ADSORPTION PROPERTIES OF CARBON MOLECULAR SIEVES PREPARED BY A CO-CARBONIZATION PROCESS

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Introduction

Carbon molecular sieves (CMSs) are microporous carbon materials whose special textural characteristics enable kinetic separation of gas mixtures, i.e., separation as a result of differences in the diffusion rates of the species involved. For a CMS to be useful for gas separation, it must possess a narrow pore size distribution (PSD) consisting of pore mouths of molecular sizes and a relatively high micropore volume, features which confer them selectivity and capacity, respectively [1]. Besides, it must show high adsorption and desorption absolute rates, as the performance for PSA cycles designed for kinetic separation is usually optimal for cycles with short time duration [2,3].

In the present work the preparation of CMS by a co-carbonization process using an activated carbon and coal-tar pitch is presented. This process results in a blockage of the pores of the starting activated carbon so that a reduction in the pore size takes place. Equilibrium and kinetic studies were done in a tapered element oscillating microbalance (TEOM) in order to test the performance of a so-prepared CMS in the separation of gases (CH_4/CO_2). The comparison of these results with those obtained with a commercial CMS (Takeda 3A) is presented. An appropriate model was proposed to extract diffusivities at zero loading.

Experimental

An activated carbon (AC) prepared by KOH activation of anthracite was used as precursor. Detailed information about the preparation and characterization of these materials is given elsewhere [4]. Table I includes the pore structure characterization results corresponding to this AC. Co-carbonization process of this AC and a coal tar pitch was carried out in a horizontal furnace under N_2 atmosphere (60 ml/min) using two different boats to dispose the pitch and the AC. Table 2 contains the coal tar pitch characterization results. The effect of different preparation conditions on the final porosity of the material was analyzed: (i) heating rate, (ii) pitch/carbon ratio, (iii) co-carbonization temperature, (iv) gas phase composition.

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Table 1. Porous texture characterization results for the AC.

Sample	S_{BET} (m^2/g)	V_{DR} (N$_2$) (cm^3/g)	V_{DR} (CO$_2$) (cm^3/g)
AC	1336	0,79	0,80

Table 2. Characterization results corresponding to the coal tar pitch.

Elemental analysis (weight %)				Insoluble content (weight %)		Softening Point (K)
C	H	N	S+O	TI	QI	
91,85	4,79	0,79	2,65	19	3	346

Textural characterization of the materials was accomplished by N_2 and CO_2 adsorption isotherms at 77 K and 273 K, respectively, using an automatic adsorption system (Autosorb-6, Quantachrome).

Equilibrium and transient adsorption experiments were carried out in a Rupprecht & Patashnick TEOM 1500 mass analyzers (100 mg sample volume). A detailed description of the TEOM operating principles is given elsewhere [5]. CO_2 adsorption isotherms at three different temperatures (298 K, 313 K and 328 K) were obtained for a CMS prepared by the co-carbonization process described previously, and for a commercial carbon molecular sieve (Takeda 3A). The sieved and almost-spherical particles in this study had an average particle radius of 0.15 mm, as determined by SEM. The isotherms were obtained by a stepwise increase of the partial pressure of CO_2 at fixed temperatures, using a thin layer of the sample, which weight was 16 mg.

In addition, kinetic studies of both samples were carried out by continuous monitoring of the mass changes during an adsorption-desorption cycle. An adsorption run was initiated by replacing the helium stream by a predetermined mixture of helium and the sample gas (CO_2 or CH_4). The feed was maintained until the sample was equilibrated as indicated by constant mass change.

Results and discussion

As a summary of the effect of the preparation variables on porous texture of the final material, Figure 1 shows the total micropore volume obtained from N_2 adsorption data at 77 K [V_{DR}(N$_2$)], and the narrow micropore volume obtained from CO_2 adsorption data at 273 K [V_{DR}(CO$_2$)] corresponding to samples prepared using different co-carbonization temperatures and different pitch/carbon ratios. These experiments were carried out by

