

Features of Nanoporous Carbon Material Synthesis

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Abstract

Creation of innovative products and technological breakthrough – phrases most often used in relation to objects located in the nanoscale area. Carbon nanomaterials (CNMs) of various morphologies and structures, which include nanotubes, graphene, nanoporous carbon, are one of the most studied materials of the nanotechnology industry at present. This is due primarily to the fact that their physico-mechanical and physico-chemical characteristics have a direct effect on the final product. At the same time, for a number of applications, the best performance is achieved at the highest possible values of specific surface parameters and porosity. Methods and an experimental technology for producing micro- and mesoporous carbon material have been developed. Depending on the feedstock and technological synthesis modes, a nanoporous carbon material is obtained with a predominance of micro- or mesopores, with a BET specific surface area in the range of 2000–4000 m²/g. The technology includes carbonization of the starting materials and subsequent chemical activation. The obtained activated carbon material can be used as sorbents for gaseous media, both in purification systems and as gas batteries for safe storage and transportation systems, as well as for solving a number of environmental problems.

Keywords

Carbon nanomaterial; nanoporous carbon; specific surface area; activation; sorbent.

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Introduction

The current period of nanoindustry development in the Russian Federation is characterized by the intensity of accumulation of knowledge about the structure, properties, methods of obtaining and areas of practical application of nanoscale structures. In the study of CNMs, two directions can be distinguished in which both fundamental and applied studies are carried out: synthesis and characterization of CNMs as a new class of materials, as well as the practical application of these materials [1–3].

Carbon materials with a developed surface and porosity are widely used in various fields of modern industry: chemical, pharmaceutical, radio electronics, etc. They are used as sorbents for air purification, protection against harmful chemical compounds, catalyst carriers, storage systems for natural gases in the energy sector and in transport [1, 4, 5].

For most applications, materials containing mesopores with a high specific volume and specific surface are most effective. According to the classification officially adopted by the International

Union of Pure and Applied Chemistry, pores are classified by size as follows: micropores (< 2 nm); mesopores (2–50 nm); macropores (> 50 nm) [6]. In real materials, pore size refers to the effective diameter calculated from the adsorption-desorption isotherms according to a theoretical model. Most often, the calculation of the surface and porosity of various materials is carried out according to the BET, BJH and DFT models, which, as a rule, are included in the programs of modern devices for adsorption measurements. For different types of materials and size ranges, this or that model is better suited. The term “nanoporous material” is also widely used, for which the pore size range is not standardized, but usually ranges from one to several nanometers, that is, it overlaps with the mesoporosity range.

To obtain porous carbon materials, carbon raw materials, various types of charcoal and fossil coal, coals obtained by carbonization of raw materials of plant or animal origin, are activated by liquid-phase or gas-phase reagents, for example, water vapor, air, carbon dioxide, nitric acid, potassium hydroxide, phosphoric acid, zinc chloride and others [7].

In industry, as a rule, the activation of carbon-containing raw materials by water vapor, air, carbon dioxide, or mixtures thereof is used, since gas-phase technology is most suitable for industrial production [8]. Active carbons are obtained by carbonization and activation of plant materials (wood, fruit seeds). Moreover, a high specific surface is achieved only for microporous coals. If activation is carried out before a larger mass of the starting carbon material is burned out, due to the burning out of the pore walls, the micropores are first enlarged into mesopores, then into macropores, but the specific surface drops sharply.

In [9], the authors propose the production of activated carbon materials by heat treatment of wood at 300–500 °C in the presence of activating reagents; moreover, phosphoric acid or diammonium hydrogen phosphate should be used as activating reagents. This results in materials containing micropores and mesopores.

The authors of [10], in order to obtain a nanostructured carbon material, carry out oxidative sulfonation of the carbon source material and activation with potassium hydroxide at 700 °C. The result is a microporous nanostructured carbon material with a pore size mainly in the mesopore range, as well as an insufficiently high specific pore volume.

