



Synthesis of carbon with bimodal porosity by simultaneous polymerization of furfuryl alcohol and phloroglucinol



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ABSTRACT

Carbon materials with bimodal porosity have shown enhanced performance in a wide variety of applications including catalysis, energy storage and fluid separation. Presence of mesoporosity is essential to lower the mass transfer limitation imposed by the microporous nature of the carbons. The synthesis approaches used to prepare bimodal carbons with controlled micro/mesopore size and narrow pore size distribution, usually involve multi step processes and the use of harsh chemicals and solvents. Herein, we present a simple one step method that can be used to synthesize carbon with bimodal pore size distribution. Simultaneous polymerization of furfuryl alcohol and phloroglucinol-formaldehyde in the presence of a structure-directing agent (Pluronic F-127) was carried out and the resultant polymer was pyrolyzed to yield the bimodal carbon. Effect of polymerization conditions such as concentrations of monomer, initiator and surfactant on the bimodal pore size distribution of the carbon was studied in detail. Pyrolyzed precursors form carbons with narrow mean micropore size of 0.5 nm and mean mesopores ranging from 3.5 to 6 nm. The range of the mesopore size could be altered by varying the polymerization parameters (acid and surfactant concentration) as well as selective oxidation using CO₂ gas.

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1. Introduction

Porous carbon materials possess unique properties such as high surface area, large pore volume, and good thermal stability. These characteristics make them suitable candidates for different applications including catalysis, gas separation, adsorption and electrodes in electrochemical capacitors for energy storage purposes [1–4]. To have acceptable performance in many applications, an interconnected porous structure with both meso and microporosity is necessary. The presence of meso and macropores facilitate mass transfer processes that are the controlling steps in many applications including membrane separation and catalysis. On the other hand, it is the micropores that provide high surface area and size selectivity at the molecular level in the adsorption process. Researchers have been using different methods to engineer the pore size and connectivity in carbon so as to tailor its properties and performance for different applications [5–13].

Carbons derived from thermosetting resins intrinsically contain micropores in the range of 0.4–0.5 nm. The porosity in these

carbons is the result of misalignment of the graphitic domains [2] and is created when the thermoset polymer is heat treated at temperatures higher than 300 °C but not above 800 °C. The micropore size of these carbons can be enlarged by either physical or chemical activation while maintaining a narrow pore size distribution [14–17]. Morphology and size of the carbon particles can also be controlled using structure-directing agents, for example during emulsion polymerization of the carbon precursor [18,19]. It has been shown that by decreasing the diameter of carbon spheres synthesized by the emulsion polymerization of furfuryl alcohol, mass transport of reactant and products inside the pores can be enhanced. This in turn improves catalytic activity in liquid phase hydrogenation reactions, while maintaining high selectivity due to microporosity [20,21].

To form pores in the mesopore range (2–50 nm) within polymer-derived carbons, it is necessary to use a template (either soft or hard) during the synthesis of the corresponding polymer [5,7]. Carbons produced via hard-templating route have interesting structures, but the post synthesis processing involves the use of harsh chemicals and the destruction of the rather expensive mesoporous inorganic oxide [8–11]. In soft-templating approach, the micellar structure formed by the self-assembly of the template molecules (usually block copolymers) is the origin of the mesoporosity in the final material [7,22–23].

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In applications such as heterogeneous catalysis, it has been shown that introducing a small amount of mesoporosity can improve the catalyst activity by an order of magnitude, through facilitated mass transport in mesopores. However, it is important to have narrow pore size distributions in both micro- and mesopore region to retain size and shape selectivity at the molecular level [20].

In the present study, we demonstrate that it is possible to use the soft-templating approach to develop carbons with well-defined bimodal pore distributions. This was made possible by simultaneous polymerization of two monomers (furfuryl alcohol and phloroglucinol) in the presence of a structure-directing agent (Pluronic F-127). The effects of polymerization conditions on the formation of micro- and mesopores were studied in detail and the role played by the surfactant molecule was elucidated.

2. Experimental

2.1. Synthesis of homo-polymers, polymer blends and polymer mixtures

Furfuryl alcohol and phloroglucinol were purchased from Sigma–Aldrich and used as received. Deionized water and ethanol were used as solvents in the synthesis of the polymers. An amphiphilic triblock copolymer (EO₁₀₆PO₇₀EO₁₀₆), Pluronic F-127, was used as the structure-directing agent (purchased from Sigma–Aldrich). Formaldehyde (37 wt% solution) and HCl (36 wt% solution) were used as linker and polymerization initiator, respectively.

