

Plasma bromination as pre-treatment of carbon fiber for acid-base catalyst preparation

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The samples of carbon fibers were brominated in low-temperature gas discharge and their physico-chemical properties were studied. It was shown that the concentration of graft bromine depended on processing time and reached 0.9 mmol/g at 20 min of treatment. Thermal desorption properties of synthesized samples were studied. It was shown that temperature range of bromine desorption from the surface of the samples was more narrow as compared to the samples obtained by liquid phase bromination, indicating that the reaction of bromination involved energetically more homogeneous surface centers. Oxidation of the fiber surface during bromination in the gas discharge was much lower compared to the modification in the liquid phase. It was shown that the synthesized materials can be used as precursors for preparing of fibers with acid SO₃H-groups in the surface layer. SO₃H-containing carbon fibers showed catalytic activity in the reaction of isopropanol dehydration. They were characterized by higher stability under reaction conditions in comparison with the samples obtained from precursors that had been brominated by liquid phase method.

1. Introduction

Acid-base catalysts are widely used in commercially important processes of chemical and petrochemical synthesis such as esterification, hydrolysis, dehydration, alkylation, isomerisation [1, 2]. Nowadays a promising trend in heterogeneous catalysis is chemical modification of carbon sorbents to manufacture the low-temperature acid-base catalytic systems. High concentration of active acidic centers can be achieved by impregnation of carbon materials with strong acids but such systems are inconvenient to use in liquid-phase reactions especially at high temperature [3, 4]. Grafting of acidic functional groups is preferable but this is rather difficult due to chemical inactivity of carbon surface. Plasma bromination of carbon materials is known to be a way to produce chemically reactive anchoring groups onto surface for covalent grafting of organic molecules [5]. Covalent bonded bromine is a reactive leaving group in nucleophilic substitution reaction and well suited for grafting of organic molecules with –NH₂, –OH or –SH groups.

Carbon fiber (CF) sorbents are microporous materials with high thermal and mechanical stability. Their structural features and physico-chemical properties made them promising materials for producing of catalysts and catalyst carriers with needed adsorption characteristics [6, 7]. Chemical specificity of CF surface layer can be improved by grafting of different functional groups. Pre-halogenation of carbon fibers and treatment of the active precursors with sub-

stances containing required functional groups were performed to prepare heterogeneous catalysts with graft acidic functional groups that are active catalytic centers [5, 8].

As it was previously found, bromination of carbon fibers in a liquid phase (liquid bromine or aqueous solution of Br₂-KBr) was accompanied with significant oxidation of surface layer [9, 10]. In this work we used plasma bromine treatment to obtain bromine-containing CF samples.

2. Experimental

Commercial Polyacrylonitrile-based carbon fibers (CFs) with S_{BET}=900 m²/g were brominated in a low-temperature gas discharge. Surface bromine was substituted by SO₃H-functional groups and obtained catalysts were tested in a model reaction of isopropanol dehydration. Physico-chemical properties of the synthesized materials were studied by chemical analysis (CA) [11], thermogravimetric analysis (TGA), and temperature-programmed desorption mass spectrometry (TPD-MS).

Bromination of CF samples: CFs (2 g) were treated with bromine in electrodeless high-frequency plasma discharge at a frequency of 27,12 MHz and under a pressure of 10,1 mm Hg. Time of treatment was 5, 10, 15 or 20 min. Before modifying the samples were dried at 120 °C for 1 h and evacuated. Bromine was purified by distillation over concentrated sulfuric acid.

Substitution of surface bromine by S-containing functional groups: Brominated CFs (1 g) were immersed in 5 ml of an aqueous solution of 25% NaSCH₂COONa or

20% Na₂S in an autoclave and heated for 12 h at 90 °C. Then the samples were boiled in 25% HCl for 2 h, washed with distilled water and treated with 30% H₂O₂ for 3 h. All samples were washed and dried in air at 120 °C.

3. Results and discussion

According to the CA data the concentration of bromine in a surface layer depends on treatment time and reaches 0,9 mmol/g when samples are brominated for 20 min under mentioned conditions. Analysis of the TPD-MS data shows that decomposition of bromine-containing samples occurs with HBr evolution in the temperature range 180–430 °C. This interval is essentially more narrow (per 80–150 °C) compared with similar data for samples brominated in a liquid phase [10]. This indicates that bromination runs with involving more energetically homogeneous surface sites. The signals corresponding to carbon monoxide and carbon dioxide are characterized by low intensity and observed at temperatures close to HBr desorption and also above 600 °C, indicating the decrease of the surface oxidation impact into bromination process compared to bromination in the liquid phase.

The TGA data demonstrate weight loss at 180–350 °C and at higher temperatures. A low temperature range corresponds to bromine desorption but its amount is only 40–60 % of the total bromine in the samples. The concentration of bromine which evolves in a high temperature range can not be determined using the TGA data because simultaneous desorption of carbon oxides from the CF surface occurs.