Common features of [11–16] are the use of carbon-containing material as a starting material and the use of reagents that enter into chemical reactions with carbon as an activating component.

In [17], the authors solve the problem of producing mesoporous carbon, combining high specific surface area and specific volume of mesopores by using a mixture of phenol-formaldehyde resin (PFR) and dextrin or carboxymethyl cellulose (CMC) with the addition of graphene or graphene plates (GNP) as a feedstock.

Comparative characteristics of the materials obtained by different authors are shown in Table 1.

The authors of this work set the task by changing the composition and ratio of substances subjected to carbonization, as well as technological activation parameters, to ensure the production of nanoporous carbon, combining a high specific surface area and specific volume of mesopores, a more effective macroscopic structure, for subsequent use as sorbents for air purification, protection against volatile chemical compounds, as well as low-pressure batteries in natural gas storage systems in the energy and transport sectors.

Experimental technique

The task of obtaining nanoporous carbon was solved by changing the composition of the starting components, including heat treatment of the starting

material containing phenol-formaldehyde resin, graphene, dextrin or carboxymethyl cellulose, mixing the heat-treated substance with potassium hydroxide, heat treatment of the mixture at the activation temperature, and post-treatment of the activated mixture.

The developed technology includes preparation (carbonization) of the feedstock and chemical activation with potassium hydroxide. Depending on the raw materials used and technological conditions, activated carbon materials with a highly developed porous surface with a predominance of micro- or mesopores are obtained.

To prepare the starting material, aqueous solutions of the starting components were mixed in a container. The container was closed with a lid, to prevent communication with the atmosphere, and placed in an oven, where step heating occurred with exposure for 4 hours at 140 °C, 160 °C, and 8 hours at 300 °C. The substance obtained after heat treatment was crushed to a particle size of not more than 0.2 mm. Next, chemical activation of the heat-treated substance with potassium hydroxide was carried out at a temperature of 750 °C in an inert gas environment for 2 hours. In this case, the mass ratio of the initial components and the technological activation parameters (temperature, heating rate, and exposure) were varied. After which the resulting material was washed and dried.

Physico-mechanical and physico-chemical characteristics – surface and porosity parameters, were determined by nitrogen adsorption using a Nova Quantachrome E1200 surface and porosity analyzer; specific surface area was determined by the BET multipoint method; pore size distribution and specific pore volume - according to the DFT method, which is the most adequate for the studied materials.

Results and discussion

As a result, nanoporous carbon materials with the following characteristics were obtained: specific surface area according to BET – 2400–3600 m²/g, specific pore volume according to DFT – 2.40–4.65 cm³/g, of which for mesopores ≈ 80 %, average diameter then – 3.5–5,0 nm.

Analyzing the research results obtained at this stage, we can draw a number of conclusions about the characteristics of the synthesized carbon material. As compared with the materials of other authors, as well as in relation to studies conducted by the authors of this work, it can be noted that the specific surface and porosity parameters depend, first of all, on the starting components used to obtain carbon-containing

