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Functionalization of carbon fibres with S-containing groups

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Surface modification of Busofit carbon fiber with sulfur vapors in the temperature range 500–800 °C with subsequent oxidation of the resulting materials with hydrogen peroxide was carried out. Samples of carbon fiber that had S-containing acidic groups on their surface were obtained. Method of temperature-programmed desorption mass spectrometry revealed that desorption of the sulfur-containing groups occurred as SO_2 in the temperature range 85–550 °C. The concentrations of S-containing groups were calculated by thermogravimetric method. It was demonstrated that quantity of the acidic groups depended on the synthesis temperature: the concentration was the highest for the sample obtained via treatment with sulfur vapors at 500 °C and it declined as synthesis temperature increased. The catalytic activity of the fibers obtained was studied in the reaction of propan-2-ol dehydration. It was demonstrated that the materials synthesized had sufficiently high catalytic activity – a complete conversion of propan-2-ol to propylene was observed for all samples modified. The temperatures of full conversion of the reagent to the resultants of reaction were 155–230 °C. It was established, that all modified carbon fibers could be arranged in order by their catalytic activity and that that sequence was analogical to the range of their sulfur group concentrations. The samples synthesized can be used as active acid-base catalysts when the reactions proceed at temperatures up to 200 °C.

Introduction

Acid-base catalysts are widely used in industrially important processes such as esterification, hydrolysis, dehydration, alkylation, isomerization [1, 2]. The development of new low-temperature active heterogeneous catalysts with thermally and hydrolytically stable acidic centers is very important and attracts the attention of scientists worldwide [3, 4].

Nowadays the preparation of the carbon catalytic system with high concentration of acidic groups is carried out by impregnation of carbon materials (active carbons, carbon fibers, etc.) with acids, sulfonation of carbonized natural organic materials or carbonization of sulfur-containing compounds, in particular S-containing aromatic hydrocarbons [5–7]. These methods of synthesis of carbon-based catalysts often resulted in obtaining products that were inconvenient to use or were unusable due to their mechanical or thermal properties. Particularly, difficulties arose when those materials were used in liquid-phase reactions, especially under heating, because of rapid inactivation and decrease in catalytic activity [6, 7].

This paper proposes a method for obtaining the carbon fibers with S-containing surface groups. Acid-base catalysts were prepared by oxidation of modified materials and their catalytic activity as well as their thermal properties was tested.

Experimental

Busofit commercial carbon fiber obtained by carbonization and activation of viscose was used as initial material. Its specific surface area determined by the BET method and its total pore volume were: S = 1380 m^2/g, V = 0.63 cm^3/g, respectively.

Functionalization of carbon fibers (Cfs) with S-containing groups was performed by treatment of the initial material with sulfur vapor at 500, 600, 700 and 800 °C. The reaction was carried out under an argon atmosphere for 1 h. Then the samples were allowed to remain for 1 h at the temperature of synthesis to remove physically adsorbed sulfur and cooled to room temperature without disconnecting the argon feeding line. Thereafter, the materials obtained were oxidized by 30 % H_2O_2 solution to prepare acidic catalysts. The temperature of sulfur vapor treatment is indicated in the sample title.

All modified carbon fibers were investigated by thermogravimetric analysis (TGA) and temperature-programmed desorption mass spectrometry (TPD-MS). Catalytic activity of the synthesized acidic catalysts was studied in the reaction of propan-2-ol dehydration. The temperature of 100% conversion of propan-2-ol to propylene was used as a measure of catalytic activity.

Results and discussion

The treatment of carbon fibers with sulfur vapors and H_2O_2 solution enabled obtaining samples with acidic S-containing surface groups. Analysis of the TPD-MS data revealed that desorption of these groups occurred with SO_2 evolution (m/z 64) in the temperature range 85–550 °C. That range was rather wide and could be divided into two parts: the low-temperature (85–250 °C) and the high-temperature (250–550 °C) ranges with maxima at 190±10 and 300±10 °C, respectively. Functional groups desorbed in the low-temperature interval could be identified as graft sulfo-ether groups and/or sulfuric acid adsorbed on the CFs surface [8]. Functional groups which decomposed in the high-temperature range could be identified as sulfo groups [8].

Analysis of the TGA data revealed that all modified samples demonstrated a significant increase in weight loss as compared to the initial samples. Also, in contrast to initial CFs, there were maxima in the temperature range 150–470 °C on the differential weight loss curves. In accordance with the TPD-MS data, those maxima could be related to desorption of S-containing groups from the modified CFs surface.

The concentration of S-containing groups was calculated from the TGA data. For all modified samples the concentrations of these groups were 0.26–0.88 mmol/g and the highest value was found for the CFs treated with sulfur vapors at 500 °C. According to concentrations of S-containing groups, all samples could be arranged in the order as follows: CFs/S/500> CFs/S/600> CFs/S/700> CFs/S/800. The concentration of surface acidic groups declined as the synthesis temperature increased. Maximum desorption of the acidic surface groups occurred at 245±5 °C and slightly differed for all samples obtained.

