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Defining effective microporosity in carbon molecular sieves

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Abstract

A pseudo equilibrium method is described for establishing the micropore distribution in carbon molecular sieves (CMS) having micropore sizes below 6 Å. The method uses a series of carefully selected molecular probes varying in their minimum Van der Waals diameter between 3.7 and 6.0 Å. Various small-pore zeolites were used to validate the method. Over the critical micropore size range these probes can establish the "effective" microporosity which can be modified by post-treatment to produce an O_2-selective CMS useful for air separation. This method coupled with kinetic measurements of O_2 and N_2 uptake indicates that pores larger than 4 Å are not highly O_2-selective. Results from these molecular probe studies in combination with porosimetry and pycnometry measurements show that the O_2-selective carbons have an unusual bimodal pore distribution with no significant mesoporosity. We found obtaining pore distributions from equilibrium analysis of N_2 or O_2 isotherms at cryogenic conditions was inappropriate on these carbons. The study clearly demonstrates the importance of the method which monitors the size and relative amounts of micropores which are O_2-selective.

Keywords: adsorbent; air separation; carbon molecular sieve; micropore size distribution; molecular probes; porosity; zeolites

Introduction

Carbon molecular sieves (CMS) are a subgroup of activated carbon which have both high internal surface area and some degree of molecular sieving capability. Walker's early research [1] was the first report of CMS adsorbents specifically prepared to demonstrate size and shape selectivity. This early work focused on equilibrium column processes for hydrocarbon separation by molecular exclusion. A decade later Jüntgen *et al.* [2] prepared a CMS which separated O_2 and N_2 by "partial molecular sieving". The first commercial use of CMS for nitrogen production was developed over a decade ago [3]. Today there are growing commercial applications for these CMS adsorbents to produce N_2 from a pressure swing adsorption (PSA) process [4]. Therefore, there is a keen interest in developing better CMS adsorbents for air separation as well as for other separation and purification applications.

CMS adsorbents used for separating air are slightly selective towards O_2 at equilibrium having similar capacities for both O_2 and N_2. However, the rate of adsorption of O_2 is about twenty to thirty times faster than that of N_2, thus imparting these adsorbents with high kinetic selectivity for O_2. This difference in uptake rate, combined with suitable PSA cycles, provides the basis for several commercial processes for producing N_2. It is widely accepted that the gate-keeping layer or surface barrier at the entrance to the micropore plays a critical and dominant role in imparting these CMS adsorbents with high degrees of kinetic selectivity [5]. Yet effective, simple methods to measure the micropore distribution of this important class of adsorbents have not been reported previously.

Although much attention has been given to the characterization of microporous-activated carbons, there are few reports describing micropore size and distribution for CMS adsorbents used in air separa-

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tion. This is largely because the standard adsorption measurements and theories which are applicable to most carbons are not applicable to CMS adsorbents where the size-discriminating micropores are of molecular dimensions. There are several excellent reviews describing the current state of the art in modeling micropore–mesopore distributions for activated carbons from adsorption data [5–7]. The Kelvin equation, the Dubinin–Astakhov equation, and, more recently, the Horvath-Kawazoe method do not adequately describe the effective micropore distribution of CMS adsorbents having a narrow-pore distribution below 10 Å. Suzuki [8] and Carrott and Sing [9] have concluded that the best approach to defining the effective pore opening in a CMS is to use a series of organic vapors varying in size and shape.

Numerous studies using different organic vapors to define microporosity of activated carbons have been made. In most cases the carbons do not have sufficient micropores small enough to demonstrate significant kinetic selectivity towards O_2 from air. Some relatively early work by Koresh and Soffer [10] demonstrated the effectiveness of using molecular probes to study the porosity of O_2-selective carbon produced by heating a carbon cloth under vacuum. A more recent study using molecular probes is briefly described by Suzuki [8] and was carried out on a series of unidentified CMS adsorbents. Takeda Chemical [11] also developed a related method, but none of these methods were described in detail.

