SYNTHESIS AND CHARACTERIZATION OF CARBON-MODIFIED SILICA GELS AND SILICA-TEMPLATED CARBONS FOR LIQUID CHROMATOGRAPHY

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Introduction

There is a strong interest in developing purely mesoporous carbons for liquid chromatography separations. Knox et al. [1] reported that porous carbons could be prepared by impregnating silica gel with phenol and hexamine followed by polymerization, carbonization, and dissolution of the template. This technique rendered a mesoporous carbon of rigid structure featuring also some micropores, having surface area of 500 m^2/g and pore volume of 2 cm^3/g. Graphitization of this material resulted in a porous graphitized carbon, which had been successfully used in chromatographic separations [2].

In this work the mesophase pitch and polyacrylonitrile (PAN), which are commonly used for preparation of carbon fibers, were used as carbon precursors. Since an intrinsic feature of carbon fibers is very low surface area [3], a combination of the carbon fiber technology with the Knox's templating method [1] allowed us to obtain almost purely mesoporous carbons. It should be noted that the petroleum pitch and PAN were used as precursors to prepare mesoporous carbons via catalytic activation with transition metal compounds but the mesoporosity counted for about 60-80% only and the metal compounds were not removed (see references in [4]).

Experimental

The synthesis of mesoporous carbons was performed using the Lichrosper Si 100 silica as template and a synthetic mesophase pitch (s.p. 237 ^oC, Mitsubishi) or acrylonitrle as carbon sources. The mesophase pitch was first treated with quinoline and only soluble components were used. Then, the silica was impregnated with quinoline solution of the mesophase at 100-250 ^oC and later the solvent was allowed to evaporate slowly. In the case of the mesoporous carbon obtained from acrylonitrile, the silica was impregnated with DMSO solution of acrylonitrile, which was allowed to polymerize under protection of an inert gas at 40-80 ^oC. The stabilization process for both kinds of impregnated silicas was the same. Both were stabilized in air between 180-330 ^oC for 24 hours. The stabilized sample was then carbonized at 1000 ^oC under nitrogen protection for 2 hours. The silica template was removed by using a hot sodium hydroxide solution. Then, the resulting carbons were thoroughly washed and dried.

Results and Discussion

Shown in Figure 1 are nitrogen adsorption isotherms at –196 ^oC for the initial silica sample, silica with coated mesophase pitch (M-Silica) and the resulting carbons (M-Carbon and PAN-Carbon) obtained by dissolution of silica from the mesophase pitch and PAN-coated samples. These isotherms exhibit gradually increasing hysteresis loops, which reflect quite broad distribution of mesopores. The corresponding pore size distributions (PSD) are shown in Figure 2. The distribution for the silica sample was calculated by the BJH method calibrated for a series of the MCM-41 samples [5]. As can be seen from Figure 2 the pore width at the maximum of PSD is about 19 nm, which is ~5 nm greater than the value obtained by commercial BJH software. PSDs for the remaining samples were obtained by using the BJH method with the statistical film thickness for the carbon surface. The latter was obtained by fitting the multilayer range of the standard data [6] to those reported in [7]. As can be seen from both figures the impregnation of the silica with the mesophase pitch and PAN reduced significantly its porosity but did not fill completely mesopores. Therefore, the mesoporosity of the resulting carbons arose from dissolved silica framework as well as from the incompletely filled silica mesopores.

Shown in Figure 3 are the α_s-plots for the pitch-silica sample as well as for the M- and PAN-carbons. These plots were prepared by using the standard adsorption data for nitrogen on non-graphitized carbon black [6]. The α_s-plot analysis showed that the presence of micropores in the carbons studied was very small, i.e., below 1-2%.

In conclusion, mesoporous carbons were prepared by combining silica templating and carbon fiber fabrication procedures. These carbons reflected not only the mesoporous structure of the silica template but also exhibited the surface properties analogous to those of carbon fibers and as latter they were practically non-microporous [8].

