CO$_2$ AS AN ADSORPTIVE TO CHARACTERIZE ACTIVE CARBON AND CARBON MOLECULAR SIEVE

J. Alcañiz-Monge, M.A. de la Casa-Lillo, D. Cazorla-Amorós and A. Linares-Solano
Departamento de Química Inorgánica. Universidad de Alicante
Apartado 99- Alicante. Spain

Introduction

In a previous study [1], we analyzed CO$_2$ adsorption at high pressures in activated carbon fibers (ACF). With the use of high pressures, N$_2$ adsorption at 77 K and CO$_2$ adsorption at 298 K could be directly compared, because a similar range of relative pressures was covered.

The results obtained showed that: i) both adsorptives show a unique characteristic curve; ii) CO$_2$ adsorption at subatmospheric pressures can be used to determine the volume of narrow microporosity (< 0.7nm) ; iii) it is a convenient technique to complement the characterization of porosity through N$_2$ adsorption at 77 K and iii) CO$_2$ adsorbs in super-microporosity at 298 K if CO$_2$ pressures of about 4 MPa are used.

The above study was carried out with ACF, that are essentially microporous materials, and at 298 K. At this temperature, the maximum relative fugacity reached was 0.76 which only covers filling of narrow micro and supermicroporosity.

In the work that will be presented and analyzed in the following, we have extended the research to different carbon materials with quite different pore size distribution. In this sense, carbon molecular sieves and active carbons with a high volume of meso and macroporosity have been analyzed. The materials have been studied by high pressure CO$_2$ adsorption at 273 K. At this temperature, relative fugacities close to 1 can be reached and the whole range of porosity can participate in the CO$_2$ adsorption.

Experimental

Four commercial carbon molecular sieves (CMS), characterized by a low or absent N$_2$ adsorption at 77 K, ACF obtained from CO$_2$ and steam activations [2], a char of phenolformaldehyde resin (A) [3] and activated carbons obtained from an almond shell char by steam activation (BH) [4], have been used in this study. Table 1 includes as an example the results corresponding to a sample of each group. It contains the volume of micropores calculated from the application of the Dubinin-Radushkevich (DR) equation to the N$_2$ adsorption at 77 K and CO$_2$ adsorption at 273 K at subatmospheric pressures. The isotherms were measured in an Autosorb-6 apparatus. The table also includes the meso and macropore volumes determined from N$_2$ adsorption at 77 K and mercury porosimetry.

CO$_2$ adsorption isotherms at 273 K and at high pressures have been obtained in a DMT high-pressure microbalance (Sartorius 4406). The maximum pressure reached is 4 MPa. The experimental results have been corrected for buoyancy effects [1].

Table I. Pore volumes of several samples studied (cc/g)

Sample	micropores			meso	macro
	CO$_2$	N$_2$	CO$_2$^{HP}		
CMS	0.17	-	0.17	-	-
A	0.26	0.27	0.27	0.39	0.04
CFS50	0.47	0.65	0.66	0.03	-
BH57	0.47	0.52	0.52	0.40	0.57

Results and discussion

Figures 1 and 2 contain the N$_2$ and CO$_2$ adsorption isotherms obtained for several materials studied. As an example, those obtained for a CMS (in which N$_2$ adsorption is not observed), an ACF (CFS50) that contains narrow micro and super-microporosity, the char A (with narrow microporosity and meso and macroporosity) and an activated carbon (BH57) with a wide pore size distribution (narrow micro, supermicro, meso and macroporosity), have been included. The isotherms are of type I of the IUPAC classification in all the cases.

The characteristic features of the pore size distribution for the above mentioned samples, are clearly reflected in the isotherms and show the different pore size distributions covered in this study. The differences observed between N$_2$ and CO$_2$ can be attributed to the different adsorption temperatures used (specially important in the filling of microporosity) and to the physico-chemical properties of both adsorbates.

In the following, the characterization of the different ranges of porosity from the high pressures CO$_2$ adsorption isotherms will be analyzed and discussed from the comparison

with the N_2 adsorption results.