These TGA data confirm the covalent binding of bromine and indicate rather high thermal stability of the samples obtained. Nevertheless, some graft bromine that desorbs in the range 180–350 °C can be substituted with other types of functional groups. Thus, the treatment of the brominated active carbons with S-containing substances (H₂S, NaSCH₂COONa, etc.) followed by hydrolysis and oxidation provides obtaining samples with SO₃H-groups in the surface layer [12]. Accordingly to the TPD-MS data, desorption of SO₃H-groups from the surface occurs as SO₂ (m/z 64) at 60–550 °C. There are signals (m/z 48) that correspond to SO desorption. They are essentially less intensive than SO₂ ones. Thermodesorption curves of SO evolution are synchronous to SO₂ indicating SO₂ dissociation in mass-spectrometer but not decomposition of some S-containing surface groups. The temperature interval of SO₂ desorption is rather wide. After mathematical treatment by Gauss function it can be divided into two parts with maxima at 230 and 330 °C. This may be due to existence of SO₃H-groups in macro/mesopores and micropores and thus different rate of desorption [12].

According to the TGA data, there are significant effect of weight loss at 150–340 °C for carbon fibers treated with S-containing reagents. Chemical analysis demonstrates the absence of bromine in these samples (or it is present in trace amounts) so this effect is proved to be a result of desorption of S-containing surface groups (according to TPD-MS).

The concentration of SO₃H-groups was calculated from the weight loss data at 150–340 °C considering CO₂ that also evolves in this temperature range. Brominated samples are revealed to be more efficient precursors than the original CFs for preparation of SO₃H-containing materials. Their weight loss in the temperature range 150–340 °C is essentially greater in comparison with non-brominated samples. The greatest concentration of graft SO₃H-groups (0.7 mmol/g) was registered for the pre-brominated CFs (20 min) that were treated with NaSCH₂COONa.

Investigation of the catalytic activity of SO₃H-containing CFs in isopropanol dehydration shows that complete conversion of isopropanol to propylene occurs at 210–260 °C. Samples obtained by using NaSCH₂COONa as S-containing reagent are more active in comparison with Na₂S. Pre-halogenation of CFs provides the lowest temperatures of dehydration; the complete conversion occurs at 210 °C. The catalytic activities of CF samples that were brominated in a gas discharge and in a liquid phase (liquid bromine or aqueous solution of Br₂·KBr) are almost similar but the catalytic activities of the first ones does not decrease with heating up to 260 °C (CFs treated with NaSCH₂COONa) and 300 °C (CFs treated with Na₂S).

When the catalysts were heated above the temperature of complete conversion of isopropanol to propylene (t_{100%}) the activity of samples obtained from plasma brominated CFs did not change being the same at temperatures that exceed t_{100%} per 40–50 °C. The activity of catalysts obtained without pre-bromination abruptly decreased at temperatures above t_{100%}. Thus, the SO₃H-containing samples that were treated with bromine in a low-temperature gas discharge are high stable under reaction conditions in comparison with non-brominated ones, so there is a possibility of using them for a longer time.

4. Conclusions

Bromination in low-temperature gas discharge is a promising technique for preparation of bromine-containing CF precursors which can be converted into materials with other surface chemical properties. Concentration of graft bromine depends on the time of treatment and reaches 0,9 mmol/g after 20 min of bromination. Surface bromine can be easily substituted by another functional groups. SO₃H-containing CF samples are active catalysts in isopropanol dehydration. They are more stable in comparison with ones prepared by brominating in a liquid phase.

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Плазмохимическое бромирование углеродного волокна как метод получения кислотно-основных катализаторов

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Получены образцы и исследованы физико-химические свойства бромированного в низкотемпературном газовом разряде углеродного волокна. Показано, что концентрация привитого брома зависит от времени обработки и достигает 0,9 ммоль/г при бромировании в течение 20 мин. Исследованы термодесорбционные свойства синтезированных образцов. Показано, что температурный интервал десорбции брома с поверхности образцов является более узким по сравнению с образцами, полученными обычным жидкофазным бромированием, что свидетельствует о прохождении реакции с участием энергетически более однородных центров поверхности. Установлено, что окисление поверхности при бромировании в газовом разряде значительно меньше, чем при модифицировании в жидкой фазе. Показано, что синтезированные материалы могут быть использованы как прекурсоры для получения волокон, содержащих на поверхности кислотные SO₃H-группы. Образцы с SO₃H-группами проявляют каталитическую активность в реакции дегидратации изопропанола и характеризуются более высокой стабильностью в условиях данной реакции по сравнению с образцами, полученными на основе прекурсоров, бромированных жидкофазным методом.

Плазмохімічне бромовання вуглецевого волокна як метод отримання кислотно-основних каталізаторів

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Отримано зразки та досліджено фізико-хімічні властивості бромованого в низькотемпературному газовому розряді вуглецевого волокна. Показано, що концентрація прищепленого броду залежить від часу обробки та досягає 0,9 ммоль/г при бромованні протягом 20 хв. Досліджено термодесорбційні властивості синтезованих зразків. Показано, що температурний інтервал десорбції броду з поверхні зразків є значно вужчим, порівняно із зразками, отриманими звичайним рідкофазним бромованням, що свідчить про перебіг реакції бромовання за участю більш енергетично однорідних центрів поверхні. Встановлено, що окиснення поверхні при бромованні в газовому розряді є значно меншим, порівняно з модифікуванням у рідкій фазі. Показано, що синтезовані матеріали можуть бути використані як прекурсори для отримання волокон, що містять на поверхні кислотні SO₃H-групи. Зразки з SO₃H-групами проявляють каталітичну активність в реакції дегідратації ізопропанолу та характеризуються вищою стабільністю в умовах перебігу даної реакції порівняно із зразками, отриманими на основі прекурсорів, бромованих рідкофазним методом.