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Stability analysis of functionalized mesoporous carbon materials in aqueous solution

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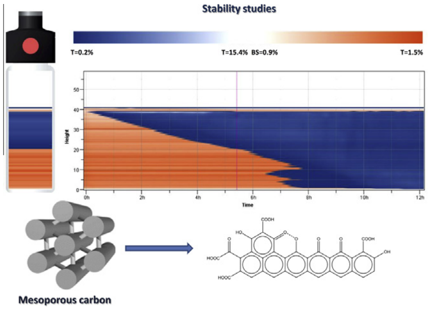
HIGHLIGHTS

- Ordered mesoporous carbons are oxidized by ammonium persulfate at 60 °C.
- Longer oxidation time is favorable for generation of high density of —COOH groups.
- Dispersion stability of mesoporous carbon is analyzed by optical methods.
- Higher transmission intensity is related with more serious sedimentation.
- The dispersion of functionalized carbons are much more stable than pure materials.

GRAPHICAL ABSTRACT



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ABSTRACT

Mesoporous carbons obtained by soft and hard template methods were oxidized by ammonium persulfate under different conditions. The functional groups present on the surface of carbon materials were identified by FT-IR and thermogravimetric studies. Longer time of oxidation process was favorable for generation of higher density of carboxylic, phenolic and etheric groups. The stability of pristine and functionalized mesoporous carbons dispersed in water was analyzed by multiple light scattering and laser diffraction methods. Additionally, the zeta potential of mesoporous carbons suspensions was measured. Particle–particle interactions, particle size and their density determined the sedimentation behavior of materials in aqueous solution. Non-modified C_{KIT-6} and C_{SBA-15} exhibited higher transmission level than the oxidized materials. Higher transmission intensity is related to more intense sedimentation. The results indicate that the dispersion of functionalized C_{KIT-6} and C_{SBA-15} in a liquid phase is much more stable than that of non-modified mesoporous carbon materials. In contrast, for the carbon samples obtained by the soft template method, the modification did not produce significant changes in the intensity of back-scattered light.

1. Introduction

Ordered mesoporous carbons (OMC) are considered as promising adsorbents of various pollutants from liquid phase. Parent and modified materials have been effective in removal of various dyes (such as methylene blue [1,2], methyl orange [3–5], chromotrope 2R [6]) and toxic heavy metal ions such as arsenic [7], mercury

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[8], lead and cadmium [9] from aqueous media. Additionally, recently mesoporous carbons have been also applied as reservoir for the storage of insoluble drugs [10] and amino acids [11]. OMC have attracted considerable attention as adsorbents because of their high surface area, large pore volume, ordered pore structure, thermal and mechanical stability [12–14]. However, the hydrophobic nature of OMC surface can be in some cases unfavorable. If so, introduction of appropriate functional groups could change the inert character of ordered mesoporous carbons. Thus, the hydrophobic surface properties are modified and the adsorbent could be more selective towards a chosen compound. So far mesoporous carbons have been functionalized via oxidation in order to introduce carboxyl groups [15,16], which can be covalently attached to their surface [17–19]. It has been recently reported that the introduction of organic functional groups can enhance the sorption properties of OMC [9,20]. As regards adsorption from liquid phase, proper characterization of adsorbent plays a significant role. Sedimentation rate of OMC, its particle size distribution and zeta potential can be useful parameters to select an appropriate adsorbent for a given adsorbate.

Sedimentation rate of OMC in various solvents can be analyzed by multiple light scattering with the use Turbiscan Lab Expert. This instrument enables monitoring the migration behavior of ordered mesoporous carbons immersed in the solvent by measuring the backscattering and transmission of monochromatic light ($\lambda = 880$ nm). During the analysis, the suspension is periodically monitored along the whole height of the sample. The analyzer is composed of near infrared light source and two synchronous detectors [21]. When light passes across the cylindrical glass cell, transmission detector receives it, while the backscattering sensor gets the light, that is scattered backward by the sample [22,23]. When the sedimentation process occurs, the transmission and backscattering profiles vary along the whole height of the samples with time. So far this technique has been used to analyze the stability of pristine and chemically oxidized carbon nanotubes (CNTs) dispersed in various polar and nonpolar solvents [24]. According to the results, CNTs dispersed in nonpolar media underwent aggregation within 2 h and their sedimentation progressively proceeded with time. When the carbon nanotubes were modified with carboxylic anion groups, the dispersibility in polar solvents was significantly enhanced as a result of a combination of polar–polar affinity and electrostatic repulsion, leading to unchanged transmission flux. The origin of electrostatic repulsion can be found from the increased zeta potential and conductivity of CNTs with carboxylic anion groups. Additionally, alkylated multiwalled carbon nanotubes dispersed in common organic solvents have also been investigated by Turbiscan optical analyzer [25]. In other studies, multiple light scattering method has been applied to measure the stabilizing abilities of the aqueous carbon nanotubes. It has been shown that the addition of surfactant enhanced the stability of CNTs dispersion [26].

