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Articles

High-Pressure CO_2 Adsorption on a Polymer-Derived Carbon Molecular Sieve

Jiahui Chen, Leslie S. Loo, and Kean Wang*

School of Chemical & Biomedical Engineering, Nanyang Technological University, Singapore

CO_2 sorption isotherms were measured on a polymer-derived carbon molecular sieve (CMS) at three temperatures and pressures up to 40 atm using the gravimetric method. The adsorption and desorption data were fitted to the Langmuir and Toth isotherms. Low-pressure CO_2 isotherms were also measured on a standard pore and surface analyzer (PSA) rig. Strong surface barriers were found at low sorption pressure, but micropore hysteresis was not seen at high sorption pressure.

Introduction

Carbon molecular sieves (CMS) and CMS membranes are promising materials for gas separation and purification.[1,2] The CMS materials comprise micropores of relatively uniform size which enable the discrimination of gas molecules with very similar dimensions.[3–5] Due to structural characteristics (ultramicropores with narrow pore size distribution, or PSD), it is impractical to characterize their structure via traditional methods such as N_2 sorption at −196 °C because of the extremely slow sorption rate. An alternative method is to analyze, at ambient temperature, the sorption isotherm of a suitable adsorbate whose rate of adsorption is much faster.[6] CO_2 sorption at room temperature appears to be a good choice because: (1) the CO_2 molecule is small in size and is capable of penetrating very small micropores, and (2) the sorptivity of CO_2 is high at room temperature. The drawbacks of CO_2 sorption may be: (1) nonideality at high pressure; (2) the molecule is not spherical in shape; and (3) CO_2−pore interaction is not purely dispersive. These factors, however, can be adequately addressed by taking into account a number of thermodynamic properties of the sorption system.[7,8]

This study will report CO_2 sorption isotherms on a CMS at multiple temperatures and pressures up to 40 atm.

Isotherm Models

The adsorption of gas molecules on microporous CMS materials generally follows the type I isotherm (IUPAC), which is described by the Langmuir equation

$$C_\mu = C_{\mu s}\frac{bP}{1+bP} \tag{1}$$

where b is the sorption affinity; P is the bulk phase pressure; C_μ is the adsorbed phase concentration; and $C_{\mu s}$ is the sorption capacity. Equation 1 is generally applicable for a homogeneous surface. For an adsorbent with structural heterogeneity, the Toth isotherm is a better choice

$$C_\mu = C_{\mu s}\frac{b_t P}{[1+(b_t P)^t]^{1/t}} \tag{2}$$

where t is the heterogeneity parameter for the sorption system. Equations 1 and 2 will be used to correlate the experimental data.

Table 1. Gas Permeation-Selectivity of KP1000 at Ambient Conditions[a]

gas	H_2	He	N_2	O_2	CF_4	CO_2
kinetic diameter σ (Å)	2.89	2.60	3.64	3.46	4.70	3.5
perm-selectivity, (P_{helium}/Pi)	0.47	1	680	29	∞	6.73

[a] Note: perm-selectivity (A/B) = permeability of A/permeability of B.

Experiments

A CMS (termed as KP1000) was prepared via the controlled pyrolysis of a polyimide thin film under vacuum. The thermal treatment program is described in the literature.[3,9] A soaking temperature of 1000 °C was used. The sample has a thickness of 23 μm and is symmetric in structure. It has been demonstrated that such a membrane has pore sizes below 7 Å and is free of pinholes.[3] The membrane possesses good perm-selectivities for many gas mixtures at ambient conditions, as shown in Table 1.

A Cahn 2000 microbalance (with a resolution of 10^{-3} μg) was utilized to measure the sorption isotherms.[10] The microbalance was placed in a high-pressure vessel in which the temperature and pressure were controlled precisely in the range from (−20 to 92) °C and (0.1 to 50) atm, respectively. The sample was crushed into small pieces and degassed at about 200 °C under high vacuum overnight. About 0.52 g of the sample was loaded in the sample basket. An aluminum block was used as the counterweight. To minimize the effect of buoyancy, gold was added in the sample basket to ensure that both the density and weight of the sample basket were (nearly) the same as those of the counterweight. This was achieved by a trial and error procedure. Helium was assumed to be the nonadsorbing gas to check the effect of buoyancy at room temperature. After the calibration and the closure of the pressure vessel, the sample was redegassed overnight at 90 °C under vacuum. The weight of the sample was monitored continuously during the degassing process until there was no obvious change within 12 h (i.e., observed weight change was less than $1 \cdot 10^{-3}$ μg). The system was then cooled down to the experimental temperature, and the zero point of the microbalance was set accordingly. Slow sorption rates (i.e., up to 2 days for the

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* Corresponding author. E-mail: mkwang@ntu.edu.sg.

