Properties of novel spherical carbon adsorbents synthesized from phosphorylated polymeric precursors

Sylwia Ronka*

Faculty of Chemistry, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

ABSTRACT

Phosphorus-containing carbon adsorbents have been prepared by the carbonization and CO_2 activation of two sets of submicroporous phosphorylated styrene/divinylbenzene copolymers in various (H^+, Cs^+, Cu^{2+}, Co^{2+} and Fe^{3+}) ionic forms. These copolymers have been synthesized in the form of beads, using the suspension polymerization technique. The polymerization was carried out in the presence of heptane and toluene in order to obtain porous material and polymers were subsequently subjected to phosphorylation. The content of the phosphinic groups in the modified polymers is ca. 4 mmol/g. Thermal degradation of the polymer precursors was monitored using thermogravimetric analysis. It was found that the carbonization yield is ca. 20% for the phosphinic acid forms and reaches ca. 60% for the various phosphinic acid salts. Scanning electron microscopy (SEM) was used to investigate the structure of the obtained carbon adsorbents. The metal ion in the phosphinic acid salt and porous structure of polymeric precursor determine the morphology and mechanical strength of the obtained carbon grains. Chemical composition were investigated using XPS, XRD and pH titrations methods. The characteristics of the porous structure of the polymer precursors and carbon materials were obtained by benzene and CO_2 adsorption. The resultant carbon adsorbents are predominantly microporous and their specific surface area is in the range of 300–1500 m^2/g depending on the ionic form and the porosity of polymeric precursors.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Activated carbons are often produced from various raw materials such as charcoal, wood peat and various kinds of stones or nut shells. Depending on the precursors, activated carbons posses different surface characteristics, including surface functional groups, surface area, porosity and pore size distribution. The shape of activated carbon affects its characteristics and performance to a great extent. Typical activated carbons are obtained in the form of granules and exhibit a wide distribution of pore size, low adsorption rate and poor mechanical strength [1]. Better adsorptive properties and lower pressure drop in column experiments are observed for carbon adsorbents having spherical shape. For the preparation of activated carbon spheres, some polymers, mainly strongly acidic ion-exchange resins and highly crosslinked polymeric adsorbents are used [1–7]. These materials have unique properties like well-defined macromolecular structure, reproducible characteristics and controlled pore size, stability in both acidic and basic media, as well as good mechanical and thermal properties, so they can

be applied as adsorbents in many separations, as catalyst supports and adsorbents for gas storage. The most important advantage is that spherical carbons obtained from polymers show good hydrodynamic properties, especially useful in separation applications e.g. for chromatographic purposes [3] as well as little resistance to the diffusion of liquids and gases, when used in a fixed-bed reactor because they can be packed into the bed homogenously [1,8].

Carbons are normally manufactured by carbonizing a carbon source under an inert atmosphere followed by further heating in the presence of chemical (H_3PO_4, $ZnCl_2$, KOH) or physical (CO_2, steam) agents, which activate the material, resulting in the increase of the adsorption capacity of the carbon. The chemical reagents may promote the formation of crosslinks, leading to the formation of a rigid matrix, less prone to volatile loss and volume contraction upon heating to high temperature [9,10]. The phosphoric acid [9–15] and another compounds containing phosphorus [14,16] are widely used in chemical activation. It is well known that by adding phosphorus compounds the yield at the activation treatment of the carbon material can be increased as well as the strength, abrasion, resistance and adsorptive properties of resultant material [14,17]. By adding phosphorus, the reaction of phosphorus and carbon produces diversified products that are continuously removed from the surface and create pores [14]. The introduction

* Tel.: +48 71 3203 871; fax: +48 71 3203 678.
E-mail address: sylwia.ronka@pwr.edu.pl

of phosphorus atoms results in the formation of complex oxygen-phosphorus compounds on the carbon surface [18]. These carbons possess acidic character and show considerable cation-exchange properties similar to those of oxidized carbons [15].

Phosphorus may also be introduced to carbons by using ion-exchanged resin containing the reactive phosphoric groups as polymeric precursor [19]. This method leads to spherical carbon adsorbents containing much fewer mineral impurities than it is observed in H_3PO_4 activation. Also, the considerably large amount of mineral species contained in coal generally restricts the porosity development in activated carbons [20]. Therefore, the carbonization of polymeric precursors allows to decrease the ash content in final product, which results in the increase of mechanical strength of the carbon [10]. The application of cation-exchange resins in manufacturing of carbon adsorbents makes possible the introduction of metal ions, by means of which the control of the pore structure of the carbons is possible [5].

In recent work [19] the carbonization of phosphorylated S/DVB gel-type (non-porous) resins substituted with metal cations (Cs^+, Cu^{2+}, Co^{2+} and Fe^{3+}) have been described. It was confirmed that the ionic form of polymeric precursor have an influence on the yield of carbonization and the physical properties of prepared materials. Based on those results, it has been decided to explore in greater details the chemical composition of polymeric precursors and additionally the effect of their porous structure on the properties of obtained carbon materials.

