CHARACTERISATION OF ACTIVATED CARBON FIBER BY CO_2 ADSORPTION AT HIGH PRESSURE AND N_2 ADSORPTION ISOTHERM AT 77K

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Introduction

N_2 adsorption isotherm at 77K is by far the most commonly way of characterising adsorbents and the basic analysis methods give a good account for non porous materials. Their extension to microporous adsorbents is limited to surface area and mesopore size determination. If the micropore volume can be attained, attempts to extract pore size distribution (P.S.D.) from the nitrogen adsorption isotherm are for now inconclusive. Dubinin classical methods are specific of microporous materials, if they are also subject to objections, their application implies to dispose of a complete adsorption isotherm for covering all the range of micropores filling. Up to now few high pressure high temperature adsorption measurements are available. With a disposal of a high pressure volumetric device we'll show, using CO_2 as adsorbate, that it is possible to improve micropore characterisation. A comparison is with N_2 adsorption measurements at 77K is made.

Experimental

The activated carbon fiber KF1500 was provided by TOYOBO Co. The high pressure volumetric device operates from 253K to 363K under pressure up to 20 bar. The N_2 adsorption isotherm was collected using an automatic sorption instrument ASAP 2000M (micromeritics).

Results and discussion

For CO_2 the density of the adsorbed phase for each temperature was evaluated following the OZAWA relation [1] :

$$\rho = \frac{\rho_e}{\exp\left[\alpha\left(T - T_e\right)\right]}$$

T_e Triple point temperature, ρ_e density at T_e

The saturated vapour pressure, P_s , is not defined above the critical temperature, T_c (304K) and we have used the DUBININ approximation : $P_s = P_c (T/T_c)^2$

(P_c, T_c refer to critical point). Owing to the non ideality of CO_2 , fugacities substitue for the pressure values in the potential expression $A = RT \, Ln \, (P_s \, / \, P)$.
Affinity coefficient, β, has been chosen equal to 0.35 for both adsorbates.
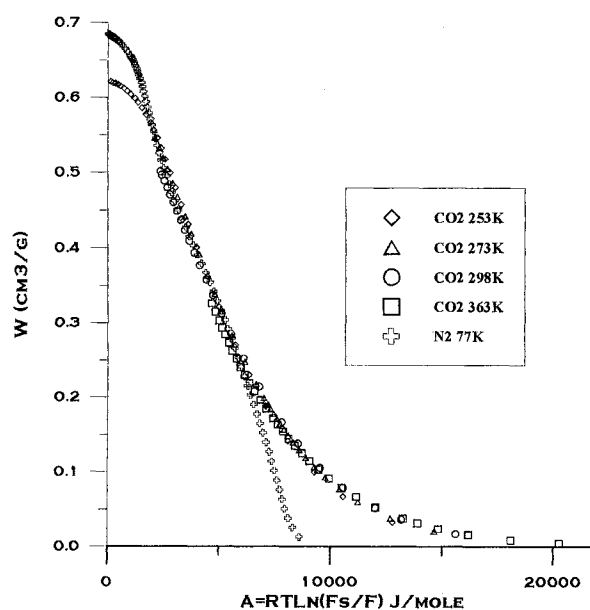Figure 1 shows the characterisitic curves (W adsorbable volume as a function of potential A).

Figure 1. Characteristic curves of CO_2 and N_2

The CO_2 one is perfectly defined at all temperatures. N_2 and CO_2 curves overlap for potential values ranging from 1800 to 6000 kJ/mole.
Below 1800 kJ/mole, the N_2 curve deviates upward and reaches a higher value of maximum adsorbable volume. This high relative pressures domain could correspond to multilayer adsorption on external surface, as mentioned by KAKEI et al.[2]. A little closed hysteresis loop observed in our desorption experiments seems to prove the existence of mesopores. This does not explain the differences between the adsorbable volume values of the two adsorbates in this domain. We can hypothesize that the density of adsorbed phase for one or other adsorbate could differ from that of micropore filling mechanism.

Further experiments with non porous adsorbents could throw light on the matter.

