Morphology and acid–base properties of porous carbon derived from poly(ethylene terephthalate) by nitric acid treatment

Abstract Activated carbon prepared from poly(ethylene terephthalate) was treated with nitric acid at ambient temperature and at the boiling point of the suspension. The morphology of the products was investigated by scanning electron microscopy, nitrogen adsorption observations and by small-angle X-ray scattering. The effect of acidic treatment on acid–base surface properties was studied by quasi-equilibrium potentiometric acid–base titration. It is found that the morphology of the products obtained after low-temperature treatment is similar, but high-temperature acid treatment induces a major reduction both in the surface area and in the fine pore structure. The intrinsic microporous character of the original carbon, however, is conserved. Both for the morphology and for the surface chemistry, the temperature of the treatment is more important than its duration. Nevertheless, while the morphology is affected significantly only at high temperature, the acid–base properties are modified in all the acidic treatments.

Keywords Activated carbon · Chemical treatment · Adsorption · Scanning electron microscopy · Small-angle X-ray scattering · Quasi-equilibrium acid-base titration

Introduction

The surface activity of carbon is affected not only by the porosity but also by the chemistry of the surface. Introduction of heteroatoms either into the graphene sheet or into the edge of the turbostratic layers may strongly influence the adsorption properties or the catalytic activity. Heteroatoms such as hydrogen, oxygen, nitrogen, halogens, sulfur, and phosphorus form nonstoichiometric stable surface compounds. Oxygen complexes formed when activated carbon is treated with various oxidative chemicals are the most frequent and most important among these surface groups.

The oxidizing agent, its concentration, the temperature and the time of the treatment influence the chemistry of the surface obtained. The oxidative treatment may, however, affect the morphology of the carbon structure as well. The aim of this paper is to reveal the effect of concentrated nitric acid treatment on both the morphology and the acid–base properties of an activated carbon prepared from poly(ethylene terephthalate) (PET).

Experimental

Sample preparation

Activated carbon (APET) was prepared from PET pellets [1, 2]. This activated carbon was treated with concentrated nitric acid at room temperature (RT) and at the boiling point (BP) of the carbon–acid suspension for 3 and/or 6 h. The acidic samples were then washed with distilled water and extracted in a Soxhlet apparatus until neutral pH was obtained. The samples were dried at ambient temperature.

References


Acknowledgments

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Further reading

The preparation and the notation of the carbon samples are listed in Table 1.

Morphology of the carbons

Scanning electron microscopy

Surface morphology investigations were performed using a JEOL 5500 electron microscope in low-vacuum mode with a secondary electron detector. The accelerating voltage was 20 kV and the working distance 20 mm. The magnification is indicated on each image. The samples were fastened to the copper sample holder by double-sided adhesive carbon.

Low-temperature nitrogen adsorption

Nitrogen adsorption/desorption isotherms were measured at 77 K and evaluated using a Quantachrome Autosorb-1 computer-controlled apparatus. (Quantachrome, Boynton Beach, FL, USA) The apparent surface area was derived using the Brunauer–Emmett–Teller (BET) model, \( S_{\text{BET}} \). The total pore volume, \( V_{\text{p, tot}} \), was calculated from the amount of nitrogen vapor adsorbed, \( V_{\text{ads}} \), at a relative pressure close to unity, on the assumption that the pores are then filled with liquid nitrogen. The average pore radius, \( r_m \), was derived from the total pore volume and the BET surface area on the basis of uniform cylindrical pores. The micropore volumes, \( V_{\text{mic}} \) and \( V_{\text{DR}} \), were computed by the Dubinin–Radushkevich (DR) and 1 methods (Halsey), respectively. The characteristic energy, \( E_0 \), was derived from the DR plot as well with \( \beta = 0.34 \). The slit size, \( L_0 \), was derived from the relation \( L_0 (\text{nm}) = 10.8/(E_0^{1/2}) \), proposed by Stoeckli for pores with \( L_0 < 1.8-2.0 \text{ nm} \).

Pycnometry

The AUTOSORB-1 was used to determine the true density of the samples with helium gas.

