

Characterization of Charcoals by Adsorption and Immersion Techniques

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Introduction

Charcoals have been obtained by carbonization in the presence or the absence of potassium hydroxide of low rank coal (1). In the present paper the micropore size distribution of these charcoals is described.

Experimental

A low rank coal (Menouna, Algeria) has been carbonized in the presence of KOH as described elsewhere (1). The KOH content before carbonization was 33 % by weight. After isothermal heat treatment at 1073 K for 1 hour the potassium salt was eliminated by refluxing in diluted HCl solution and then washed in distilled water (sample M-T). A coal sample M was also carbonized in absence of KOH.

Adsorption isotherms of CO₂ at 273 K were carried out volumetrically using a Micromeritics 2100 D equipment. Enthalpies of immersion at 307 K into benzene, n-hexane, cyclohexane, carbon tetrachloride and α -pinene were measured in a calorimeter of the Calvet type using a procedure described elsewhere (2).

Results and Discussion

Carbon Dioxide Adsorption. The adsorption characteristics of the charcoals have been determined by using the Dubinin-Astakhov equation,

$$W = W_0 \exp \left\{ - \left| \frac{RT \ln (p_0/p)}{\beta E_0} \right|^2 \right\} \quad (1)$$

where W_0 , E_0 and β are the well known parameters of the Dubinin theory. From the linear section of the Dubinin plots one obtains W_0 , the micropore volume and E_0 , the characteristic free energy for the adsorption of a reference gas. In the case of CO₂ the affinity coefficient β is equal to 0.414. The adsorption characteristics of the two samples are given in Table 1.

Table 1. Adsorption Characteristics of the Charcoals.

Charcoal	E_0 (kJ/mole)	W_0 (cm ³ /g)
M	24.2	0.17
M-T	25.4	0.39

It is seen that the micropore volume of sample M-T carbonized in the presence of KOH is two times larger than for the other sample.

Enthalpy of immersion. Stoeckli and Krähenbühl (2) have shown that the enthalpy of immersion of active carbon into organic liquids is given by the following equation, provided that the wetting of the external surface is negligible

$$-\Delta H_i \text{ (J/g)} = \beta W_0 E_0 (1 + \alpha T) \sqrt{\pi/2} V_m \quad (2)$$

where α = thermal expansion coefficient of the liquid filling the micropores and V_m = molar volume of the liquid. Hence, knowing β , α and V_m for a given liquid one may determine the volume of micropores W_0 filled by the liquid by measuring ΔH_i and using equation (2). The enthalpy of immersion of sample M into the liquids listed in Table 2 is negligible, indicating that only CO₂ can penetrate into the micropore system. Moreover, the contribution of the external surface to ΔH must be also necessarily negligible. The enthalpies of immersion of sample M-T as well as the micropore volume

Table 2. Enthalpy Immersion Characteristics of Sample M-T.

	$-\Delta H_i$ (J/g)	W_0 (cm ³ /g)	A (%)	ϕ nm
Benzene	126	0.37	95	0.37
n-Hexane	110	0.36	92	0.40
Cyclohexane	50	0.18	47	0.56
CCl ₄	44	0.13	34	0.60
α -Pinene	18	0.06	15	0.80

filled by each liquid are indicated in Table 2. The percentage A of volume filled by each liquid as compared to the total volume of micropore determined by CO₂ adsorption, is also given in Table 2 with the molecular size ϕ of each liquid.

It is seen that 95 % of the micropore volume determined by CO₂ adsorption is also available to benzene. Comparing this result to the one obtained for sample M, it appears that the presence of KOH during carbonization increases the width of the micropores. However, molecular sieve effects and/or a distribution of micropore sizes are still present since larger molecules like α -pinene are considerably less

adsorbed in the micropore system.

Conclusion

Carbonization of a low-rank coal in the presence of KOH increases the micropore volume of the resulting charcoal. A molecular sieve effect has been revealed for this type of charcoal.

References

1. P. Ehrburger, A. Addoun, F. Addoun and J.B. Donnet : this Conference.
2. H.F. Stoeckli and F. Krähenbühl, Carbon, 19, pp. 353-356, 1981.