

Surface modification of microfibrous materials with nanostructured carbon



Irina V. Krasnikova^{a, b, *}, Ilya V. Mishakov^{a, b}, Aleksey A. Vedyagin^{a, b}, Yury I. Bauman^a, Denis V. Korneev^c

^a Borekov Institute of Catalysis SB RAS, pr. Ac. Lavrentieva, 5, Novosibirsk 630090, Russia

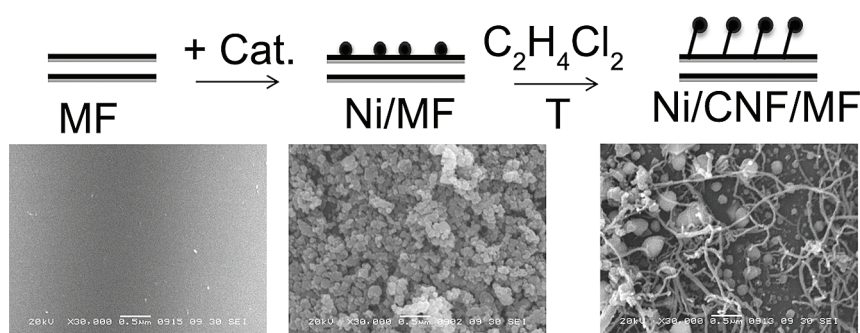
^b National Research Tomsk Polytechnic University, Lenin av., 30, Tomsk 634050, Russia

^c State Research Center of Virology and Biotechnology VECTOR, Koltsovo, Novosibirsk Region 630559, Russia

HIGHLIGHTS

- The microfibers of different nature were coated with nanostructured carbon layer.
- Features of CNF growth and characteristics of hybrid materials were studied.
- Appropriate anchorage of CNF layer on microfiber's surface was demonstrated.

GRAPHICAL ABSTRACT



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ABSTRACT

The surface of fiberglass cloth, carbon and basalt microfibers was modified with carbon nanostructured coating via catalytic chemical vapor deposition (CCVD) of 1,2-dichloroethane. Incipient wetness impregnation and solution combustion synthesis (SCS) methods were used to deposit nickel catalyst on the surface of microfibrous support. Prepared NiO/support samples were characterized by X-ray diffraction analysis and temperature-programmed reduction. The samples of resulted hybrid materials were studied by means of scanning and transmission electron microscopies as well as by low-temperature nitrogen adsorption. The nature of the support was found to have considerable effect on the CCVD process peculiarities. High yield of nanostructured carbon with largest average diameter of nanofibers within the studied series was observed when carbon microfibers were used as a support. This sample characterized with moderate surface area (about 80 m²/g after 2 h of CCVD) shows the best anchorage effect. Among the mineral supports, fiberglass tissue was found to provide highest carbon yield (up to 3.07 g/g_{FC}) and surface area (up to 344 m²/g) due to applicability of SCS method for Ni deposition.

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1. Introduction

Microfibrous materials (microfibers, fibre, clothes) are known to possess high strength along with low density, thus stipulating its

* Corresponding author. Borekov Institute of Catalysis SB RAS, pr. Ac. Lavrentieva, 5, Novosibirsk 630090, Russia.

E-mail address: tokareva@catalysis.ru (I.V. Krasnikova).

wide application as reinforcement additives for constructional composites based on polymers, concretes or bitumen; as catalyst supports and conductive layers of membranes etc. [1–4]. The market segment of microfibrinous materials is represented by carbon microfibers (CMF), fiberglass items (FG) and basalt microfibers (BMF) which belong to different price categories and can be applied to improve conductivity, corrosion stability and thermal insulation, respectively.

The industrial production techniques used to manufacture mentioned materials are quite different. Thus, high modulus carbon fibers are produced via polyacrylonitrile graphitization at 1000–2000 °C [5]. An extrusion of whinstone melt through the dies is usually used for basalt fibers fabrication. In this case, the use of natural raw stocks makes the process of BMF production more ecological friendly and cheaper if compare with fiberglass that is produced from special glass melts with thermostabilizing additives [6]. In all cases, the resulting smooth fibers are characterized with low surface area (0.1–8 m²/g). The adhesion between reinforcement additive with flawless inert surface and polymer matrix is quite poor [7,8]. In aim to improve the interaction of matrix and additive, a lot of physical and chemical approaches are being developed to increase the surface defectiveness and corrosive resistance [3,9–13].

The catalytic chemical vapor deposition (CCVD) technique applied for nanomodification of microfibers surface is of great interest nowadays. As a result of carbon-containing precursor decomposition, the surface gets covered with carbon nanofibers (CNF) [14–16] or carbon nanotubes [17]. This technique requires, as a rule, using of pure gases (ethylene, acetylene, ethanol, etc.). Depending on the nature of microfibers the final hybrid product can be applied in electrochemical capacitors [16,17] or as reinforcing agents for polymers [18,19]. Additional post-functionalization of the latter in corresponding media allows introducing oxygen- and nitrogen-containing functional groups into CNF composition. Such approach significantly enhances surface area, thus improving strength characteristics of reinforced polymers, especially in the case of CNF/matrix chemical linkage.