To make mesoporous carbon, phloroglucinol was polymerized as described in Dai's work [23]. In a typical synthesis, 8.5 g water and 9.4 g of ethanol were mixed. 2.5 g of pluronic F-127 and 2.5 g of phloroglucinol were then added to this solvent. After complete dissolution of the solid powder in the solvent, 0.2 g HCl was added as the polymerization initiator. After 30 min of stirring, 2.6 g formaldehyde was added and polymerization was continued for an additional hour. At this step, phase separation occurred and water rich phase (upper phase) was removed. The polymerization continued for an additional 12 h at room temperature; then the polymer was placed in an oven at 100 °C for 12 h. Finally the resultant polymeric solid was pyrolyzed at 850 °C under an argon atmosphere. The mesoporous carbon made using phloroglucinol is referred to as Ph-C. A sample was synthesized under exactly the same conditions with furfuryl alcohol. Basically, all other parameters and amounts were kept constant except that 2.5 g of furfuryl alcohol was added instead of phloroglucinol. This sample is referred to as FA-Plu-C. To study the effect of surfactant, furfuryl alcohol alone was polymerized in a water/ethanol solution under the same conditions used for preparation of FA-Plu-C, but without any surfactant (FA-C).

Both monomers were also simultaneously polymerized as follows: 8.5 g of water was mixed with 9.4 g of ethanol. To this solution, 2.5 g pluronic F-127 and 2.5 g phloroglucinol were added. After complete dissolution of the solid powders in the solvent mixture, 0.2 g HCl was added and the solution stirred for few minutes; this was followed by addition of the second monomer: furfuryl alcohol. The solution was stirred for 30 more minutes until the color turned to light pink. At this point, 2.6 g formaldehyde was added to the solution and the polymerization was continued for an additional hour after which phase separation occurred with the polymer-rich phase in the bottom of the beaker and water-rich phase above. The water-rich phase was separated and polymerization in the polymer-rich phase was continued overnight (almost 12 h). The result of the polymerization was a rubbery polymer film that was placed in an oven at 90 °C for 12 h. The dried polymer was pyrolyzed at 850 °C for 5 h to obtain porous carbon (FA-Ph-C). In another experiment, in order to make a physical blend of the two homopolymers, 1 g of synthesized PFA was added to solution during the polymerization of phloroglucinol; this was done in the

presence of pluronic F-127 (2.5 g) using 0.2 g HCl as initiator and 2.6 g of formaldehyde as the linker (PFA-Ph-C). The effects of polymerization conditions on porosity of the resultant carbons were studied by varying the concentration of the monomers, acid and surfactant.

2.2. Characterization of synthesized polymers and carbon

Field Emission Scanning Electron Microscopy (FEI Nova Nano-SEM 630) was used to examine the morphological and textural properties of the synthesized polymers and carbons. Field Emission Transmission Electron Microscopy (JEOL 2010F) was used to image the carbon structure and the pore arrangement. The pore size distribution and the total pore volume of the synthesized carbon samples were determined by methyl chloride gas adsorption combined with the Horvath-Kawazoe model for micropore region [24] and the Kelvin equation for mesopore region. The BET surface areas were measured using nitrogen gas adsorption in a Micromeritics (ASAP 2020) instrument.

3. Results

3.1. Characterization of homopolymer-derived carbons

Our previous studies have shown that carbons derived from polyfurfuryl alcohol by acid-catalyzed polymerization results in a microporous material with a narrow pore size distribution centered around 4–5 Å [19,24]. In this study, we have synthesized PFA in a water/ethanol solvent both with and without Pluronic F-127. As seen before, PFA made without surfactant present, was purely microporous with a pore size around 0.5 nm [25]. However, the PFA synthesized in the presence of surfactant (FA-Plu-C), had both micropores similar to PFA and a broad mesopore distribution ranging from 2 to 20 nm as shown in Fig. 1. As can be seen in this figure, when PFA is synthesized without surfactant (Fig. 1c), a rather smooth monolithic carbon structure without any mesopores is obtained upon pyrolysis. In the sample made with surfactant, the existence of mesopores is evident from FESEM image (Fig. 1d), which can be attributed to the gaps between small carbonaceous domains that are agglomerated during pyrolysis. The micropore volume of FA-Plu-C (0.12 cc/g) was slightly less than FA-C (0.18 cc/g) while significant mesopore volume ~0.064 cc/g (35% of total porosity) was generated. (see Table 1).

The effect of acid concentration on the pore size distribution was also studied. In general, the micropore volume increased from 0.09 cc/g to 0.15 cc/g when the acid concentration was increased from 0.04 M to 0.18 M, as shown in Table 2.

Phloroglucinol-derived carbon was predominantly mesoporous with narrow pore size distribution centered on 8.2 nm and a small volume of micropores centered at about 0.6 nm. The mean mesopore size was a strong function of the acid concentration, while the micropore size and volume were invariant. By increasing the HCl concentration from 0.04 M to 0.18 M, the mean mesopore size can be increased from 4.7 to 11 nm. The total mesopore volume also scaled with increase in acid concentration with the cumulative pore volume reaching 0.7 cc/g, as shown in Fig. 2a and b. The porous texture of the carbon was examined using FESEM and STEM imaging as shown in Fig. 2c and d, respectively. The interconnected mesoporosity in these carbons can be visualized as the gaps between dense carbon domains, as depicted in both dark and bright field TEM images (Fig. 2d).

3.2. Characterization of bimodal porous carbons

Next, we systematically varied the relative amounts of furfuryl alcohol and phloroglucinol while keeping the concentrations of

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