

MICROPORE SIZE DISTRIBUTIONS OF ACTIVATED CARBONS AND CARBON MOLECULAR SIEVES ASSESSED BY N₂ ADSORPTION AND HIGH PRESSURE CH₄ AND CO₂ ADSORPTION ISOTHERMS

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Introduction

Characterization of pore size distribution is very important for the design and utilization of improved porous carbons in a lot of applications. N₂ at 77K is the most widely used gas for the characterization of porous solids. However, the main disadvantage of N₂ adsorption at 77K is that when it is used for the characterization of microporous solids, diffusional problems of the molecules inside the narrow porosity range (size < 0.7 nm) occur [1]. Moreover, there is an additional experimental difficulty in the adsorption of subcritical nitrogen because very low relative pressures (10⁻⁸-10⁻⁴) are required to extend the range of porosity studied to narrow microporosity. To overcome these problems, the use of other adsorptives has been proposed. In previous studies it has been shown that a good alternative to complement N₂ adsorption could be the use of CO₂ adsorption at 273 K [2,3]. In order to cover the same range of relative pressure as the N₂ adsorption, CO₂ adsorption has to be carried out up to 3 MPa. On the other hand, high pressure methane adsorption isotherms (up to 4 MPa) has been shown to be another way for characterizing the porous texture [4].

The main objective of this work is to characterize in terms of micropore size distribution (MPSD) some of the carbon materials prepared in our laboratory (activated carbons and carbon molecular sieves, CMS). The comparison of the MPSDs assessed by two different adsorptives (CO₂ and CH₄) at high pressures is presented.

Experimental

Four carbon materials with different micropore structures have been selected for this study: i) a carbon molecular sieve (KUA1B8) prepared in our laboratory and ii) three activated carbons prepared by chemical activation with KOH of a Spanish anthracite (KUA1GC, KUA1L26 and KUA1L34). The samples have been chosen in such a way that their micropore volume and their MPSDs are very different.

Porous texture analysis of all the samples has been carried out by subatmospheric N₂ and CO₂ adsorption at 77K and

273K, respectively, in an Autosorb 6 apparatus. Table 1 contains the BET surface area and micropore volumes obtained by applying the Dubinin Radushkevich equation to the N₂ and CO₂ adsorption data. CO₂ and CH₄ adsorption isotherms at high pressures and at 273K and 298K, respectively, have been obtained in a Sartorius high-pressure microbalance. Isotherms fittings of both type of isotherms have been obtained by applying the Toth equation.

Table I.- Surface area and micropore volume for all the samples.

Sample	BET surface area (m ² /g)	V (N ₂) (cm ³ /g)	V (CO ₂) (cm ³ /g)
KUA1B8	-	-	0.2
KUA1GC	2021	0.83	0.80
KUA1L26	3290	1.45	0.81
KUA1L34	2402	1.07	0.52

Results and discussion

Figure 1 has the N₂ adsorption isotherms at 77 K of the three activated carbons. The isotherm corresponding to the carbon molecular sieve (KUA1B8) is not shown because this sample presents a very narrow microporosity, making that the kinetics of N₂ adsorption is extremely slow at 77K [2,3].

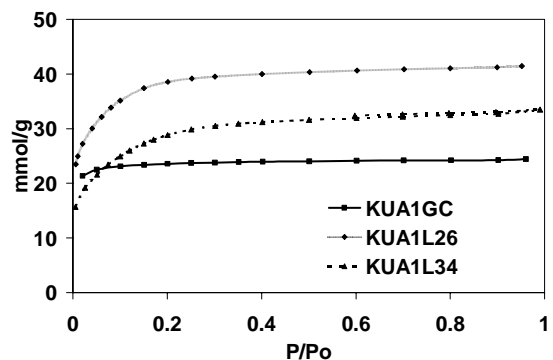


Figure 1.- N₂ adsorption isotherms at 77K.

Figure 1 and the characterization results presented in Table I show that the samples chosen for this study have

significant differences in pore size distribution. The sample KUA1GC presents the lowest difference between both micropore volumes ($V_{N_2}-V_{CO_2}$), which indicates that this sample has a narrow MPSD. On the other hand, the sample KUA1L34 has the widest MPSD.

Figure 2 presents the experimental CO_2 adsorption isotherms (sub-atmospheric and high-pressure adsorption data) obtained at 273 K (points) and the Toth fittings (lines). It can be observed that there is a good continuation in the measurements done at subatmospheric (volumetric system) and high pressures (gravimetric system) despite the different experimental systems used. The CMS, whose N_2 isotherm can not be measured, does present adsorption of CO_2 at 273K, and its isotherm can be easily measured.

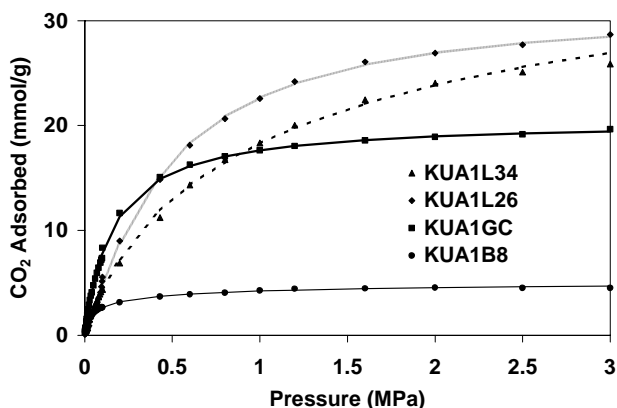


Figure 2.- CO_2 adsorption isotherms at 273 K (experimental and fittings).