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Table 2. CO_2 Isotherm Data on KP1000 CMS Membrane

pressure kPa	adsorbed $\mu mol \cdot g^{-1}$	pressure kPa	adsorbed $\mu mol \cdot g^{-1}$	pressure kPa	adsorbed $\mu mol \cdot g^{-1}$	pressure kPa	adsorbed $\mu mol \cdot g^{-1}$
$T = 298$ K							
52.588	1321.4	1961.9	3259.3	3175.9	3259.3	100.12	1849.9
102.14	1695.7	3003.6	3303.4	2103.5	3259.3	52.588	1413.8
208.33	2180.2	4045.2	3299.0	1061.9	3105.2	30.339	991.02
490.48	2691.2			540.03	2818.9	12.136	739.96
991.07	3021.5			208.33	2246.3	1.0113	88.090
$T = 333$ K							
50.565	845.67	1001.2	2603.1	3135.0	2981.9	206.31	1722.2
104.16	1237.7	1992.3	2898.2	2083.3	2907.0	103.15	1299.3
201.25	1629.7	3054.1	2973.0	1041.6	2664.7	55.622	991.02
501.60	2215.5	5026.2	2995.1	546.10	2303.6		
$T = 353$ K							
49.554	590.20	1010.3	2259.5	3104.7	2722.0	204.28	1343.4
100.12	902.93	1992.3	2581.0	2133.9	2620.7	101.13	946.97
201.25	1294.9	2983.3	2700.0	1051.8	2312.4	50.565	660.68
496.55	1841.1	4550.9	2730.8	504.6	1871.9		

equilibrium to be reached) were observed at the low-pressure end, possibly due to the diffusion barrier of the small micropores toward CO_2 adsorption. The slow sorption kinetics of molecules such as CO_2 and N_2 at supercritical temperature have also been reported by other researchers on ultramicroporous carbons[11] and CMSs.[12,13] For the purpose of comparison, CO_2 isotherms were also measured for the sample using a standard PSA rig (pore and surface analyzer, BEL Inc., Japan). The PSA uses volumetric technology and can measure the sorption at pressures ranging from $(0.133 \text{ to } 1.33) \cdot 10^5$ Pa.

Results and Discussion

Table 2 lists the CO_2 isotherm data measured at three temperatures (298 K, 333 K, and 353 K). The experimental data are plotted in Figure 1 with the adsorption data (shown as solid symbols) and desorption data (shown as hollow symbols). Slow sorption rates were noted (especially for the first pressure point); however, the adsorption and desorption data virtually overlap with each other, and no evidence of micropore hysteresis was observed in this system. Also shown in Figure 1 are the fits using the Langmuir isotherm (solid lines) and the Toth isotherm (dashed lines). It is seen that both models can adequately fit the experimental data, but the Toth isotherm gives a slightly better fit. Table 3 shows the optimal model parameters and the goodness of fit (in terms of the average relative error, or ARE) of the two models.

The heterogeneity parameter of the Toth isotherm ($t \approx 0.7$) suggests that KP1000 has a relatively homogeneous surface compared to commercial activated carbons (in which t generally ranges from 0.2 to 0.5).[12] This is in agreement with the molecular probe experiments which show that the pore sizes of KP1000 are below 7 Å (effective pore size, wall to wall).

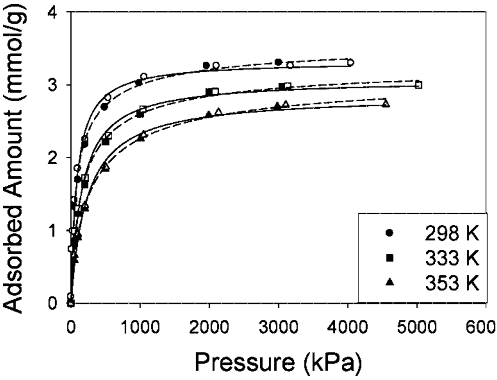

Figure 1. CO_2 isotherms on a KP1000 CMS measured with a microbalance. —, Langmuir; ----, Toth; ●, ■, ▲, adsorption; ○, □, Δ, desorption.