2. Material and methods

2.1. Preparation of the polymer precursors

The starting materials: styrene (S) and divinylbenzene (DVB) copolymers were prepared by typical suspension polymerization using 0.5 wt.% of benzoyl peroxide as initiator. The nominal crosslinking degree of S/DVB copolymers (R1 and R9) was 20 wt.%. Synthesis of polymers was carried out in the presence of inert diluents in order to obtain porous structure. The applied mixture of inert diluents was: heptane/toluene 1:9 v/v (for resin R1) and 9:1 v/v (for resin R9). After polymerization the polymer beads were washed with hot and cold water, acetone and dried. Then, the polymer was swollen in toluene and extracted with this solvent for 9 h in a Soxhlet apparatus.

Both types of S/DVB copolymers were modified by phosphorylation. Thus, dry polymer beads were placed in a round bottom flask together with an excess of PCl_3 and swelled for 30 min. Then, powdered aluminum chloride was added and the entire mixture was refluxed for 6 h. After that time beads are filtered off, washed briefly with dioxane and dropped into a beaker containing ice and sodium chloride solution. After washing with distilled water the beads were transferred to a ca. 3 M NaOH solution and left in it overnight followed by standard conditioning with distilled water, 1 M HCl, distilled water, 1 M NaOH, distilled water, 1 M HCl and finally with distilled water. Thus obtained resins contain phosphinic acid groups.

Metal ions were introduced to the phosphorylated polymer using an aqueous solution of CsOH, $Cu(NO_3)_2$, $Co(CH_3COO)_2 \times 4H_2O$ and $Fe(NO_3)_3 \times 9H_2O$ and applying 2 × metal ions excess in respect to phosphinic groups. After the ion exchange treatment the resins were washed with deionized water to in order to remove the excess cations and then dried.

2.2. Carbonization and activation

Approximately 6 g samples were thermally treated in quartz tubes in horizontal carbonization furnace. Carbonization experiments were carried out under a 100 ml/min argon flow. The samples were first heated to 110 °C at a rate of 11 °C/min and held at that temperature for 0.5 h to stabilize. Then, they were heated to 850 °C at a rate of 0.83 °C/min, kept for 0.5 h at the final temperature, and then cooled to room temperature under an Ar stream. Finally, chars have been CO_2 activated at 850 °C to 10% burn off.

2.3. Methods

Acid capacity was measured by immersing a known amount of the centrifuged polymer (in the protonated form) in 50 ml of 0.1 M sodium hydroxide solution for 24 h and titrating the resultant solution with 0.1 M hydrochloric acid. Water regain of the resins was measured using centrifugation method.

The phosphorus content in the polymer precursors and in carbon materials was determined by digesting a sample (ca. 20 mg) in a hot concentrated sulfuric acid followed by analysis of the solution using the standard molybdate blue method. Readings were taken at 700 nm.

Metal concentration was measured (after mineralization of resin and carbon samples (ca. 0.1 g)) using atomic absorption spectroscopy method on a Perkin-Elmer AAnalyst 100 with wavelength set at 324.8, 240.7, 248.3 nm for Cu(II), Co(II), Fe(III), respectively, and using atomic emission spectroscopy with wavelength 852.1 nm for Cs(I).

The pyrolysis behavior of the polymer precursors was determined by thermogravimetry using a Netzsch STA 409 C analyzer. Thermal stability was monitored by heating the samples at 3 °C/min to 850 °C in an inert argon atmosphere.

Morphological features of polymer and carbon samples were obtained with a scanning electron microscope (JEOL, JSM-5800LV).

The crystal structure of carbon materials were examined with an X-ray diffractometer (XRD, Siemens D5000). The X-ray diffraction patterns were obtained using Cu $K\alpha$ radiation (λ = 0.15409 nm). Data were collected at 2θ from 5 to 60° with a step size of 0.2° min^{-1}.

The chemical composition of the carbons and state of phosphorus atoms were investigated by X-ray photoelectron spectroscopy (XPS). XPS has a sampling depth which depends on the material density but it is around 10 nm for organic/polymeric materials and ca. 3–5 nm for metal/oxide materials. XPS experiments were carried out using SPECS UHV System equipped with PHOIBOS 100 spectrometer and SPECLAB software. X-ray was generated using Mg anode operating at 100 W (wide angle scan) and 200–300 W (high resolution spectra). The spectrometer energy scale was calibrated using Au ($4f_{7/2}$), Ag ($3d_{5/2}$) and Cu ($2p_{3/2}$) lines at 84.2, 367.9 and 932.4 eV, respectively. The analyzer mode was set on constant serving of energy of 30 eV (survey scan) and 5 eV (narrow scan). The detection angle was normal near the surface. The base pressure in the UHV analysis was below 1×10^{-9} mbar. The peaks were fitted and derived with SPECSLAB and Origin 7.0 professional software packages using Gaussian–Lorenzian curve profile and Shirley baseline.

The pH titrations of activated carbon samples were carried out using the method described by Helfferich [21]. A set of samples was prepared with successively larger amounts of 0.1 M NaOH and/or HCl added to the different samples using a micro-pipette. 10 milliliters of 0.1 M NaCl solutions was added to each flask to keep a high background electrolyte concentration. A total batch volume of 15 ml was made up by adding distilled water to maintain the solution volume to sorbent weight ratio constant. The pH of these solutions were measured as blank. Samples of (75 mg each) powdered carbons were weighed into the flasks. The flasks were stirred for 48 h. Finally, the equilibrium pH of the solutions were measured.