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Effect of pyrolysis temperature and thermal oxidation on the adsorption properties of carbon cryogels

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ABSTRACT

The effect of pyrolysis temperature (500 °C and 930 °C) and partial oxidation by oxygen (250 °C–450 °C) of resorcinol–formaldehyde cryogels (RF) and their graphene derivatives (RFGO) on adsorption capacity for Pb(II) and methylene blue were investigated. Increasing temperature of partial oxidation causes increase in adsorption capacity for Pb(II) from 0.09 to 0.20 (RF) and 0.10 to 0.29 mmol g^{-1} (RFGO) for samples pyrolysed at 500 °C resp. from 0.20 to 0.23 (RF) and 0.16 to 0.27 mmol g^{-1} (RFGO) for samples pyrolysed at 930 °C. Partial oxidation does not affect adsorption capacity for methylene blue. The adsorption capacity of carbon cryogels for both adsorbates increased with higher pyrolysis temperature about 90% for RF and 60% for RFGO. The presence of graphene in the structure does not improve the adsorption properties of prepared carbon cryogels.

1. Introduction

Adsorption of heavy metal ions [1] or ionic dyes [2] from aqueous solution is one of the intensively studied applications of carbon aerogels, cryogels and xerogels. Affinity of polar species to non-polar carbon surface is generally low [3]. Therefore physical or chemical activation is often needed before adsorption application. Physical activation of carbon surface is based on partial oxidation (e.g. by H_2O or CO_2) at high temperature and leads to development of microporosity often interconnected with enlarging the surface area, but without significant changes in surface chemistry [4,5]. Formation of oxygen containing surface groups is typical for chemical activation with hydroxides [5] and for partial oxidation of carbonaceous matter either in gas or liquid phase e.g. Ref. [6].

Gas phase surface oxidation by air or oxygen was tested on various activated carbons. It was found that increasing temperature of oxidation leads to higher amount of surface acidic oxygen containing groups [7,8]. Available temperature range for the oxidation is determined by reactivity of the carbonaceous material and for activated carbons is about 200 °C–400 °C [7–9]. Partially oxidized activated carbons show higher adsorption capacity for adsorption of dibenzothiophene [7], water vapour [8], ammonia [9] or heavy metal ions [8]. Excellent adsorption properties of graphite oxide [10] demonstrate the fact that more oxidized carbons act as better adsorbents.

Aim of this work was to explore the possibility of gas phase oxidation of carbon gels by oxygen and to test the effect of oxidation on adsorption properties of these materials. Resorcinol–formaldehyde carbon cryogels and their derivatives containing graphene were selected as substrates for partial oxidation.

2. Materials and methods

2.1. Preparation of carbon cryogels

Preparation of used materials was derived from literature [11,12] and modified. Graphite oxide (GO) was produced by Hummer's method [12,13]. Briefly, graphite powder (0,5 g) was added to 23 ml of 96% H_2SO_4, followed by the addition of $NaNO_3$ (0,5 g) and solid $KMnO_4$ (3 g) under stirring. The temperature of the mixture was kept at 0 °C for 1 h. Then, the temperature was increased to 40 °C and the mixture was stirred for 1 h. Distilled water (40 ml) was slowly added to the suspension which caused increase of the temperature to 90 °C–100 °C. After 30 min, the suspension was diluted with distilled water (100 ml) and 30% H_2O_2 was added until the colour of the mixture changed from brown to yellow. The suspension was washed with aqueous HCl (1:1) to remove metal ions and then with water to remove the acid. The resulting graphite oxide was isolated by centrifugation (4000 G, 10 min) and freeze dried (52 Pa, 72 h). The graphene oxide was obtained by ultrasonic treatment (3 h) of suspension of prepared

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graphite oxide in water. Obtained suspension was used for cryogel preparation below.

Synthesis of organic cryogels (RF and RFGO, the second doped with graphene oxide) was based on sol–gel polymerization of resorcinol (R) and formaldehyde (F) in aqueous solution with sodium carbonate (C) as catalyst. The molar ratio of R:F in initial mixture was 1:2 and R:C was equal to 200:1. The content of R + F in the reaction mixture was 4 wt%. GO was added to the initial mixture (1 wt%) for sample RFGO. The reaction mixture was mixed with intensive stirring, poured into glass vials and then transferred to an autoclave container for 72 h at 85 °C. After gelation the wet organic gels were freeze dried at 52 Pa for 24 h. Dry organic cryogels were pyrolysed at 500 °C or 930 °C under inert atmosphere (nitrogen) for 3 h. After this thermal treatment the graphene oxide sheets should be reduced to graphene sheets. Four types of cryogels were prepared for this study, concretely resorcinol–formaldehyde cryogel marked as RF-P500 or RF-P930 according to pyrolysis temperature and resorcinol–formaldehyde cryogel containing graphene marked as RFGO-P500 or RFGO-P930. The total amount of prepared carbon cryogels reached several milligrams (cca 200 mg).

2.2. Characterization of carbon cryogels

Infrared spectroscopy measurements were carried out at room temperature in ambient atmosphere using a Nicolet 6700 (ThemoScientific) spectrometer. FT-IR spectra of the prepared sample were recorded in the range of 4000–400 cm^{-1} using the ATR technique equipped with a diamond crystal. The spectra were obtained from 124 scans with the resolution of 4 cm^{-1}.