The surface barrier effect (i.e., slow sorption rate when molecules penetrate the narrow necks of micropores) generally occurs for gas sorption on CMS materials, and this effect is significant on the KP1000 sample. Figure 2 shows CO_2 isotherms measured with a standard pore and surface analyzer (PSA). The PSA uses a different measuring methodology (volumetric) compared to the microbalance (gravimetric) and is capable of measuring sorption at pressures as low as 0.133 Pa. The criteria used for the PSA to decide the *EQUILIBRIUM* for a dosing is set so that the pressure variation must be less than 0.133 Pa in 5 min. With such a criterion, it is seen in Figure 2 that the desorption data (hollow symbols) significantly deviate from the adsorption data (solid symbols) at all experimental temperatures. These hystereses are indications of surface barriers at low sorption pressure, confirming the existence of a portion of small micropores in KP1000 which are difficult for CO_2 molecules to penetrate. This surface barrier becomes much stronger in the case of N_2 sorption at 77 K so that the equilibrium criteria ($\Delta P < 0.133$ Pa in 5 min) can not be met for the first isotherm point within days, making it impractical for the standard N_2 sorption measurement.

Figure 2b combines the adsorption isotherms of CO_2 measured by the two methods at 333 K (on the logarithmic scale). It is seen that, considering the experimental error and different techniques, the two isotherms (methods) agree well with each other at a similar pressure range.

Conclusions

Adsorption/desorption isotherms of CO_2 were measured on a CMS membrane at three temperatures and a wide range of pressures. The data were fitted reasonably well by the Langmuir

Table 3. Optimal Isotherm Parameters[a]

	Langmuir isotherm			Toth isotherm			
temp K	$C_{\mu s}$ $mmol \cdot g^{-1}$	b kPa^{-1}	ARE	$C_{\mu s}$ $mmol \cdot g^{-1}$	b_t kPa^{-1}	t	ARE
298	3.32	$1.19 \cdot 10^{-2}$	10.7	3.65	$2.46 \cdot 10^{-2}$	0.63	8.99
333	3.07	$6.44 \cdot 10^{-3}$	4.57	3.31	$9.69 \cdot 10^{-3}$	0.725	2.65
353	2.86	$4.36 \cdot 10^{-3}$	2.91	3.21	$6.36 \cdot 10^{-3}$	0.70	1.31

[a] Note: the average relative error (ARE) is defined as: ARE $= 100 / N \sum_{k=1}^{N} |Y_{\text{model}} - Y_{\text{exptl}}| / Y_{\text{exptl}}$.

isotherm as well as by the Toth isotherm. Isotherm analysis suggests that: (1) micropore hysteresis is not significant at high pressure; (2) the membrane sample has a relatively uniform structure with a portion of small micropores; and (3) the surface barrier is significant at low sorption pressure.

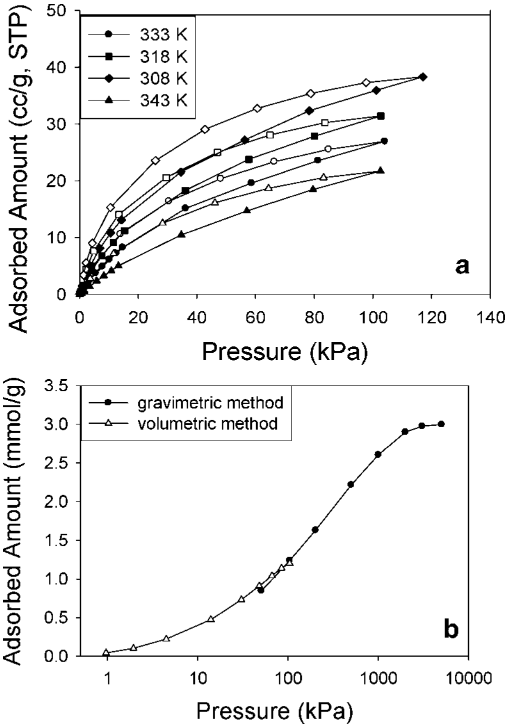

Figure 2. (a) CO_2 isotherm measured by the PSA (volumetric technology). Solid symbol, adsorption; hollow symbol, desorption. (b) The combined adsorption isotherm of CO_2 on the CMS at 333 K.

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