We wanted to determine the influence of effective micropore size and distribution on the O_2 uptake rates of CMS adsorbents after different treatments. The effects of pore size modification on the kinetic O_2 selectivity by hydrocarbon deposition is reported elsewhere [12–14]. This paper describes the molecular probe technique we used and our attempts to use standard adsorption methods for studying CMS adsorbents. Further, this work shows how molecular probes can be used to monitor small, but very important changes in microporosity which are not currently possible using conventional approaches with a single adsorbate, such as N_2 or CO_2.

Experimental

The carbons used in this work were in granular or pelleted form (2–3 mm) and representative of CMS adsorbents generally referred to as 3A, 4A, 5A, and activated carbon. The activated carbon, grade 203C from Suitcliffe Speakman, was a granular, highly microporous coconut shell-derived adsorbent labelled CSS for this work. Commercial samples of CMS-4A and CMS-5A were obtained from Takeda Chemical Industries. Commercial samples of CMS used in air separation processes are available from several sources. The data given here are typical for a commercial air separation adsorbent produced in 1990. These adsorbents are labelled in this paper as CMS-3A; however, as our studies show, the majority of the effective microporosity is larger than 3 Å.

Adsorption of the organic vapors was measured on a McBain–Bakr-type balance. Approximately 5 g of the carbon samples were loaded into quartz sample cylinders and suspended from individual helical quartz springs. Pelleted samples do not ordinarily require crushing or grinding provided representative samples of the material can be obtained. Powders can also be used, but special precautions must be taken to prevent loss of sample from the sample containers during evacuation and heating. Weight changes due to adsorption were determined from the spring extensions and spring constants. The cumulative error associated with reading the spring extensions is 0.005 ml/g. The carbon samples were outgassed under vacuum for 16 h at 110°C to a final pressure of 10^{-5} Torr prior to exposure to the organic vapor. A fresh carbon sample was used for each vapor measured. With the exception of the water and *n*-butane vapor measurements, the samples and vapor source were thermostated at 28°C and exposed to the organic vapors at a relative pressure (P/P_0) of 0.5. This pressure is sufficiently high to assure the adsorption measurement is being made on the plateau of the isotherm but low enough to eliminate any potential errors due to condensation. All *n*-butane measurements were done at 0°C in order to obtain the desired relative vapor pressure of 0.5. We found a P/P_0 of 0.9 was required for water to be an effective probe. Adsorption of each vapor was measured

24 h after initial exposure. All hydrocarbons were of a minimum 99% purity and were further purified by the freeze–pump–thaw technique. The amount of organic vapor adsorbed at the desired relative pressure is expressed as the volume of liquid adsorbed per gram of adsorbent, assuming the density of the adsorbed phase is the same as the density of the bulk liquid.

Results and discussion

Molecular probe studies

Molecular probe studies have been used by many researchers to measure the porosity of activated carbons. In almost all cases the adsorption isotherms of the probe molecules are measured at equilibrium conditions. Most researchers then analyze the isotherm data using a proposed model such as the Dubinin–Radushkevich equation or Sing's α_S method to obtain a micropore volume for each vapor [7]. From these data an estimate of the micropore size range can be made. For materials like activated carbons that have pores greater than 5 Å in diameter, this approach is reasonable. It is not appropriate for characterizing air separation carbons in which the bulk of the pore size is less than 5 Å. Equilibrium isotherms of some vapors could take weeks to measure on these materials. Our approach was to pursue a molecular probe technique based on a single adsorption point measurement of a series of carefully selected vapors varying in molecular diameter by approximately 0.3 Å. This method extended previous work of Nishino [11]. Based on results for PVDC-based chars, Ainscough and Dollimore [15] suggested that the total pore volume measured for a given adsorbate could not be related to the relative micropore sizes due to pore constrictions and activated diffusion effects. However, we found that the apparent pore volume determined after a 24-h exposure varies greatly depending on the size of the organic vapor. This indicates that the Gurvitsch rule is not obeyed and that these pores are effective molecular sieves for the range of vapors being used. In this way we can obtain an "effective" micropore size distribution of the adsorbent over a range of 3.7–6.0 Å within a few tenths of an angstrom in a reasonable period of time. Using a twelve-port McBain–Bakr balance, we measured micropore size distributions within this range on twelve CMS materials in twelve days.