Micropore volumes have been quantified from high pressure CO_2 adsorption isotherms (see Table 1). DR equation has been applied and the results have been compared with those obtained from N_2 at 77 K and from CO_2 at subatmospheric pressures at 273 K.

In this sense, we observe that those samples in which N_2 adsorption at 77K is kinetically restricted (i.e., CMS), the volumes obtained from CO_2 are higher than from the first adsorbate and that the values determined from CO_2 at high and at subatmospheric pressures coincide. For those samples in which N_2 volume is higher than the CO_2 are at subatmospheric pressures (i.e., the samples contain super-microporosity), the micropore volumes from high pressure CO_2 adsorption agree with the N_2 one. This confirms the conclusion deduced previously [1] that CO_2 adsorption is sensitive to the narrow microporosity (< 0.7nm) and to the supermicroporosity, if high pressures are used. The results also reveal a good overlapping between the characteristic curves of N_2 adsorption at 77 K and CO_2 adsorption at 273 K performed at subatmospheric and high pressures.

All these results deduced from a wide variety of samples, agree with the conclusions proposed from the study of ACF by high pressure CO_2 adsorption at 298 K [1].

Because the CO_2 measurements have been carried out at 273 K, we have been able in our experimental system to reach relative pressures close to 1 and, hence, to follow the adsorption of CO_2 in the wider porosity. In this sense, it is observed that only those samples which contain a considerable contribution of mesoporosity, the CO_2 adsorption isotherms deviate upwards at relative pressures higher than 0.9 (Figure 2), whereas this happens in the N_2 isotherms from relative pressures higher than 0.3-0-4 (Figure 1). The differences between both adsorbates can be attributed to the different surface tension of both liquids, that influences their capillary condensation. Hence, applying Kelvin equation to both adsorbates, it is obtained that condensation in pores of size 2 nm happens at $p/p^0 = 0.3$ and 0.9 for N_2 and CO_2, respectively. These differences indicate that N_2 is more sensitive than CO_2 to meso and macroporosity as its adsorption happens in a wider range of relative pressures.

Conclusions

CO_2 adsorption follows the same mechanism than N_2 in the whole range of porosity (micro, meso and macroporosity) if both adsorptives are compared in a similar range of relative pressure. CO_2 is much more sensitive to narrow microporosity, not accessible to N_2 and, hence, it is necessary to characterize CMS and, in addition, it is a good complement to characterize the porosity of activated carbons.
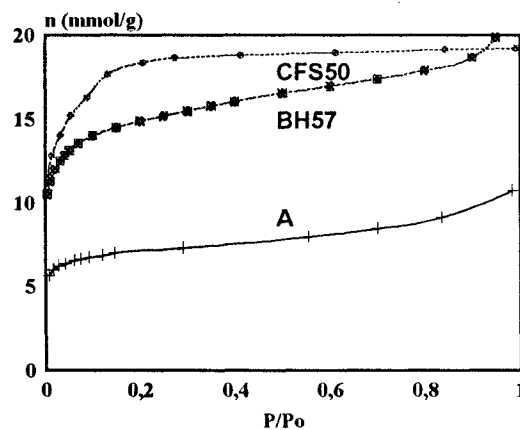

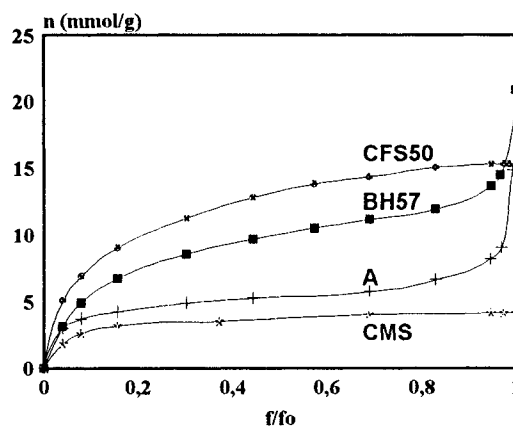**Figure 1.** N_2 adsorption isotherms at 77 K.

Figure 2. CO_2 adsorption isotherms at 273 K.

Acknowledgments

References

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