introducing the AC and the pitch in the furnace when the co-carbonization temperature was already reached.
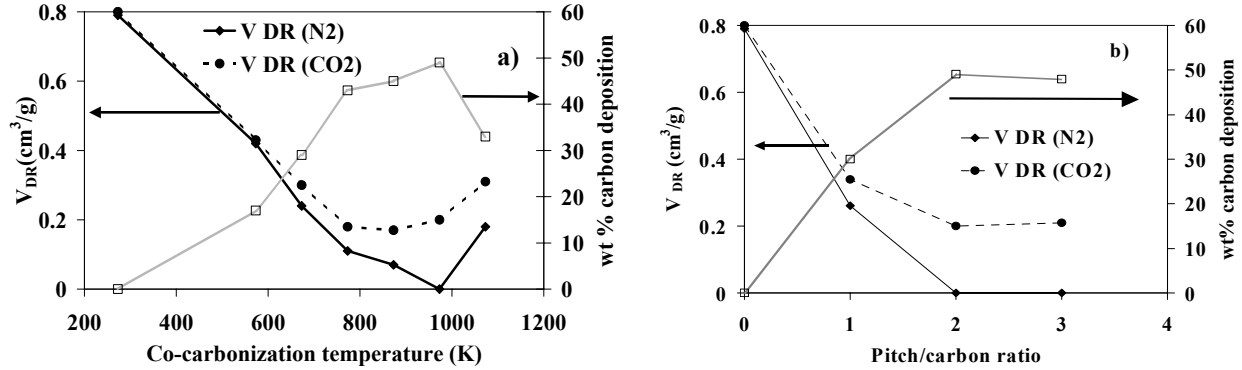

Figure 1. Micropore volume and wt% carbon deposition corresponding to materials prepared using (a) different co-carbonization temperatures and a 2/1 pitch/carbon ratio; (b) different pitch/carbon ratios at 973 K.

In Figure 1(a) it can be seen that, up to 973 K, the higher the temperature the lower the micropore volume [$V_{DR}(N_2)$] and the higher the wt % carbon deposition. The narrow micropore volume [$V_{DR}(CO_2)$] follows a similar trend as [$V_{DR}(N_2)$] up to 773 K, however, it increases at higher temperatures. For temperatures higher than 973 K, the general trend is inverted. There is a decrease in the wt% carbon deposition and consequently a smaller blockage of the porosity (increase of micropore volume).

It should be mentioned that the sample prepared at 973 K does not present adsorption of N_2 at 77 K but it still presents CO_2 adsorption at 273 K [$V_{DR}(CO_2) = 0.2$ cm^3/g], which is an indication that this sample could present molecular sieve properties [6,7]

From the results presented in Figure 1(b) it can be said that the carbon deposition obtained with a lower pitch/carbon ratio (1/1) is not sufficient to prepare a carbon molecular sieve.

Considering the interesting porous texture of the sample prepared at 973 K and using a 2/1 pitch/carbon ratio (sample B8), further studies of this sample by the TEOM technique were done, and compared with a commercial CMS, Takeda 3A (sample T3A).

Figure 2 presents the CO_2 adsorption isotherms at two different temperatures for samples B8 and Takeda 3A. Points represent experimental results and lines are the Tóth model fits. For adsorption on heterogeneous adsorbents such as activated carbon, the Tóth model is often used to correlate isotherm data [8,9]

$$q = q^{sat} \frac{Kp}{[1+(Kp)^m]^{1/m}}$$ (1)

where q is the amount adsorbed, q^{sat} is the saturation amount adsorbed, K is the equilibrium constant, p is the pressure, and m is the parameter that characterizes the system heterogeneity [9]. The extracted values of the adsorption parameters in the Tóth model for three different temperatures are listed in Table 3. It can be seen that the Tóth model gives a good description of the adsorption isotherms of CO_2, and the extracted saturation amount for sample B8 is slightly higher than that forT3A.
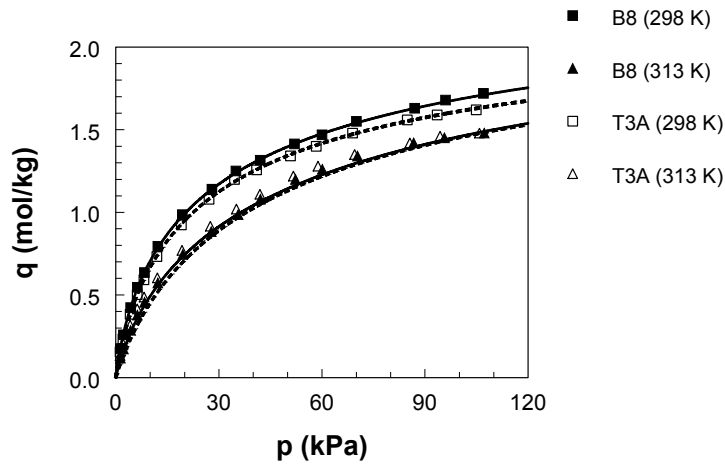

Figure 2. CO_2 adsorption isotherms at 298 and 313 K on samples B8 and T3A.

