

## Bromination of carbon fibers as a route to formation of active functional surface

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Bromination of PAN-based carbon fibers (CFs) by liquid bromine and aqueous solution of Br<sub>2</sub>-KBr complex was carried out and chemical and thermo desorption properties of the samples synthesized were studied. It was established that bromination of carbon fibers resulted in grafting onto surface layer up to 0,5 mmol/g of bromine and its concentration slightly depended on the method of bromination. Graft bromine is hydrolytically stable at 30–100 °C. It was established that thermal desorption of bromine as HBr occurs within the temperature range 100–600 °C. The amount of HBr desorbed in the temperature ranges of 100–300 and 300–600 °C is approximately the same. It was found by TGA and TPD-IR methods that the concentrations of carbon monoxide and dioxide for brominated CFs are higher in comparison with initial carbon fibers that indicate a parallel process of surface oxidation which results in formation predominantly phenolic groups. Treatment brominated CFs with alcoholic solutions of different amines under heating leads to the complete removal of the bromine and grafting N-containing functional groups onto the surface layer. Concentration of amino groups in the surface layer of samples equals 0,5–1,0 mmol/g.

Carbon fibers (CFs) in comparison with other carbon materials with large surface and porous structure possess high thermal and mechanical resistance, so they are competitive materials for application in adsorption and catalysis [1, 2]. Their properties can be varied by the modification of the surface with different functional groups [3, 4]. One of the most common synthetic approaches used in organic synthesis for obtaining various compound derivatives is the initial preparation of halogen-containing precursors with active halogen that can be substituted by other functional groups.

In the present work bromination of carbon fibers using liquid bromine and aqueous solution of Br<sub>2</sub>-KBr complex was carried out and brominated precursors were treated with amines for synthesis of N-containing carbon materials.

### Experimental

Commercial Polyacrylonitrile-based carbon fibers (CFs) were used as an initial material. The samples of CFs with functionalized surface were obtained as follows.

*Bromination with liquid bromine (method B1) or aqueous solution of Br<sub>2</sub>-KBr complex (method B2):* carbon fibers (5 g) were treated with 10 ml of liquid bromine or 50 ml of aqueous solution containing 10 % Br<sub>2</sub> and 15 % KBr at room temperature for 1 hour. Then the samples were treated with 10 % solution of potassium oxalate (200 ml) till carbon dioxide evolution was ceased. The samples were filtered and washed with distilled water until Br<sup>-</sup> ions were not detected in washing waters. Modified fibers were dried

at 120 °C. The samples obtained are designated as CF/B1 and CF/B2.

*Substitution of bromine by the amine residues:* samples CF/B1 or CF/B2 were mixed with excess of 20 % ethanol solution of amine and heated at 90 °C for 15 hours in an autoclave. Thereafter, the fibers were washed with water and dilute sulphuric acid to remove physically adsorbed amine, then with 1 % sodium carbonate solution for renewal of basic state of amino groups. The samples were washed with distilled water to neutral pH of washing water and dried at 120 °C. For CFs modification the following amines were used: ethylenediamine (En), diethylamine (Et<sub>2</sub>N), monoethanolamine (MEA) and piperazine (Pi).

The synthesized samples were investigated by chemical (CA) [5] and thermogravimetric (TGA) analysis, temperature-programmed desorption with IR spectrometric registration of gaseous products of desorption (TPD-IR) and temperature-programmed desorption mass spectrometry (TPD-MS).

### Results and discussion

According to CA data bromination performed under condition of mentioned above techniques provides obtaining up to 0.5 mmol/g of bromine in carbon surface layer. This concentration weakly depends on the chosen method of treatment.

Analysis of TPDMS data revealed the presence of the fragments with m/z 80 and 82 (HBr) in desorption products in an equal amount that corresponds to the natural ratio of

isotopes of bromine. Signals of the fragments with  $m/z$  79 and 81 (Br) are significantly less intensive and completely synchronous to the temperature dependences of HBr evolution, indicating the formation of Br as a result of HBr dissociation in the mass spectrometer but not as the decomposition of Br-containing groups on CFs surface. Desorption of HBr occurs in a wide temperature range, which indicates the energy inhomogeneity of surface sites involved in bromination process. The amount of HBr which is desorbed in the temperature ranges of 100–300 and 300–600 °C is approximately the same.