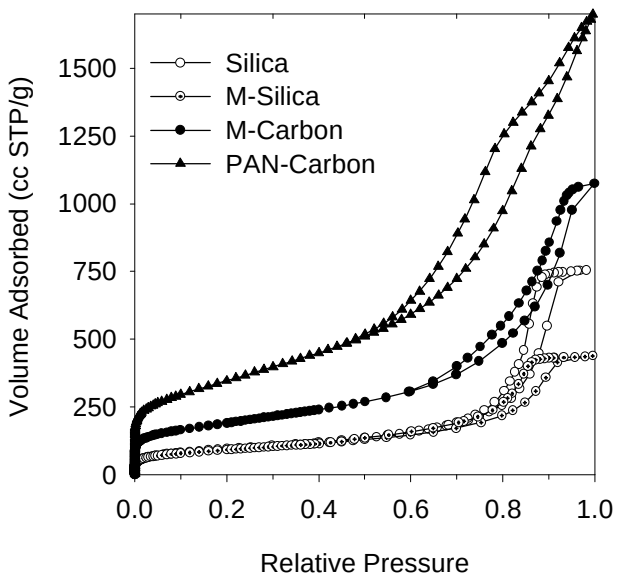

Figure 1. Nitrogen adsorption isotherms for the initial silica, the mesophase pitch-silica hybrid (M-Silica) and the mesoporous carbons obtained by dissolving silica from the hybrid samples at –196 ^{o}C.

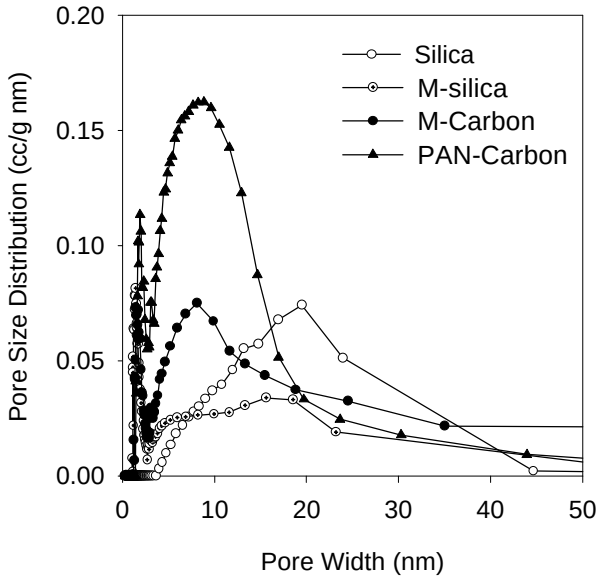

Figure 2. Pore size distributions for the initial silica, the mesophase pitch-silica hybrid (M-Silica) and the mesoporous carbons obtained by dissolving silica from the hybrid samples calculated according to the BJH method from nitrogen adsorption isotherms shown in Figure 1.

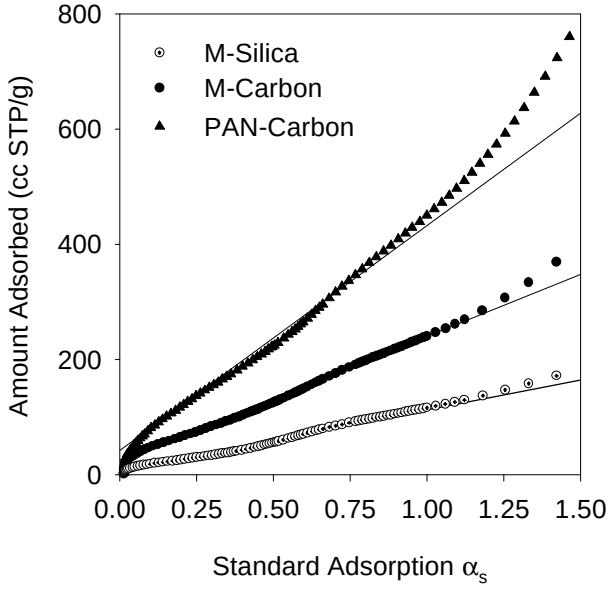

Figure 3. The α_s-plots for the samples studied prepared by using standard adsorption data reported in [6].

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