Small-angle X-ray scattering

Small angle X-ray scattering (SAXS) measurements were made on the BM2 beam line at the European Synchrotron Radiation Facility, Grenoble, France. To cover the wide q range required \((0.01 < q < 10 \text{ nm}^{-1})\), two different incident X-ray energies, 7.9 and 16 keV, were selected, with sample–detector distances between 30 cm and 210 m. A two-dimensional charge-coupled device detector was used (Princeton Instruments), with exposure times between 1 and 50 s, depending on the sample and the q range explored. Corrections were made for the detector dark counts and for background scattering from the mica windows of the sample cell.

Characterization of acid–base properties

The “fully automatic” \([3, 4]\) quasi-equilibrium acid–base titration was performed under a CO_2-free atmosphere using NaCl back-ground electrolyte. Carbon \((0.15-0.25 \text{ g})\) was suspended in 50 ml 0.01 M NaCl solution. Solutions were prepared from fresh Millipore water. The washed and hot water extracted carbon samples were immersed in the aqueous electrolyte solution and ultrasonicated for 15 min, then stirred and bubbled with purified nitrogen for 1 h. The initial pH was measured before the titration. A laboratory-developed computer-controlled titration system (GI-MET1) consisting of 665 Dosimat (Metrohm) burettes, nitrogen bubbling, a magnetic stirrer, and a high-performance potentiometer was used. The equilibrium criterion for continuation of the titration was conditioned by the pH stability of the suspension and arbitrarily set as \( \Delta \text{pH} \text{ min}^{-1} < 0.012 \). A Radelkis OP-0808P (Hungary) combination pH electrode was calibrated for three buffer solutions to check the Nernstian response. The concentration dependence of the hydrogen ion activity was determined from a background electrolyte solution titration, so that the electrode output could be converted directly to hydrogen ion concentration instead of activity.

The detailed description of the titration procedure for surface charge characterization of amphoteric solid particles is given elsewhere \([5]\). The reversibility of the titration was tested in a cycle of forward and backward titrations starting at the initial pH of the carbon suspension (pH~8.5 for original APET and pH~4.5-2.7 for the acid-treated APET samples), going down to pH 3 then up to pH 10, and finally returning to the lower pH limit. NaOH (0.1 M) and HCl (0.1 M) solutions were used in forward and backward titrations, respectively. Titration cycles were completed within 2–8 h, depending on the samples. The specific amount of proton surface excess \((\delta n'_+ \text{, millimoles per gram})\), i.e. the difference between the surface excess amounts of \( H^+ (n'_{H^+}) \) and \( OH^- (n'_{OH^-}) \), was derived directly from the initial and equilibrium concentrations of the solute \([6]\). The values of \( n'_{H^+} \) and \( n'_{OH^-} \) were calculated at each point of the titration, and \( \Delta \delta n' = n'_{H^+} - n'_{OH^-} \) was plotted as a function of the equilibrium pH.

Table 1 Sample preparation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acidic treatment</th>
<th>Temperature</th>
<th>Duration (h)</th>
<th>Extraction with water</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APET2002</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>APET2002 V</td>
<td>–</td>
<td>–</td>
<td>+</td>
<td>100</td>
<td>–</td>
</tr>
<tr>
<td>APET2002 H3SEN</td>
<td>Room temperature</td>
<td>3</td>
<td>+</td>
<td>100</td>
<td>–</td>
</tr>
<tr>
<td>APET2002 M3SEN</td>
<td>Boiling point</td>
<td>3</td>
<td>+</td>
<td>94.5</td>
<td>–</td>
</tr>
<tr>
<td>APET2002 H6SEN</td>
<td>Room temperature</td>
<td>6</td>
<td>+</td>
<td>110</td>
<td>–</td>
</tr>
</tbody>
</table>

Results and discussion

Morphology of the carbons

According to the adsorption/desorption isotherms in Fig. 1, the carbons have a microporous structure. The ratio of the microporosity exceeds 90%, except for the M3SEN sample. The boiling water extraction results in a small increase in the surface area and all relevant parameters, probably by removing water-soluble tarlike plugs from the pores.

The RT acidic treatments, as illustrated in the scanning electron microscope (SEM) images (Fig. 2), do not affect significantly the surface structure of the sample either on a macroscopic scale or at the nanometre