In present work CCVD method was applied to modify the surface of carbon and basalt microfibers, and fiberglass cloth. 1,2-dichloroethane (DCE) was used as a carbon source. The choice of DCE was motivated by a number of ecological, economical and practical reasons. Firstly, DCE is known to be complicated utilizing industrial waste of polyvinylchloride production [20]. Secondly, its decomposition allows one to obtain in one stage highly defective carbon nanostructures slightly doped with Cl atoms and with developed surface area [21]. Thirdly, using of wastes may be favorable in terms of cost of the surface modification process.

The aim of this work was to study the influence of microfiber's nature on characteristics of carbon coating (thickness, morphology and uniformity of CNF layer). Also we varied the catalyst deposition methods and estimated the coating strength for CNF/microfiber systems.

2. Experimental

2.1. Starting materials

The following fibrous materials were used in the present study: chopped carbon microfibers UKN-M 5000 (LLC “Argon”, Russia); basalt microfibers SV-B-13-4S (LLC “Basalt Fiber Technology”, Russia); fiberglass cloth (LLC “Argon”, Russia). The first two types of fibers represent bundles of single microfibers (filaments) and the later consists of bundles interwoven in cloth. Characteristics of the materials are presented in Table 1.

2.2. Deposition of the catalyst

An active component (Ni) was deposited on the surface of fibrous materials via incipient wetness impregnation with aqueous solution of nickel nitrate Ni(NO₃)₂·6H₂O. The method implies one step impregnation where volume of solution should be equal to the pore volume of a support [22]. As a result, a precursor deposits quantitatively. Practically, pore volume was determined with preliminary test on aliquot samples and then appropriate amount of solution was used in accordance to the measurements [23]. Mass of the salt was calculated in order to obtain nickel loading of 2.5 wt% in all impregnated sample. After the impregnation procedure the samples were dried at 120 °C and calcined at 350 °C resulting in NiO formation. The samples were labeled as 2.5Ni/CMF, 2.5Ni/FG and 2.5Ni/BMF, respectively. Amount of metal loading was controlled by weighing of ash residual after combustion in air atmosphere.

Deposition of Ni on fiberglass cloth was also performed by means of solution combustion synthesis (SCS). Prior to SCS procedure, the fiberglass strips (1.5 cm × 8 cm) were washed out in acetone, dried at 120 °C and calcined at 600 °C (1 h). Water solution of nickel nitrate and lemon acid used as a fuel additive was evenly distributed throughout surface of fiberglass strips by impregnation at constant heating. The “precursor salt/fuel additive” ratio was equal to 1:4 by weight. Samples were dried at -60–70 °C, placed over the warmed-up electric stove, and one edge of strip was brought to a contact with the electric spiral heated to 400 °C. Thus the propagation of combustion front over the strip's surface was initiated. Described technique was used to prepare the series of xNi/FG-scs samples with varied Ni loading (where x is 0.5, 2.5 or 5 wt%).

2.3. Modification of the fiber surface

Catalytic decomposition of DCE was carried out in vertical quartz reactor. As prepared samples (after nitrate decomposition) were placed in reactor and heated in Ar atmosphere up to 600 °C. In some cases, preliminary reduction in a hydrogen flow (6 l/h) during 20 min at reaction temperature was used to reduce NiO. Then, an argon flow was passed through the saturator with DCE and mixed with hydrogen flow before feeding the reactor loaded with a sample. Finally, the reaction mixture contained 7.5 vol% of DCE, 37.5 vol% of H₂ and Ar as a balance. Hydrogen was used to stabilize the performance of catalyst that could be partially poisoned with chlorine during the reaction. Peculiarities of the process are given elsewhere [24]. Reaction gas space velocity was 15 l/h. The duration of CCVD process was varied as follows: 180 min for kinetic studies; 10, 30 or 120 min for distinct syntheses. Heating and cooling procedures were performed in argon atmosphere.

2.4. Characterization of the samples

The microstructure of the prepared samples was examined by scanning electron microscopy (SEM) using JSM 6460 instrument (Jeol, Japan). The microscope ensured magnifications from 8 × to 300,000×.

The elemental composition of the materials was determined by EDX using an energy-dispersive spectrometer fitted with a Si(Li) detector with an energy resolution of 130 eV and a microprobe spot size down to 10 nm.

Specific surface area (S_{BET}) of the modified fibers was measured by low-temperature nitrogen adsorption/desorption using an ASAP 2400 instrument (Micromeritics, USA).

Temperature programmed reduction (TPR) analysis was used for evaluating the reduction properties of NiO deposited on fiberglass cloth, carbon and basalt fibers. TPR measurements were performed

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