The sedimentation behavior can be also explained by particle features in particular their size. In order to determine the particle size distribution the laser diffraction (LD) method can be applied. The measurement is based on the principle that the particles of a given size diffract light at a given angle that increases logarithmically with decreasing size [27,28]. The phenomenon of LD produced by the particles dispersed in the colloidal systems is studied. The collected data are analyzed in term of the Fraunhofer and Mie theories that explain the scattering of light by the particles [29].

It should be added that the dispersed systems are used in various application areas. Their stability is a key parameter both in fundamental research and industrial processes. Therefore, the aim of this work was to apply the optical methods to analyze the sedimentation behavior of functionalized and non-functionalized mesoporous carbons in water to evaluate the effect of their functionalization on their stability.

2. Experimental

2.1. Sample preparation

2.1.1. Synthesis of carbon materials

Mesoporous carbons (C_{KIT-6}, C_{SBA-15}) were synthesized by hard template method with the use of ordered silica materials KIT-6 (regular structure) and SBA-15 (hexagonal structure) as templates and sucrose as the carbon source, according to the reported procedures [4,6].

C_{ST} was prepared by co-assembly of carbon precursors and triblock copolymer F127 ($EO_{106}PO_{70}EO_{106,}$ Aldrich) – the soft template method. In a typical synthesis 1.875 g of block copolymer F127 and 1.875 g of resorcinol (Aldrich) were dissolved in 15.375 g of ethanol to afford a homogenous solution. After stirring for 10 min, 0.12 mL of concentrated HCl (36–38 wt.%) and 1.875 mL of formalin (37 wt.%, Chempur) were added to the above solution. The homogenous solution formed was stirred for 60 min, followed by transferring into petri dishes. Ethanol evaporation took 12 h at room temperature and thermopolymerization took 24 h at 100 °C in an oven. The as-prepared product was scraped from the petri dishes and ground into fine powder. Carbonization was carried out in a tubular furnace at 800 °C for 3 h under nitrogen flow (flow rate of 100 mL/min) at the ramp of 2 °C/min below 600 °C and 5 °C/min between 600 and 800 °C.

2.1.2. Surface functionalization

Mesoporous carbons C_{KIT-6}, C_{SBA-15} and C_{ST} were treated with a mild oxidant of 1 M ammonium persulfate solution (Aldrich) – APS (prepared in 2 M H_2SO_4) at 60 °C. Oxidation was performed for two different times (6 and 12 h) to achieve different levels of surface modification.

For a typical treatment, 0.5 g of mesoporous carbon and 30 mL of freshly prepared 1 M acidic APS solution were added into a round flask. The mixture was stirred and refluxed at 60 °C for 6 or 12 h. In the next step, the solid was filtered, washed with water as well as ethanol and dried at 60 °C for 12 h.

The functionalized samples were denoted as C_{KIT-6} – APS – x, C_{SBA-15} – APS – x, C_{ST} – APS – x, where x stands for the treatment time (h).

2.2. Sample characterization

To identify the functional groups present on the surface of carbon materials, they were subjected to FT-IR study. The mesoporous molecular sieves were mixed with dried potassium bromide, at the rate of 1 mg of carbon per 200 mg KBr. Fourier transform infrared spectra in the range 400–4000 cm^{-1} were collected on an FT-IR Bruker spectrometer IFS 66v/S.

The content of the surface oxygen functional groups, both acidic and basic, was determined by standard neutralization – titration with HCl and NaOH, according to the Boehm method [30]. Briefly, when functionalization was performed with acidic groups, a portion of 0.25 g of dry sample powder was shaken for 24 h in 25 mL of the 0.1 N NaOH solution. After that the suspension was filtrated through a membrane filter and titrated with 0.1 N HCl solution. For basic groups the converse procedure was applied.

Thermogravimetric analysis was performed on an SETSYS 12 made by Setaram. The samples (10 mg) were heated at the rate 10 °C/min, in nitrogen atmosphere. Analysis lasted for 100 min and the temperature during the decomposition was varied from 20 to 1000 °C.