For potential value higher than 6000 kJ/mole as commonly observed, the N_2 curve deviates downward due to restricted diffusion or thermal effects. Comparing our N_2 experimental results with the KAKEI et al.[1] ones, we have found a more pronounced deviation. Probably our commercial equipement does not provide so high resolution on the low pressure range and maybe thermogravimetric measurements are not so affected by by thermal effects

One cannot collect information from that experimental values in this domain that accounts for the narrower micropores.

In our earlier study [3] the D.R. analysis of our CO_2 adsorption measurements displays four linear domains on the DR plot. The multi-stage micropore filling mechanism proposed by KAKEI et al.[1] have been supported but we have put in evidence an additional domain which could correspond to narrower micropore filling on the high potential range.

Low pressures CO_2 adsorption measurements have been used frequently for characterise microporosity but due to the high value of the saturated pressure it was not possible to get complete information owing to the limited relative pressures range. With high pressure high temperature measurements disposal it is now possible to improve on microporosity characterisation.

It does not exist, up to now, an absolute method of determination of P.S.D. Neverthless DUBININ STOECKLI (D.S.) [4] method had proved to be consistent for a lot of active carbons, giving results in agreement with the molecular probe method. We recall the fundamental relations :

$$W = $$

$$\frac{W_o}{2\sqrt{1+2m\sigma^2 A^2}}\exp\left[\frac{mX_o^2 A^2}{1+2m\sigma^2 A^2}\right]\left[1+erf\left(\frac{X_o}{\sigma\sqrt{2}\sqrt{1+2m\sigma^2 A^2}}\right)\right]$$

$$m=\frac{1}{\beta^2 K^2} \qquad K = 13.028\text{-}1.53.10^{-5}\,(E_o.10^{-3})^{3.5}$$

E_o being characteristic energy expressed in J/mole, the average half-width of the slit-shaped pores, X_o is deduced from the D.S. relation :

$X_o = K / E_o$. σ is the dispersion.

The parameters E_o , σ have been determined by non linear least square method applied to n experimental points for minimizing :

$$\frac{\sum_i \left(W_i - W(T_i, P_i, E_o, \sigma)\right)^2}{n}$$

The resulting curve is shown in figure 2.
the mean squared error is $< 1.10^{-4}$
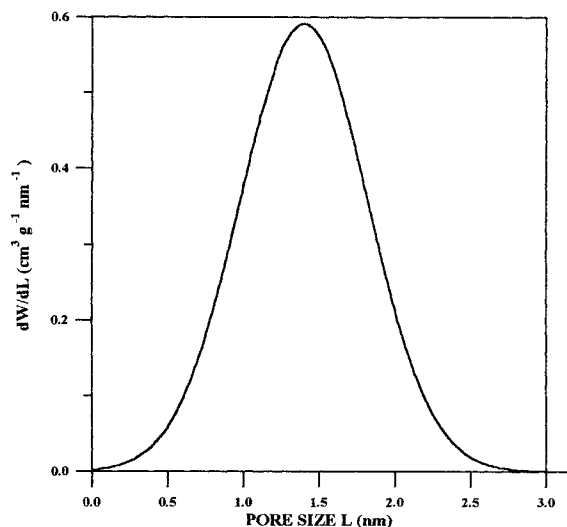we determine $L_o = 1.4$ nm and $\sigma = 0.4$ nm

Figure 2. Pore size distribution given by D.S. analysis

For nitrogen, due to the lack of experimental points in the low relative pressures range, application of the D.S. analysis leads to higher values of X_o and σ. Comparative methods as the M.P. one [5] lead to physically unrealistic P.S.D.

Conclusions

The use of high pressure high temperature adsorption measurements for characterising microporous adsorbents seems attractive : it is relatively simple with regards to the gravimetric method that imply a uneasy buoyancy correction. The possibility of specific quadupolar intreaction between the CO_2. and the carbon surfaces can raise an objection. We are studying the adsorption of CO_2 adsorption on non porous carbons and methane adsorption experiments are under study in order to understand this point. Neverthless we recall that that any characterisation method require an independent confirmation of the results. Particulary, knowledge of heats of adsorption by calorimetric methods could be helpful.

References

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