There are many methods of estimating effective molecular size. Ainscough and co-workers [15,16] have shown that these different methods all give different values and in several cases may alter their relative molecular size. Many studies on adsorption and diffusion in molecular sieve materials have shown the proper relative molecular size is achieved for most cases using the smallest molecular dimensions [10]. Therefore the minimum Van der Waals cross-sectional diameter which gives a measure of the size of the molecule in its equilibrium state provides the best measure of relative size for this study. In a recent review on the diffusivity in CMS-4A and -5A Karger and Ruthven [17] state that for these systems it is more satisfactory to correlate molecular transport to molecular size than the critical kinetic diameter. Table 1 summarizes the physical properties and minimum Van der Waals diameters for the molecular probes used in this study.

We established how appropriate it is to use Van der Waals diameters to gauge the micropore size by using small-pore zeolites to standardize the correlation. The results are given in Table 2. We measured uptakes for water (3.2 Å), methylene chloride (4.0 Å), isopentane (4.9 Å), and carbon tetrachloride (6.0 Å) over KA (3.0 Å), NaA (4.2 Å), CaA (4.8 Å), and Ca chabazite (3.7 × 4.2 Å). The agreement between the minimum Van der Waals diameters of the probes and the accepted pore size of the zeolite in most cases is very good [21]. In particular, note that the pore volume obtained for water is the same as that reported elsewhere [21]. Methylene chloride, which has a Van der Waals diameter of 4.0 Å, goes into all the zeolites having a free pore aperture in excess of 4.0 Å. The adsorption uptake for chabazite is significantly less than the larger-pore 5A zeolite having similar internal void volume suggesting that under the conditions of these studies ($P/P_0 = 0.5$ after a 24-h exposure) the chabazite sample has not reached equilibrium. Presumably this is due to the kinetic constraints on the adsorption arising from the similarity in size of the pore and molecule.

TABLE 1

Molecular probe properties

Vapor	Liquid density[a] (g/ml)	Saturation vapor pressure at 28°C[b]	Minimum Van der Waals diameter[d] (Å)
H_2O	0.996	28	3.2
CS_2	1.2610	400	3.7
CH_2Cl_2	1.3266	442	4.0
n-C_4H_{10}	0.6012	760[c]	4.3
$CHCl_3$	1.4832	200	4.6
i-C_5H_{12}	0.6201	720	4.9
CCl_4	1.5867	120	6.0

[a] From CRC Handbook of Chemistry and Physics.
[b] Measured experimentally.
[c] Measured at 0°C.
[d] Refs. 18–20.

TABLE 2

Sorption of molecular probes on zeolites

Adsorbent[a]	Sorption (ml liquid/g)						
	CCl_4 (6.0 Å)	i-C_5H_{12} (4.9 Å)	$CHCl_3$ (4.6 Å)	n-C_4H_{10} (4.3 Å)	CH_2Cl_2 (4.0 Å)	CS_2 (3.7 Å)	H_2O (3.2 Å)
CaA (4.8 Å)	0.003	0.019	0.146	0.19	0.20	0.21	0.28
Ca chabazite (3.7 × 4.2 Å)	0.006	0.011	0.023	0.16	0.19	0.22	0.25
KA (3.0 Å)	0.001	0.004	0.002	0.004	0.001	0.001	0.23
NaA (4.2 Å)	0.001	0.007	0.001	0.007	0.17	0.17	0.28

[a] The zeolites were dehydrated to 400°C under a dynamic vacuum of $<10^{-5}$ Torr at 2°C/min with 1-h holds at 150 and 250°C and maintained at 400°C for at least 12 h.