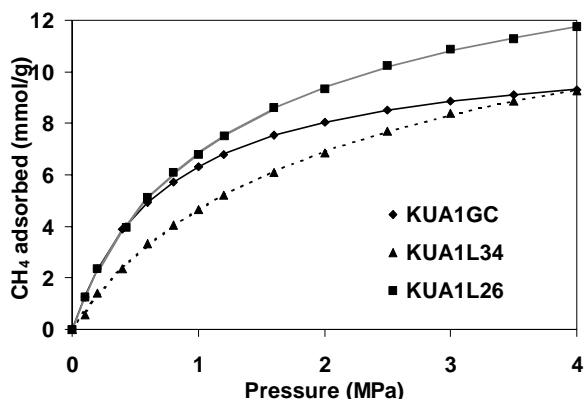


Figure 3.- Methane adsorption isotherms at 298 K (experimental and fitting).

Figure 3 presents the experimental CH_4 adsorption isotherms at 298 K for all the samples studied, shown as points, and the associated curve fittings obtained by applying the Toth equations (lines). As happened in the case of N_2 adsorption, the isotherm of the CMS (KUA1B8) does not appear in this figure because this sample has a very narrow microporosity. It can be observed that the

shape of the CO_2 and CH_4 isotherms is very different for all the samples, indicating the different MPSDs.

MPSDs have been calculated from both the high pressure CO_2 adsorption isotherms using the approach proposed by Cazorla-Amorós et al [3] and the high pressure methane isotherms using the procedure developed by K.A. Sosin and D.F. Quinn [4]. The pore sizes obtained by these approaches are the size available for the gases, i.e. the additional width of a carbon atom is not considered. Figure 4 and 5 present the MPSDs obtained from the CO_2 and CH_4 adsorption data, respectively.

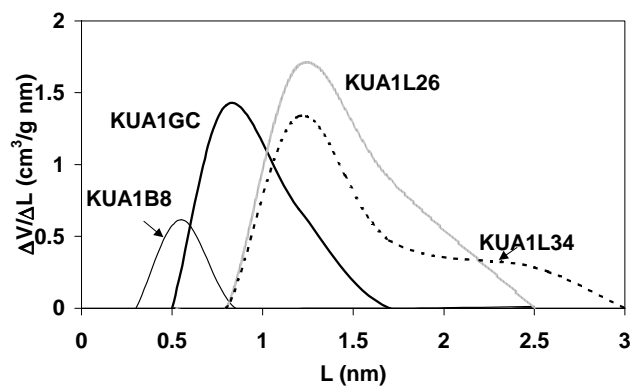


Figure 4.- MPSDs assessed from the subatmospheric and high pressure CO_2 adsorption isotherms.

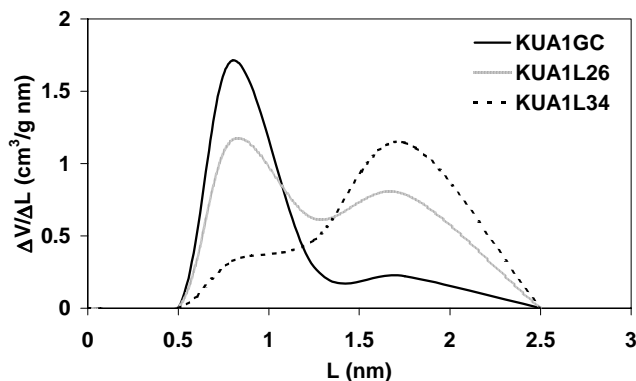


Figure 5.- MPSDs obtained from the high pressure CH_4 adsorption isotherms.

In Figure 4 it can be seen that, as expected, the narrowest MPSD corresponds to the CMS (sample KUA1B8). This sample presents a very homogeneous MPSD with most of the porosity having a pore size around 0.5 nm. The mean pore size of this sample should be between 0.3 and 0.4 nm (this sample has shown good separation capabilities for CH_4 and CO_2), which suggests that, in the case of this sample with very narrow pores, the obtained MPSD is slightly shifted to higher pore sizes. This could be due to the fact that the equation relating the mean width (L) and

the characteristic energy (E_0) is an empirical equation and, probably, is not very precise for samples with very narrow pore sizes. The sample KUA1GC has also a quite narrow MPD. This sample presents the maximum at around 0.8 nm, which agrees with the pore size expected according to its similar $V(N_2)$ and $V(CO_2)$ [1] and NLDFT calculations for CO_2 adsorption [5]. The sample KUA1L34 presents the widest MPDs.

Figure 5 presents the MPDs obtained from the high pressure methane adsorption isotherms. It can be observed that bimodal distributions (centered at around 0.8 nm and 1.7 nm, approximately) are obtained. Depending on the shape of the methane isotherm the contribution of each mode is different, i.e., the wider the MPD the lower the contribution of the first mode and the higher the contribution of the second mode.

Comparing the MPDs obtained with these two different adsorptives (CO_2 and CH_4) and different experimental temperatures (298 and 273 K, respectively), which corresponds to different adsorption conditions (subcritical and supercritical adsorption conditions), it can be said that a reasonable consistence between both MPDs exists for all the samples.

Conclusions

MPDs have been deduced from the high pressure CO_2 and CH_4 isotherms, according to two different approaches proposed in previous independent works. The results are very consistent with the characteristics of the samples, suggesting that both methods are suitable for a reliable analysis of the MPDs of microporous samples. The use of CO_2 adsorption at 273 K allows us to characterize CMS with very narrow microporosity, which can not be characterized with N_2 (77 K) or CH_4 (298 K) adsorption.

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