POSTER

ANALYSIS OF N_2/77 K AND CO_2/273 K ADSORPTION DATA OF ACTIVATED CARBONS BY THE SIMPLEX FLEXIBLE METHOD.

A. Marcilla-Gomis[(a)], A.N. García-Cortés[(a)] and J.M. Martín-Martínez [(b)*]

(a) Department of Chemical Engineering. University of Alicante. Apartado 99. 03080 Alicante. Spain.
(b) Department of Inorganic Chemistry. University of Alicante. Apartado 99. 03080 Alicante. Spain.

INTRODUCTION

It has been widely shown[1,2] that the application of the Dubinin-Radushkevich (DR) equation to activated carbons gives a more pronounced deviation of the linearity as the burn-off increases.

On the other hand, the micropore volume (V_0) calculated from N_2/77K and CO_2/273K adsorption isotherms do not correlate adequately in activated carbons with a high degree of burn-off and the conventional method of calculation of V_0 by extrapolating the linear part of the DR plot may lead to uncertainties, especially for highly activated carbons.

Thus, the objective of this study is to apply a mathematical method for analyzing the N_2/77K and CO_2/273K adsorption isotherms on a series of CO_2 activated carbons, stating their advantages and limitations in the quantification of the microporosity of activated carbons.

EXPERIMENTAL

Olive stones were carbonized in nitrogen at 1123 K and activated in CO_2 at 1098 K for different periods of time. Activated carbons with burn-off degrees ranging from 8 % to 80 % were obtained. N_2/77 K as well as CO_2/273 K adsorption isotherms were determined. Details of the experimental method and the results obtained can be found elsewhere[3].

SUGGESTED PROCEDURE

In the present study, the overall adsorption isotherm has been represented by a single type of micropores (1-DR) or by a sum of two different types of micropores (2-DR). These ranges of micropores are considered to follow either the Dubinin-Radushkevich (DR) or the Dubinin-Astakhov (DA) equation. Consequently, the isotherms were fitted to an equation of the type:

$$W(\mathrm{mmol/g}) = \sum_{i=1,2} W_{oi} \cdot \exp\left[-B_i \cdot \left(\frac{R \cdot T}{\beta} \right)^{n_i} \cdot \ln^{n_i} \left(\frac{P^o}{P} \right) \right]$$

where: W is the amount of adsorbate within the pore structure at a relative pressure P/P^o; W_{oi} is the amount of adsorbate retained in a given range of micropores; B_i is a parameter related to the micropore size distribution; P^o is the saturation pressure of the adsorbate at the adsorption temperature; T is the adsorption temperature; β is the affinity coefficient; and n_i is the exponent of the DR or DA equations. β used was 0.33 (N_2/77K) and 0.35 (CO_2/273K).

The parameters W_{oi}, B_i and n_i have been optimized using a Simplex Flexible Method[4]. This is a method for nonlinear functions which minimizes the sum of the squares of the deviations. The selected objective function minimized in this study has been the following:

$$O.F. = \sum_i \left(W_{i,cal} - W_{i,exp} \right)^2$$

where the subscripts *cal* and *exp* represent the calculated and experimental values, respectively. Because the microporosity of activated carbons can be considered completely filled at P/P^o=0.4, only the adsorption data at P/P^o<0.4 have been considered in this study.

The results obtained showed that a single equation (one micropore distribution) does not properly represent the adsorption data within the 0-0.4 relative pressure range, especially in carbons with high burn-off while the two micropore distributions adequately represent the experimental adsorption data.

Different sets of W_0, B and n values may provide similar fittings of DR or DA equations and only a set of them (if any) has a real physical meaning. Nevertheless, if all the N_2/77K isotherms (or CO_2/273K isotherms) of the series of activated carbons are fitted together, the values of the optimized parameters obtained, which may be a function of the burn-off of each carbon, may have an improved physical meaning. To obtain these functions, separate fits must be carried out to obtain the general trends of the parameters of each carbon as a function of its burn-off degree, and furthermore representative empirical functions of such trends should be obtained. Afterwards, all the N_2/77K (and CO_2/273K isotherms) isotherms must be fitted together, expressing the corresponding

parameters as a function of the burn-off of the activated carbon. Figure 1 shows an excellent agreement between the experimental and calculated N_2/77K adsorption isotherms when two DR distributions of micropores are considered.

RESULTS

Table 1 shows the results obtained for V_{o1} and V_{o2} expressed as cm^3 of liquid/g_{carbon} (the following density values were considered: $\rho N_2(l)$ = 0.808 g/cm^3; $\rho CO_2(l)$ = 1.023 g/cm^3), obtained from the adsoption of N_2/77K (2-DR models).

DISCUSSION AND CONCLUSIONS

From the results obtained we may conclude that: *i)* some degree of overlapping exists in the microporosity measured by N_2/77K and CO_2/273K, *ii)* the microporosity measured with both adsorbates is heterogeneous, and *iii)* the narrow micropores measured with N_2/77K (2-DR model) consider two types of micropores which can also be evidenced by adsorption of CO_2/273K.

The results of this study also show that the 2-DR equation allows a clearer interpretation of the experimental results and a better agreement between CO_2/273K and N_2/77K adsorption data than 2-DA, probably as a consequence of the inter-relation between n and B in this model.

The exponent n of the DA equation in the series of activated carbons seems to be better correlated with the burn-off degree rather than with the parameter B of the DR equation.

The volumes of micropores obtained by N_2/77K (V_{o1}) and CO_2/273K (V_{o1} + V_{o2}) adsorption data are in good agreement when all isotherms are fitted together and using 2-DR equation (see Table 1).

Further information will be provided during the Conference.

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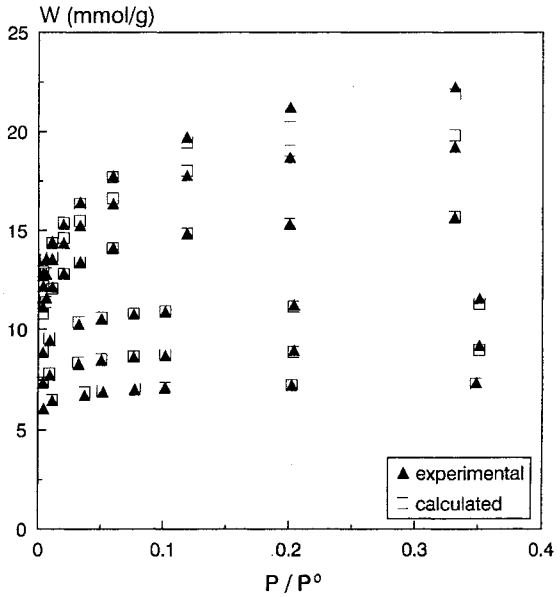

Figure 1. Agreement between experimental and calculated (2-DR) N_2/77K adsorption isotherm

Table 1. Micropore volumes of activated carbons (cm^3/g_{carbon}). DR equation.

	N_2/77K (2-DR Model)			CO_2/77K (2-DR Model)		
BD (%)	V_{o1}	V_{o2}	$V_{o1}+V_{o2}$	V_{o1}	V_{o2}	$V_{o1}+V_{o2}$
8	0.25	0.006	0.26	0.25	0.003	0.25
19	0.30	0.01	0.31	0.29	0.01	0.30
34	0.36	0.03	0.39	0.36	0.02	0.38
52	0.44	0.12	0.56	0.40	0.04	0.44
70	0.51	0.20	0.71	0.45	0.06	0.51
80	0.54	0.25	0.79	0.47	0.08	0.55