

ADSORPTION CHARACTERIZATION OF ACTIVE CARBONS MODIFIED BY DEPOSITION OF SILICA

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Introduction

Surface properties carbonaceous materials are often modified by chemical deposition in order to expand the range of their applications [1]. However, the exact nature of the chemical deposition process is not completely understood. The layers of deposited material may exhibit a high degree of inhomogeneity, which results in inadequate performance of the modified material in the targeted applications. The goal of the current work is to improve our understanding of the chemical deposition of silica on the carbon surface.

Experimental

Materials. Active carbon used for preparation of the silica-carbon (SC) hybrids was obtained from Calgon Carbon Corporation. Silicon tetrachloride used for surface modification was purchased from Aldrich.

Chemical deposition. The SC materials containing various amounts of deposited silica were prepared by multi-cycle chemical deposition. Each deposition cycle consisted of two steps: 1) adsorption of silicon tetrachloride onto the surface of carbon particles; 2) conversion of silicon tetrachloride into silica via the reaction with water vapor. Details on the deposition method can be found elsewhere [2].

Adsorption measurements. Prior to sorption measurements the SC samples were outgassed at 200°C for 2 hours under the vacuum of 10^{-4} Torr. Measurements of nitrogen adsorption isotherms were carried out at -195.5°C using a model ASAP 2010 (Micromeritics, Inc., Norcross, GA), high-resolution volumetric sorption analyzer.

Calculation methods. The standard analysis of adsorption isotherms included evaluation of the specific surface area according to the BET method [3], the total pore volume according to the single point method [3], and the micropore volume analysis by the t-plot [3].

Advanced numerical algorithms based on the regularization procedure were used to evaluate the pore size and the adsorption energy distributions for the SC

samples. The pore size distributions were evaluated using the entire range of the adsorption isotherms employing the DFT software [4]. The adsorption energy distributions (AEDs) were calculated from the submonolayer range of the adsorption isotherms using the INTEG software [5]. The local adsorption was modeled by Fowler-Guggenheim equation for patchwise distribution of adsorption sites.

Results and Discussion

Adsorption isotherms for the selected SC samples are shown in Figure 1. As can be seen an increase in the amount of the deposited silica causes decrease in the adsorption capacity of the samples (see also Table 1).

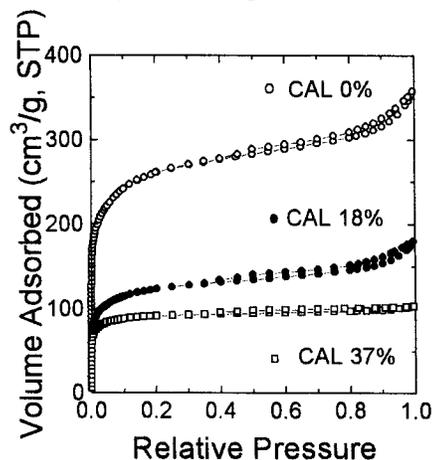


Figure 1. Nitrogen adsorption-desorption isotherms on the SC samples at -195.5°C.

Moreover, adsorption isotherms for the SC hybrids containing up to 34% of silica exhibit a pronounced hysteresis loop, which indicates on the presence of mesopores in the porous structure. However, the samples containing 37% of silica (or more) practically do not show hysteresis loop. It may indicate that for these samples the mesopores are practically blocked.

These findings are in a good agreement with the values of the micropore and total pore volumes (Table 1).

For the samples containing more than 34% of silica, a further deposition practically does not effect the micropore volume, while the total pore volume approaches the volume of micropores.

Table 1. Characterization of the modified carbons.

SiO ₂ %	S _{BET} m ² /g	S _{EXT} m ² /g	V _{TOTAL} cm ³ /g	V _{MICRO} cm ³ /g
0	870	116	0.53	0.36
11	724	76	0.42	0.31
18	485	63	0.26	0.18
34	403	25	0.21	0.17
37	295	17	0.16	0.14
41	303	14	0.15	0.14
42	284	8	0.14	0.13

Analysis of the pore size distributions clearly shows a gradual decrease in mesoporosity. As can be seen from Figure 2, the deposition of silica mostly occurs in the mesopores. Thus, the CAL 37% sample practically has no mesopores.

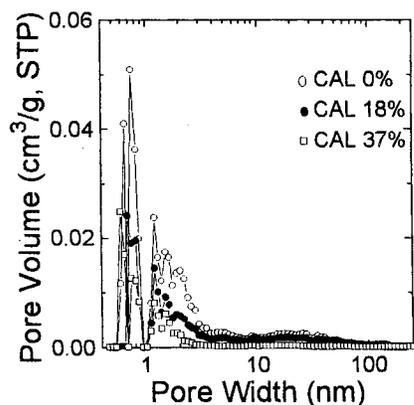


Figure 2. Pore-size distributions for the SC samples.

Additional information about the influence of the chemical deposition on the surface energetics was obtained from the analysis of the adsorption energy distribution functions for the SC samples. Typically, the AED for a microporous sample contains two peaks: a high energy peak that may be related to adsorption in the micropores, and a low energy peak that may correspond to adsorption in the mesopores (see AED for CAL 0% in Figure 3). As the amount of silica increases the energy spectrum undergoes certain changes. As can be seen from Figure 3, the AED for the CAL 37% sample has no low energy peak, which may indicate an absence of active sites related to adsorption in mesopores. The high energy peak has a broad shape, which can be attributed to micropores.

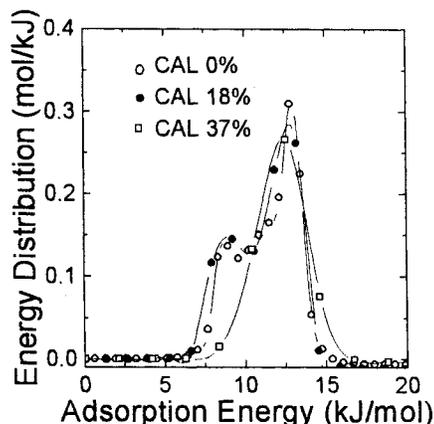


Figure 3. Adsorption energy distribution functions for the SC samples.

Conclusions

The analysis of the structural and surface properties for a series of the SC materials showed a gradual decrease in mesoporosity caused by the deposition of silica on the external surface of mesopores (Table 1). The changes in the microporous structure seemed to be smaller than those related to mesopores. Fine micropores appeared to be inaccessible to relatively big molecules of silicon tetrachloride. A consecutive deposition of silica increased the thickness of the mesopore walls, causing the blockage of some micropores, and finally led to the complete filling of small mesopores.

A comparison of the AED functions for silica-modified carbon samples shows a gradual decrease in their energetic heterogeneity with the increasing amount of deposited silica. It appears that the deposition of silica influences mainly the low energy part of the AEDs due to a gradual filling of the mesopores. The current work demonstrates the utility of the AED analysis for investigating the silica deposition process on active carbons and for characterizing the gradual changes in the porous structure of the resulting hybrid materials.

References

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