Table 3. Extracted values of adsorption isotherm parameters in the Tóth isotherm

Sample	T (K)	q^{sat} (mol/kg)	K (kPa^{-1})	m
B8	298	2.62	0.0757	0.5945
	313	2.62	0.0384	0.6174
	328	2.62	0.0207	0.6383
T3A	298	2.35	0.0672	0.6620
	313	2.35	0.0302	0.7522
	328	2.35	0.0146	0.8341

The uptake measurements for single components CO_2 and CH_4 in adsorbents B8 and T3A were carried out at 298, 313, and 328 K and at different feed pressures. Figure 3 presents the normalized uptake curves of CO_2 in B8 and T3A at 298 K and a feed pressure of 1.3 kPa, where Q is defined as $q(t)/q(\infty)$. The lines represent the fits obtained with a model, in which diffusion inside the micropores of the carbon materials is described by Fick's law with a concentration-dependent diffusivity that is expressed by Darken's relation. The model describes the uptake curve of CO_2 in adsorbent B8 very well, while it does not match the uptake curve in adsorbent T3A. The estimated values of the micropore diffusional time constant at zero loading, i.e. D_0/R^2, as the only fitting parameter in the model are 5.5×10^{-4} and 2.6×10^{-4} s^{-1} at 298 K and 1.3 kPa for

CO$_2$ in samples B8 and T3A, respectively. It should be remarked that no significant mass change by methane adsorption on both carbon adsorbents was observed with the TEOM under the same experimental conditions within 1000 s, indicating the separation ability of CO$_2$ and CH$_4$ mixtures by adsorbents B8 and T3A.

From the results presented in Figure 3 and those obtained at different temperatures and feed pressures, it is clearly seen that the diffusivity of CO$_2$ in the CMS prepared in the laboratory (sample B8) is considerably higher than that in the commercial CMS (sample T3A). This property of sample B8 is very interesting from an application point of view, considering that the performance of a PSA equipment designed for kinetic separation is usually optimal for cycles with short time duration [2,3].
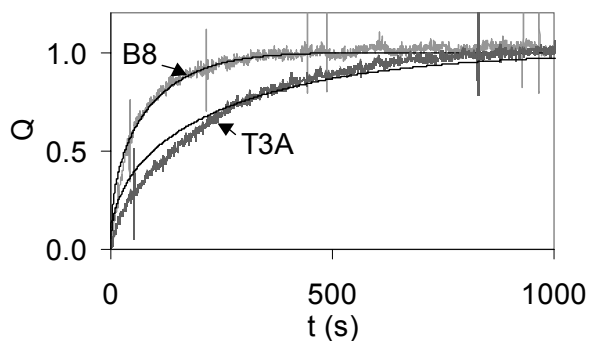

Figure 3. Normalized CO$_2$ uptake profiles at 298 K and a feed pressure of 1.3 kPa in both CMS. Thin lines are the fits by the micropore diffusion model.
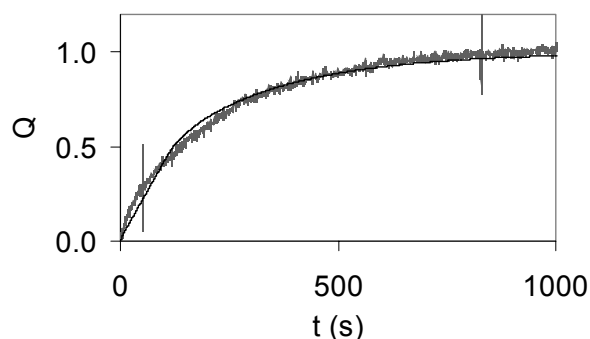
Figure 4. Normalized CO$_2$ uptake profile at 298 K and a feed pressure of 1.3 kPa in T3A. Thin line corresponds to the model fit by the dual resistance model.

