INVERSE GAS CHROMATOGRAPHIC APPROACH OF ADSORBENTS OBTAINED BY CHEMICAL TREATMENT

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Introduction

Most porous solids are interesting because of their high adsorption capacity and allows their use in many industrial processes. Among these materials the active carbons usually contain a wide range of pores of different size and shape. Furthermore, the surface energy for porous materials may be dependent on the geometric curvature of the surface. Inverse gas chromatography (IGC) is one of the most convenient methods for studying the gas-solid interface providing thermodynamic parameters of adsorption. So the surface energy of solids can be measured using IGC at infinite dilution (IGC-ID) according to Gray's method [1].

Experimental

Two commercial active carbons (A, B) were selected for this study. A and B were obtained by chemical activation with phosphoric acid starting from wood material. It was noticed that sample A was already impregnated with H_3PO_4 therefore A was washed with distilled water in a Soxhlet apparatus during 8 hours and oven-dried at 110 °C and so denoted AW.

Changes in the surface chemistry were also monitored using Diffuse Reflectance Infrared Fourier Transform (DRIFT) BIO-RAD FTS 185.

The chromatographic experiments were performed with a CP 9001 apparatus (Chrompack) equipped with a flame ionization detector. The stainless steel columns were filled with carbon particles of size ranging 0.1-0.2 mm. The experimental temperature was 250°C and helium was used as a carrier gas with a flow rate of about 30 ml/min.

Results and Discussion

Treatment with phosphoric acid was found to promote an expansion of the wood structure and chemical modifications. Structural parameters calculated from sorption of benzene and carbon dioxide are collected in Table 1. The BET surface areas range from 1704-1967 m^2/g and samples showed a trace amount of desorption hysteresis, indicating some mesopore character. Elemental analysis of the above carbonaceous materials (Table 2) revealed high oxygen contents (between 8.99 and 24.5 wt %) due to the chemical activation process and specially for sample A which had a remainder of phosphorus (5.78 wt %).

The dispersive component of surface energy γ_s^d and the adsorption free energy ΔG_{CH2} was calculated from the exponential relationship [2] of the net retention time versus number of carbon atoms for alkanes from pentane to octane (Figure 1). Inverse gas chromatography results are reported in Table 3. Activated carbons leads to high values of γ_s^d, between 202 and 244 mJ/m^2. Moreover γ_s^d increases after sample A was washed in distilled water; the value then become 242 mJ/m^2. It can be noted that the increasing of γ_s^d value is quite similar to the BET surface evolution (~15%). IGC-ID surface measurements can be considered as a good indicator of the evolution of the non-specific surface energy of active carbon.

Examination of the DRIFT spectra (Figure 2) confirms the loss of impregnated acid phosphoric indicated by the disappearance of a band at 990 cm^{-1} which was attributed to phosphates.

Conclusion

IGC appears to be a most sensitive and well-suited method for the characterization of solids with surface as complex as those of active carbons. Mesoporous materials are distinguished by their high dispersive component of surface energy γ_s^d corresponding to the average of the high adsorption energy sites.

References

1 GM Dorris, DG Gray, J. Colloid Interface Sci. 1979;**71**:93.
2 Watzig H, Ebel S, Holley A, Fresenius J. Anal. Chem. 1992;344:354-356.

Table1. Structural characteristics of Active Carbons

Sample	V micro (cm^3/g)	V meso (cm^3/g)	S_{BET} (m^2/g)
A	0.6	0.638	1726
AW	0.648	0.722	1967
B	0.497	0.779	1704

Table 2. Elemental analysis

Sample	C (%)	H (%)	O (%)	P (%)
A	63.4	3.1	24.5	5.78
AW	73.5	2	18.5	1.1
B	82.96	2.5	8.99	1.06

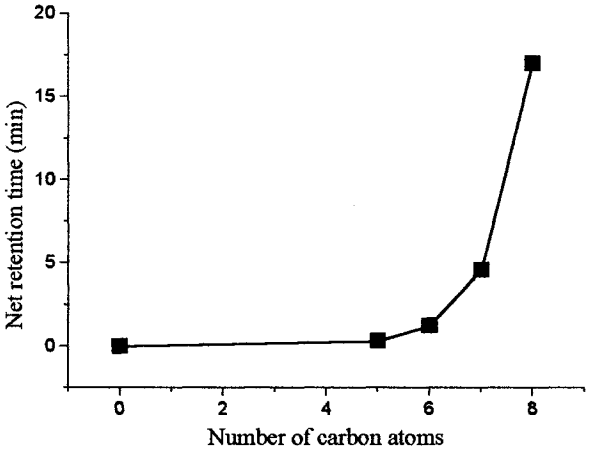

Figure 1. Typical evolution to apply Wätzig algorithm

Table 3. Inverse gas chromatography results at 250°C

Sample	ΔG_{CH2} (kJ/mol)	γ_S^D (mJ/m^2)
A	4.85	202
AW	5.3	242
B	5.32	244

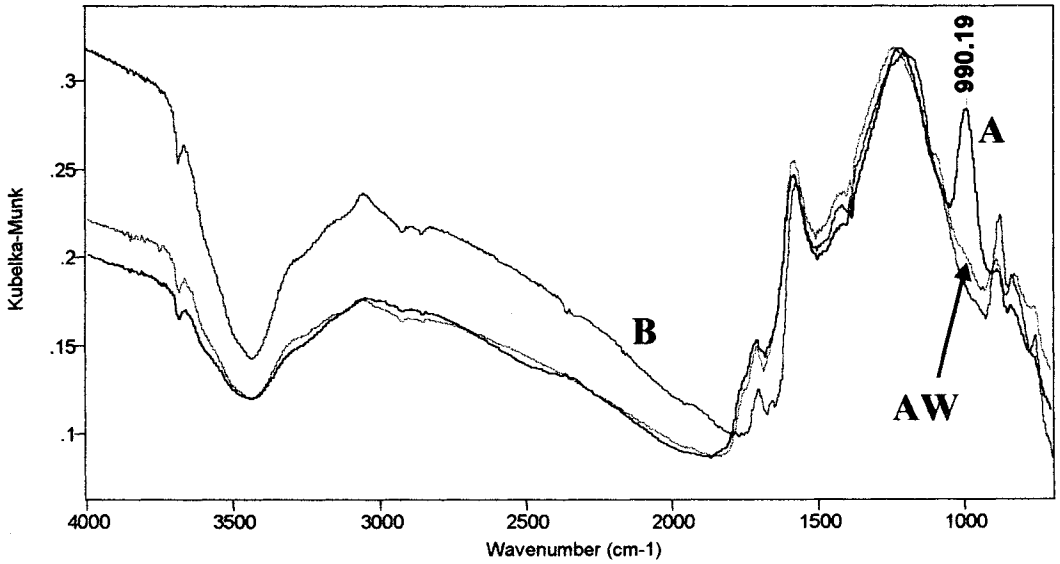

Figure 2. DRIFT spectra for active carbons