The investigation of the catalytic activity revealed that 100 % conversion of propan-2-ol to propylene was observed for all samples modified. The temperature of 100 % conversion was 155–230 °C. The catalytic activity of the samples completely corresponded to the concentrations of oxidized S-containing groups on the surface and the highest value was observed for sample CFs/S/500. All modified CFs could be arranged in order by their catalytic activity and this sequence was analogical to the one given above. Catalytic activity of these catalysts was preserved during repeated use. Initial fibers appeared to be inactive in the propan-2-ol dehydration when tested at temperature up to 240 °C.

Thus, the treatment of carbon fibers with sulfur vapor followed by oxidation with hydrogen peroxide ensured obtaining samples with acidic S-containing groups in the surface layer. These materials have a sufficiently high thermal stability and can be used as effective low-temperature acid-base catalysts in the reactions that proceed at temperatures up to 200 °C.

1. Стайлз Э. Б., *Носители и нанесенные катализаторы,* Москва, Химия, 1991.

2. Танабе К., *Катализаторы и каталитические процессы,* Москва, Мир, 1993.

3. Егиазаров Ю.Г., Потапова Л.Л., Радкевич В.З., Солдатов В.С., Шункевич А.А., Черчес Б.Х., *Химия в интересах устойчивого развития*, 2001, (9), 417–431.

4. Diyuk V.E., Zaderko A.N., Grishchenko L.M., Yatsymyrskiy A.V., Lisnyak V.V., *Catal. Commun,* 2012, (27), 33–37.

5. Ставицкая С.С, Стрелко В.В., Тарковская И.А. *Каталитические свойства активных углей, пути их регулирования и использования,* Киев, 1995.

6. Hara M., Yoshida T., Takagaki A., Takata T., Kondo J.N., Hayashi S., Domen K. A., *Angewandte Chemie International Edition,* 2004, **43** (22), 2955–2958.

7. Toda M., Takagaki A., Okamura M., Kondo J.N., Hayashi S., Domen K. A., Hara M., *Nature,* 2005, **438** (10), 178.

8. Діюк В.Є., Гріщенко Л.М., Савицька А.М., Яцимирський В.К. *Вопросы химии и химической технологии*, 2008, (2), 96–101.

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Функціоналізація вуглецевого волокна S-вмісними групами

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Проведено модифікування поверхні вуглецевого волокна Бусофіт парами сірки в температурному інтервалі 500–800 °С з подальшим окисненням отриманих матеріалів пероксидом водню, в результаті чого отримано зразки вуглецевого волокна, що містять на поверхні S-вмісні кислотні групи. Методом термопрограмованої десорбційної масс-спектрометрії показано, що десорбція сірковмісних груп відбувається у вигляді SO_2 в температурному інтервалі 85–550 °С. Методом термогравіметричного аналізу розрахована концентрація S-вмісних груп. Показано, що кількість кислотних груп залежить від температури синтезу зразка: вона є найбільшою для зразка, отриманого при обробці парами сірки при 500 °С, і зменшується при підвищенні температури синтезу. Досліджено каталітичну активність отриманого волокна в реакції дегідратації ізопропілового спирту. Показано, що синтезовані матеріали характеризуються досить високою каталітичною активністю – при використанні всіх модифікованих зразків відбувається повне перетворення ізопропілового спирту в пропілен. Температура повного перетворення реагенту в продукти реакції складає 155–230 °С. Встановлено, що ряд каталітичної активності повністю узгоджується з рядом по концентрації сірковмісних груп. Показано, що синтезовані зразки можуть бути використані як активні кислотно-основні каталізатори при проведенні реакцій в інтервалі температур до 200 °С.

Функционализация углеродного волокна S-содержащими группами

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Проведено модифицирование поверхности углеродного волокна Бусофит парами серы в температурном интервале 500–800 °С с последующим окислением полученных материалов пероксидом водорода, в результате чего получены образцы углеродного волокна, содержащие на поверхности S-содержащие кислотные группы. Методом термопрограммированной десорбционной масс-спектрометрии показано, что десорбция серосодержащих групп происходит в виде SO_2 в температурном интервале 85–550 °С. Методом термогравиметрического анализа рассчитана концентрация S-содержащих групп. Показано, что количество кислотных групп зависит от температуры синтеза образца: она является наибольшей для образца, полученного при обработке парами серы при 500 °С, и уменьшается при повышении температуры синтеза. Исследована каталитическая активность полученного волокна в реакции дегидратации изопропилового спирта. Показано, что синтезированные материалы характеризуются достаточно высокой каталитической активностью – при использовании всех модифицированных образцов происходит полное превращение изопропилового спирта в пропилен. Температура полного превращения реагента в продукты реакции составляет 155–230 °С. Установлено, что ряд каталитической активности полностью согласуется с рядом по концентрации серосодержащих групп. Показано, что синтезированные образцы могут быть использованы как активные кислотно-основные катализаторы при проведении реакций в интервале температур до 200 °С.