THE INFLUENCE OF SYNTHESIS CONDITIONS ON THE STRUCTURAL AND SURFACE PROPERTIES OF CARBON NANOFIBROUS MATERIALS PREPARED BY CATALYTIC DECOMPOSITION OF METHANE

Kuvshinov G.G., Ermakova M.A., Glushenkov A.M., Chukanov I.S., Kuvshinov D.G.
Novosibirsk State Technical University
pr. K. Marksa, 20, Novosibirsk, 630092, Russia

The process of catalytic decomposition of methane is useful for the production of hydrogen and carbon nanofibrous materials [1]. Nanofibrous carbon is considered to be a promising carbon material. It is supposed to be used as a catalyst and catalyst support, an adsorbent for extraction of liquid and gaseous components, a material for porous electrodes, a component of hydrogen fuel cell and a filler for composite materials [2,3]. The material forms catalytically over nanoparticles of VIII group metals and their alloys. Growing nanofibers interlace with each other to form porous carbon matrix during hydrocarbon decomposition. The structural and surface properties of the nanofibrous carbon materials can be modified by the number of factors such as the temperature of the process, the nature of carbon precursor and catalyst composition.

The properties of carbon materials are the main factor providing their successful application in different areas. As a consequence, the development of methods of carbon properties control is an extremely important task. The main goal of this work is to study factors which influence the structural and surface properties of carbon nanofibrous materials prepared by catalytic decomposition of methane.

The samples of carbon materials were synthesized by decomposition of methanecontaining gases over Ni, Ni-Cu, Fe-Ni and Ni-Pd catalysts. Pure methane, methane+argon mixture and natural gas were used as a carbon-containing feedstock. The catalysts were prepared by different methods and processed different composition.

The methods of transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and low-temperature nitrogen adsorption were used to study structural and surface properties of carbon materials.

The structure of carbon materials produced over Ni, Ni-Cu and Fe-Ni catalysts is consistent with that described previously [4].

The structure of carbon nanofibers produced over Ni catalysts at 550 °C consists of the system of stacked cones. The samples obtained over Ni-Cu catalysts at 550 °C represent octopus-like fibers with a "card pack" structure. The structure of carbon nanofibers formed over Fe-Ni catalysts is similar to the structure of multi-walled nanotubes. The method of catalyst preparation does not influence the structural properties significantly.

The study of the properties of carbon materials formed over Ni-Pd catalyst showed the pronounced dependence of the morphology and structure of the material on the temperature and the method of process initiation. Octopus-like and bidirectional fibers form at 600 °C. The structure of nanofibrous carbon produced at 800 °C depends on the way of temperature increase and the presence or absence of the initial stage of carbon formation at lower temperature. The material can be grown as encapsulated catalytic nanoparticles, octopus-like fibers or hollow nanofibers with conical orientation of basal planes.

The textural properties of nanofibrous carbon depend significantly on the temperature and the nature of catalyst used. The samples synthesized over Ni-Cu and Ni-Pd catalyst at a relatively low temperature of 550-600 °C have large surface area of the value up to 325 m^2/g. The porous structure of the carbon materials consists mainly of micro- and mesopores. Figure 1 represents the typical curves of pore size distributions.

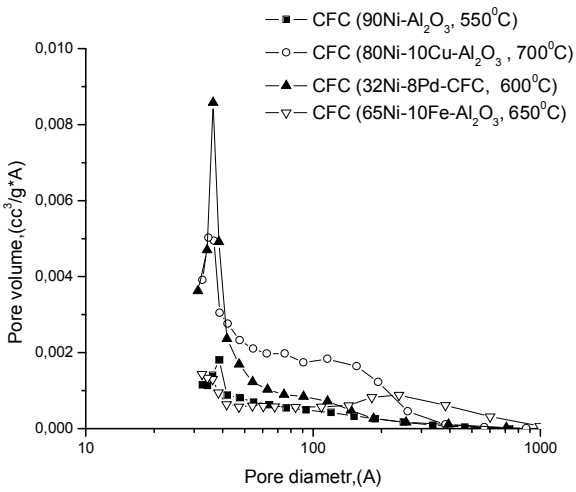

Figure 1. The pore size distribution of the CFC.

Surface properties of carbon nanofibers were studied as well. The study of the surface chemistry of carbon nanomaterials formed by decomposition of the natural gas over Ni, Ni-Cu and Fe-Ni catalysts showed that the surface of these materials contains mainly basic sites.

The surface chemistry of the carbon materials after treatment with KOH, NH_3 or HNO_3 was also investigated.

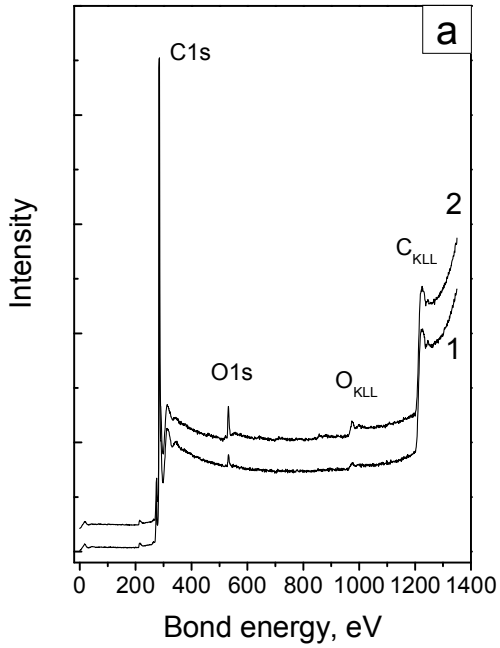

Figure 2. XPS spectra of the CFC (90%Ni-Al_2O_3): 1 – initial sample, 2 – after the treatment with KOH.

The treatment of carbon nanofibers with KOH leads to the destruction of fibers and dramatic increase in the surface area. XPS data (fig. 2) show the increase in the width of the C1s line. This feature is caused by the larger amount of defects in activated nanofibrous carbon in comparison with the initial material.

The treatment with ammonia leads to a small increase in the surface area, slight increase of pH and increase of the number of basic sites on the surface of the material.

The treatment with nitric acid leads to the oxidation of the surface of nanofibrous carbon. The amount of acid sites is bigger. According to the XPS data, it is a consequence of the formation of carboxylic groups on the surface of carbon nanofibers

References

1. Kuvshinov D. G. The processing of associated oil gases and production of novel carbon materials. PhD thesis. - Novosibirsk, 1999.
2. K. P. de Jong and J. W. Geus. Carbon nanofibers: Catalytic synthesis and applications. Catal. Rev. – Sci. Eng. 2000; 42:481-510.
3. Frantsuzov V. K., Petrusenko A. K., Peshnev B. V., Lapidus A. L. Filamentous carbon and its applications. Khimiya tverdogo topliva 2000; 2: 52-66.
4. T. V. Reshetenko, L. B. Avdeeva, . R. Ismagilov, V. V. Pushkarev, S. V. Cherepanova, A. L. Chuvilin, V. A. Likholobov. Catalytic filamentous carbon: Structural and textural properties. Carbon 2003; 41: 1605–1615.