demonstrates that carbon-metal material in the form of mixture of carbon fibers and encapsulated in unstructured carbon of nickel particles with diameter from 10 to 150 nanometers is produced by catalytic pyrolysis of ethanol at atmospheric pressure. Chemically active catalyst in the form of nickel oxide and magnesium deposited on the surface of graphite foil as inert substrate in pulverized or granular state is placed in the closed sealed volume which regularly maintain constant temperature of 600 - 750 ° C. Through this input collector is fed vaporof ethanol and gaseous pyrolysis products are removed from the output manifold. Ethanol vapor is diluted with inert gas such as argon at weight ratio of ethanol: inert gas of 1:4 ...5. The time of active chemical synthesis is from 1 to 180 minutes. Thetechnologydeveloped bytheauthors relates to chemical technology of heterophase reactions of solids with gas or thermal decomposition. Carbon-metal material is mixture of carbon fibers and encapsulated in unstructured carbon ofnickel particles with diameter from 10 to 150 nanometers. Carbon atomic fibers are characterized substantially by constant diameter, ratio of length to diameter as 10:1 with crystal structure of the ordered carbon atoms having an outer diameter in the range between 18 and 62 nanometers. Ratio ofcarbon atomic fibers and encapsulated particles ofnickel is 3..4:1[1].

The purpose of this paper is to analyze the producing carbon-metallic material by catalytic pyrolysis of ethanol.

It is known the method of carbonization of carbonaceous materials comprising feeding of bundles of treated carbonaceous material in the reactor containing thermally insulated housing with muffle, moving of bundles through the reactor chamber while supplying simultaneously hot and cold inert gas and removal of pyrolysis products with additional influence of temperature on gas during pyrolysis and selection of the treated bundles in the intermediate amount when cooling (UK patent GB 2,184,819 МПКD01F 9/22, D01F 9/32, 1987). The disadvantage of this technical solution [2] is low productivity of chemical carbonization process. It is associated with inability to maintain constant temperature environment while moving in the cavity of the ovenbundles with the material to be treated. The technological process is also associated with restrictions of temperaturewiththe danger of overheating of the product which leads to the deterioration of its properties and inability to obtain encapsulated in unstructured atomic carbon of nickel particles. Another disadvantage is the need for processing of raw material before carbonization and unsuitability of this method to obtain the desired products by catalytic pyrolysis.

Material and research methods. The most promising technological direction is the way to handle original gaseous hydrocarbon products. In this particular case pre-treatment of raw material in the majority of the cases are minimized. The U.S. patent №5165909, МПК D01F 9/10, 1992[5] describes the process ofcontinuous production of carbon atomic fibers which comprises contacting formation of fibers on catalyst containing metallic particles with gas, containing atomic carbon. However according to the known method ([RF patent № 2296827, МПК DOIF 9/127, 9/133 DOIF], 2005 [4] the process has technological disadvantage of formation of carbonatomic fibers and encapsulated in carbon fibers ofnickel particles. In this case there is technological impossibility to obtain encapsulated inunstructured carbon ofnickel particles. It is also known the method of [6] obtaining inorganic nanotubes from renewable raw materials (application for invention № 2008113245МПК S07S 1/00. 2009), the method comprises the following stages: a) synthesis of alcohol (s) by fermentation, b) dehydration of alcohol, c) introduction into the fluidised bed in the second reactor of the catalyst powder at temperature of 450-850 ° C which contains at least one metal, wherein catalyst is supported on inert solid support with diameter of catalyst pellets less than 300 mu.m; d) reduction of alkene obtained in stage b) into contact with powdery catalyst of the stage c) to form carbonhydrogen nanotubes andhydrogen on the surface of the mentioned catalyst by catalytic decomposition of the mentioned alkene, and e) recovering carbon nanotubes obtained in the d) stage. However the above mentioned technical method, contact of ethanol vapor occurs with suspended catalyst layer, which leads to instability of conditions of nanotubes growththroughout the volume of the machine and inability to obtainencapsulated in unstructured carbon of catalyst particles.

Results and discussion. The scientific basis for producing carbon-metallic material is catalytic pyrolysis of ethanol. Therefore in this case it is appropriately the result isknown as technical solution adopted for the prototype the method of producing carbon nanotubes with encapsulated particles of nickel and cobalt (RF patent number 2,310,601, МПКC01V 31/02, 2007). According to this known solution - the method [3] is prepared solution of cobalt acetylacetonate or nickel in benzene or in mixture with ethanol. For this purpose theglass vessel is filled with liquid. Then it is filled with bubbler benzene. Then the represented installation is sealed and is filled with nitrogen from the cylinder. The quartz reactor made with possibility of heating in high temperature furnace heated in nitrogen stream is fed from the container. Then the vessel with reaction mixture is suppliedwith nitrogen under pressure and is sprayed solution of cobalt acetylacetonate or nickel through the capillary in the reaction zone of the reactor with producing of appropriate catalyst. Thereafter the reactor is supplied with bubbler benzene resulting in the decomposition of benzene on the catalyst.

This method utilizes as carbon source benzene which is more costly raw material than ethanol, since ethanol is produced of renewable sources. In produced material nickel particles of encapsulated in carbon nanotubes rather than unstructured carbon and have not the form nearly to the spherical shape. Thus the use of volatile catalyst solution of nickel or cobalt acetylacetonate in benzene or its mixtures with ethyl alcohol complicate considerably the process of control of chemical technological synthesis process compared with using powdered or granular catalyst.

Conclusion. Thus the proposed method of producing carbon-metal material in the form of mixture of carbon fibers and encapsulated in unstructuredcarbon nickel particles with diameter from 10 to 150 nanometers of catalytic pyrolysis of ethanol. New technical solution lies in the fact that catalyst in the form of nickel oxide and magnesium is applied on the surface of inert substrate and is placed in the closed and sealed volume. While maintaining constant temperatureethanol vapor is fed through the inlet manifold and through the outlet manifold gaseous pyrolysis products are removed. The distinguishing features are that ethanol vapor is diluted with inert gas in a ratio ethanol: inert gas of 1:4 ... 5. Argonis used as inert gas for diluting ethanol vapor. The catalyst is used in the form of alloy of nickel oxide (II) and Mg in a weight ratio of NiO: MgO 4:1. The temperature is maintained at constant value that synthesis in the range of 600 to 750 °C. Chemical technological synthesis technology is carried out at atmospheric pressure. The catalyst applied on the surface of inert substrate in the form of graphite foil is used in pulverized or granular state in chemical processes.

References:

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[3] Russian patent number 2,310,601 МПКC01V 31/02, 2007

[4] RF Patent number 2296827, МПК DOIF 9/127, DOIF 9/133, 2005

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