Bromination of carbon fibers that was carried out according to the proposed techniques was accompanied by a significant oxidation of the carbon matrix. As a result of the parallel oxidation of CFs surface various oxygen-containing functional groups were formed. Significant desorption of water and carbon oxides all over temperature range studied was registered.

Graft bromine is sufficiently stable and does not hydrolyze upon prolonged storage of brominated CFs at room temperature, both in air and in water. Hydrolysis occurs while samples are treated with concentrated alkali solutions, particularly when heated.

According to TGA data desorption of bromine from the surface of the CF/B1 and CF/B2 samples are registered in the range of 170–320 ± 10 °C with a maximum at 220 °C and at higher temperatures. The concentration of bromine determined by TGA in a low temperature range equals 30–50 % of the total amount of bromine in the samples. The concentration of bromine which desorbs in a high temperature range can not be determined by this method because

simultaneously intensive desorption of carbon oxides from the CFs surface occurs.

After treatment of CF/B1 and CF/B2 samples with alcoholic solutions of amines the absence of bromine was observed and a new peak of weight loss appeared on TGA curves at 260 ± 20 °C, indicating to the substitution of bromine by amino groups. As it was found by TGA the concentration of amino groups in the samples was equal 0,5–1,0 mmol/g. The samples obtained have sufficient thermal stability and can be used both as adsorbents and catalyst carriers [6] with large specific area and functional surface layer.

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## Бромирование углеродных волокон как метод формирования активного поверхностного слоя

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Проведено бромирование углеродного волокна на основе ПАН жидким бромом и водным раствором комплекса  $\text{Br}_2 \cdot \text{KBr}$ . Исследованы химические и термодесорбционные свойства полученных образцов. Установлено, что бромирование приводит к введению в поверхностный слой волокна до 0,5 ммоль/г брома и его концентрация мало зависит от метода бромирования. Привитой бром является гидролитически устойчивым при температурах 30–100 °С. Установлено, что выделение брома происходит в температурном интервале 100–600 °С в виде бромоводорода, количество  $\text{HBr}$ , которое десорбируется в температурных интервалах 100–300 и 300–600 °С, приблизительно одинаково. Показано, что для бромированных образцов по сравнению с исходным углеродным волокном наблюдается увеличение концентрации оксидов углерода, особенно монооксида, что свидетельствует о параллельном окислении поверхности образцов с образованием преимущественно фенольных групп. Обработка бромированных образцов спиртовыми растворами аминов различной природы при нагревании приводит к полному удалению брома и введению в поверхностный слой N-содержащих функциональных групп. Концентрация аминогрупп в поверхностном слое волокна составляет 0,5–1,0 ммоль/г.

## Бромовання вуглецевих волокон як метод формування активного поверхневого шару

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Проведено бромовання вуглецевого волокна на основі ПАН рідким бромом і водним розчином комплексу  $\text{Br}_2 \cdot \text{KBr}$ . Досліджено хімічні і термодесорбційні властивості отриманих зразків. Встановлено, що бромовання призводить до введення в поверхневий шар волокна до 0,5 ммоль/г бромоводорода і його концентрація слабо залежить від методу бромовання. Прищеплений бром є гідролітично стійким при температурах 30–100 °С. Показано, що термодесорбція бромоводорода спостерігається в температурному інтервалі 100–600 °С у вигляді бромоводорода, кількість  $\text{HBr}$ , який десорбується в температурних інтервалах 100–300 і 300–600 °С, є приблизно однаковою. Встановлено, що порівняно з вихідним вуглецевим волокном, для бромираних зразків спостерігається збільшення концентрації оксидів вуглецю, особливо монооксида, що свідчить про паралельне окислення поверхні зразків з утворенням переважно фенольних груп. Обробка галогенованих зразків спиртовими розчинами амінів різної природи при нагріванні призводить до повного видалення бромоводорода і введенню в поверхневий шар N-вмісних функціональних груп. Концентрація аминогрупп в поверхневому шарі волокна становить 0,5–1,0 ммоль/г.