Raw materials and parameters of the obtained carbon materials

Reference	Carbon-containing feedstock for carbonization and activation	Characteristics of the resulting activated carbon material
[8]	Vegetable carbon-containing raw materials (wood, seeds of fruit crops)	The BET specific surface area corresponding to micropores is 800–1000 m ² /g, mesopores 100–200 m ² /g, for macropores 0.2–0.5 m ² /g
[9]	Plant-based carbon-containing raw materials (wood)	The specific surface area according to BET is 950–1780 m ² /g. Moreover, the volume of mesopores (0.07–0.20 cm ³ /g) is much smaller than the volume of micropores (0.48–0.67 cm ³ /g)
[10]	Various carbon-containing raw materials	Specific surface area according to BET 3100–4150 m ² /g; specific micropore volume 1.0–1.2 cm ³ /g
[11]	Fossil coals (anthracite, brown coals); plant biomass (wood)	The BET specific surface area (for anthracite) is 3240 m ² /g, with a total pore volume of 1.77 cm ³ /g, and an average pore diameter of 2.2 nm. The BET specific surface area (for brown coal) is 2003–2680 m ² /g, pore volume 0.86–2.12 cm ³ /g, average pore diameter 1.98–3.00 nm. The BET specific surface area (for wood) is 822–2050 m ² /g, with a total pore volume of 0.42–1.05 cm ³ /g, and an average pore diameter of 1.97–2.19 nm
[12]	Graphene nanoplateles	The BET specific surface area is 2400–3100 m ² /g; it contains mainly mesopores with an average diameter of 4 nm. The total specific volume of micro- and mesopores is – 2 cm ³ /g
[13]	Phenol formaldehyde resin	The specific surface area according to BET is 590–2019 m ² /g (with the prevalence of micropores)
[14]	A mixture of polymers: (phenol formaldehyde resin + polyethylene)	The BET specific surface area is 1765 m ² /g, the total pore volume is 1.00 cm ³ /g, of which for micropores – 0.68 cm ³ /g, meso-pores – 0.32 cm ³ /g; the average pore diameter of 2.5 nm
[15]	Phenol formaldehyde resin	The BET specific surface area is 900–1840 m ² /g, the total pore volume is 0.52–0.96 cm ³ /g, of which 77–88 % for micropores and 12–23 % for mesopores
[16]	Phenol formaldehyde resin	The BET specific surface area is 2653 m ² /g, the total pore volume is 1.26 cm ³ /g, of which micropores are 0.80 cm ³ /g; the specific volume of mesopores is 0.46 cm ³ /g, the average pore diameter is 2.7 nm
[17]	1. Phenol-formaldehyde resin, graphene plates, carboxymethyl cellulose. 2. Dextrin, graphene, phenol-formaldehyde resin	1. Specific surface area according to BET – 2479 m ² /g; the average pore diameter of 4.5 nm; specific pore volume – 2.49 cm ³ /g; specific micropore volume (0.85–1.8 nm) – 0.35 cm ³ /g; the specific volume of mesopores (2.34–8.00 nm) is 2.08 cm ³ /g. 2. Specific surface area according to BET – 3202 m ² /g; the average pore diameter of 3.627 nm; specific pore volume – 2.496 cm ³ /g; specific micropore volume (0.85–2.00 nm) – 0.53 cm ³ /g. The specific volume of mesopores is 1.97 cm ³ /g

substances and their percentage ratio, as well as on technological activation modes (temperature, activation time, gas exchange mode, etc.). In addition, a number of points can be noted:

– the resulting nanoporous carbon on the specific surface (BET) corresponds to or exceeds this characteristic of materials obtained by other authors, while significantly exceeding them in average pore size and specific volume of mesopores. This provides accessibility for large ions and molecules, which, in turn, improves the operational characteristics of these materials as sorbents;

– the addition of graphene changes the structure of the obtained material, contributing to the availability of mesopores for ions and molecules, however, an increase in its content in the initial mixture of components leads to a certain decrease in the specific surface and to an increase in the cost of the product;

– an increase in the content of PFS in the starting material leads to a decrease in pore size (the proportion of micropores increases).

Conclusion

The conducted experiments showed that the obtained data are a justification for the choice of the region of the mass ratio of the components in the starting material and the technological parameters of activation. And the resulting mesoporous carbon can be used as a universal sorbent for gaseous media [18–22].

The next stage of research is to conduct comprehensive tests of nanoporous (in the area of mesopores) carbon materials as gas sorbents, both in purification systems and as storage substances (gas accumulators) used in transportation and storage. This direction is promising and meets the current level of development of equipment and technologies, ensuring the creation of safe storage systems for gaseous media and the solution of a number of environmental issues.

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