The slow uptake of CO$_2$ in T3A at 298 K in the initial stage might be attributed to barrier resistance. Liu and Ruthven [10] investigated the diffusion of CO$_2$ in BF CMS, in which CO$_2$ showed a transition from barrier resistance control at lower temperatures to diffusion control at higher temperatures. We also observed the same trend. Indeed the uptake curves of CO$_2$ in T3A at 313 and 328 K are well described by the diffusion control model, and the estimated values of D_0/R^2 for CO$_2$ in T3A are slightly smaller than those in B8 under the same conditions. A dual resistance model, i.e. the overall uptake is controlled by both barrier resistance and micropore diffusion, shows a better description of the CO$_2$ uptake curve at 298 K, as indicated in Figure 4.

This kinetic study seems to predict a better CO$_2$/CH$_4$ separation performance for sample B8 than for sample T3A, due to higher CO$_2$ diffusion in sample B8. These results also reflect that pore mouths in sample B8 are slightly wider.

Conclusions

The present study has shown that a co-carbonization process using an activated carbon and coal-tar pitch is a good method for the preparation of CMS. This process results in a blockage of the pores of the starting activated carbon so that a reduction in the pore size takes place. Equilibrium CO_2 adsorption measurements at different temperatures carried out using the TEOM technique give a slightly higher CO_2 adsorption capacity for a CMS prepared by the co-carbonization process (sample B8) than for a commercial CMS (Takeda 3A). In addition, CO_2 uptake measurements at different temperatures show higher CO_2 overall diffusion for sample B8 than T3A. The experimental uptake profiles in both samples at different temperatures and different CO_2 partial pressures, except that in sample T3A at 298 K, can be described by a micropore diffusion model. A dual resistance model has been used to fit the CO_2 adsorption profile in sample T3A at 298 K. Both equilibrium and kinetic studies seem to predict a better CO_2/CH_4 separation performance for sample B8 than for sample T3A, due to the existence of slightly wider pore mouths in sample B8.

Acknowledgements

References

[1] Foley HC. Carbogenic molecular sieves: synthesis, properties and applications. Microporous Materials 1995; 4(6): 407-433.
[2] Kapoor A, Yang RT. Kinetic separation of methane-carbon dioxide mixture by adsorption on carbon molecular sieves. Chemical Engineering Science 1989; 44(8): 1723-1733.
[3] Kawabuchi Y, Kawano S, Mochida I. Molecular sieving selectivity of activated carbons and activated carbon fibers improved by chemical vapor deposition of benzene. Carbon 1996; 34(6): 711-717.
[4] Lozano-Castello D, Lillo-Rodenas MA, Cazorla-Amoros D, Linares-Solano A. Preparation of activated carbons from Spanish anthracite: I. Activation by KOH. Carbon 2001; 39(5): 741-749.
[5] Zhu W, van de Graaf JM, van den Broeke LJP, Kapteijn F, Moulijn JA. TEOM: A unique technique to measure adsorption properties. Light alkanes in Silicalite-1. Industrial & Engineering Chemistry Research 1998; 37(5): 1934-1942.
[6] de la Casa-Lillo MA, Alcañiz-Monge J, Raymundo-Piñero E, Cazorla-Amoros D, Linares-Solano A. Molecular sieve properties of genera-purpose carbon fibres. Carbon 1998; 36(9):1353-1360.
[7] de la Casa-Lillo MA, Moore BC, Cazorla-Amoros D, Linares-Solano A. Molecular sieve properties obtained by cracking of methane on activated carbon fibres. Carbon 2002; 40(13):2489-2494.
[8] Valenzuela DP, Myers AL. Adsorption Equilibrium Data Handbook, Prentice-Hall:New Jersey, 1989.

[9] Do DD. Adsorption analysis: Equilibrium and Kinetics, Imperial College Press:London, 1998.

[10] Liu H, Ruthven DM. Diffusion in Carbon Molecular Sieves. Proceedings of the 5th International Conference on the Fundamentals of Adsorption. LavVan MD. Ed.; Kluwer Press:.Boston (USA) 1996: 529-536.