Surface characteristics of the carbon cryogels were determined from physical adsorption of N_2 (−196 °C) and CO_2 (30 °C) at absolute pressure range from 0 to 1 bar measured by volumetric analyser PCTPro E&E (Setaram). The weight of the dried sample for testing was approximately 0.20–0.27 g. The N_2 adsorption isotherms were used to calculate the specific surface area (S_{BET}). The CO_2 adsorption data were evaluated according to Dubinin–Radushkevich and Medek equation to determine micropore surface area (S_{micro}) and micropore volume (V_{micro}). Although the CO_2 adsorption measurement provides information about surface area of micropores (pore diameter <2 nm), the N_2 adsorption gives information about surface area of mesopores and perhaps even coarser pores (external surface area).

The morphology of samples was examined by scanning electron microscopy (JEOL, JSM-6610LV) after coating the samples by Au film (120 s).

2.3. TG measurements

Thermoanalytical study of pyrolysis was conducted using simultaneous TG-DSC (SetsysEvolution, Setaram) coupled with mass spectrometer QMG 700 (Pfeiffer) by SuperSonic system (Setaram). Pyrolysis of organic cryogels (RF and RFGO) and graphite oxide (GO) was performed in crucible from α-Al_2O_3 (without standard) with 10–11 mg of sample under an argon (flow rate 20 ml min^{-1}) from 15 °C to 1000 °C with heating rate 10 K min^{-1}.

Simultaneous TG-DTA (NETZSCH, STA 449C) experiments was used for studying of the oxidation of the prepared samples in atmosphere of 80% O_2 and 20% N_2 (100 ml min^{-1}) from 30 °C to 1000 °C, heating rate 10 K min^{-1}. The experiments were performed with 8–13 mg of the sample in crucible from α-Al_2O_3 without standard.

2.4. Adsorption experiments

Adsorption experiments of Pb(II) ions and methylene blue from aqueous solutions were conducted in the batch mode. Sample (10–12 mg) was added to 10 ml of adsorbate solution with initial concentration of 1 mmol dm^{-3}. The experiments were carried out with contact time 24 h (Pb(II) ions) or 30 min (methylene blue) for equilibration of the system. The Pb(II) ions concentration before and after adsorption tests was determined by AAS (Varian FS 240). Quantification of methylene blue in solutions was performed by

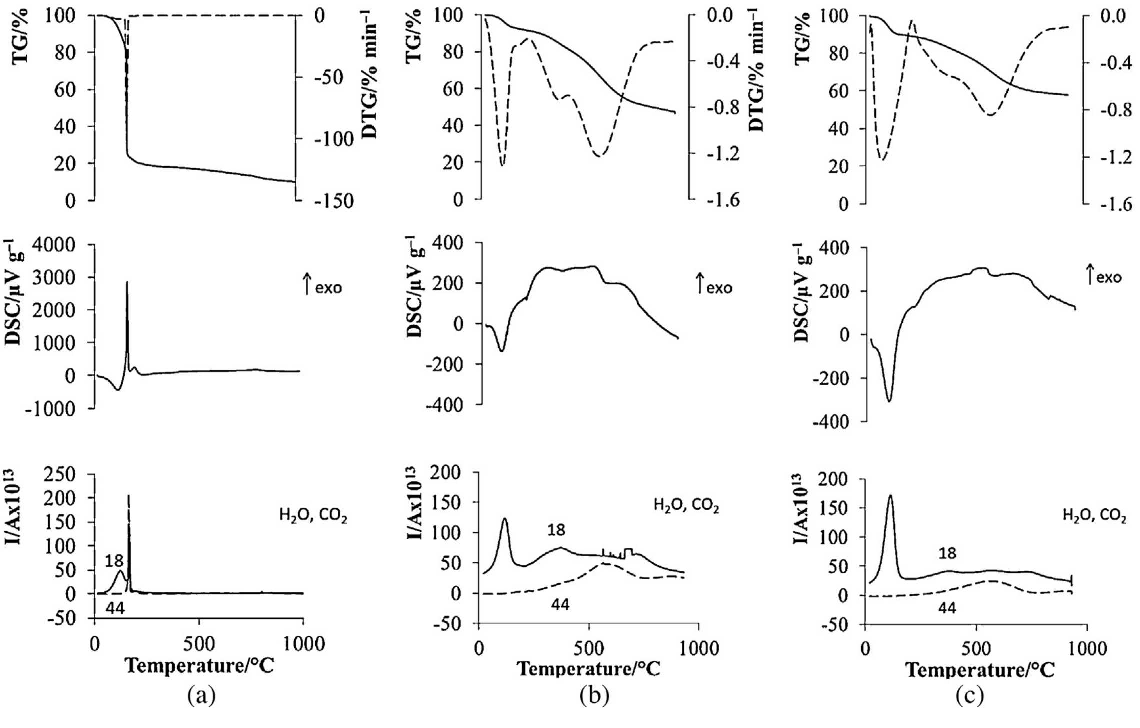

Fig. 1. TG–DSC/MS curves of pyrolysis of GO (a), RF (b) and RFGO (c).