The pore properties, selectivity, and equilibrium volumetric O_2 capacities for the carbons used in this study are given in Table 3. Micropore volumes in Table 3 are those pores accessible to helium but not mercury (~30 Å is the minimum pore diameter at a Hg intrusion pressure of 60 000 p.s.i. and a contact angle of 130°). From this bulk porosity data there are no obvious trends, and it is impossible to predict the extent of O_2 selectivity found. The O_2 capacities at equilibrium differ by no more than 10%.

We used molecular probe studies on a variety of carbon adsorbents to guide our synthetic approaches for producing a superior O_2-selective CMS. We carried out molecular probe studies on CMS-4A and CMS-5A and compared them to commercial CMS-3A used in air separation. These results are shown in Figure 1. Comparison of the conventional pore data (Table 3) for the 3A, 4A, and 5A shows that 3A and 4A have a lower micropore volume than CMS-5A. However, the molecular probe studies (Fig. 1) show that the CMS-5A actually has more micropores accessible to CS_2 (3.7 Å) than CMS-3A. We suspect that 3A has many small micropores (<3.5Å) which are inaccessible to oxygen but will adsorb helium and contribute substantially to the total micropore volume. This result points out the importance of the molecular probe studies which monitor the size and relative micropore volume which is O_2-selective. We postulate that the higher microporosity for CMS-5A would allow us to make an O_2-selective CMS from 5A which has higher working capacity if we optimize the hydrocarbon cracking to produce an effective selective barrier on the micropore. The molecular probe studies show that the commercial CMS adsorbents (4A and 5A) have most of their microporosity at about 1 Å greater

TABLE 3

Properties of base carbons

Sample	O_2/N_2 selectivity[a]	O_2 capacity at 25°C[b] (ml/ml)	Hg density[c] (g/ml)	He density[d] (g/ml)	Total pore volume[e] (ml/g)	Micropore volume[f] (ml/g)
CMS-3A	37	8.0	1.0	1.96	0.47	0.16
CMS-4A	<10	8.1	1.0	2.01	0.48	0.17
CMS-5A	1	8.1	0.91	2.01	0.60	0.20
CSS	1	7.2	0.92	1.91	0.56	0.21

[a] Ratio of mass transfer coefficients (k) at 23°C (calculated from $N(t)=N(s)[1-e^{-kt}]$, where N is the amount adsorbed at time t and at saturation s.

[b] Volumetric O_2 capacity obtained from gravimetric O_2 capacity at 1 atm O_2, 25°C corrected for the pellet density and initial adsorption of chemisorbed oxygen.

[c] Density measured by Hg porosimetry (Micromeritics, 60 000 p.s.i. Hg).

[d] Density measured by He pycnometry (Micromeritics).

[e] [(1/Hg density)−(1/He density)].

[f] [Total pore volume]−[Pore volume from Hg porosimetry to 60 000 p.s.i. Hg].

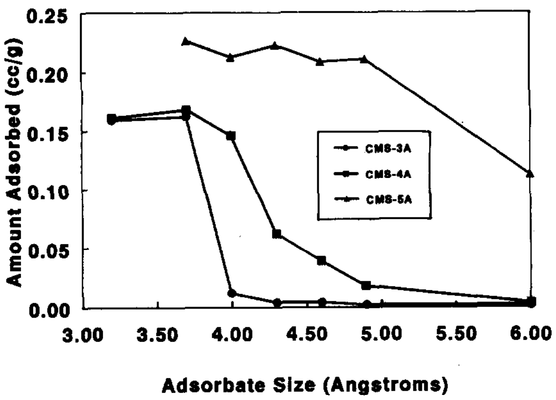

Fig. 1. Micropore distribution for carbon molecular sieves measured by the molecular probe method.

than the size implied by its name. In other words, 4A has pores which adsorb 5-Å molecules but not 6-Å molecules.

The method provides a *relative* measure of accessible or effective pore size and depends heavily on the assumption that adsorption under pore-filling conditions is only effected by the pore size. We used the molecular probe method to measure micropore size distribution over a narrow but critical range.

We initially measured the adsorption of six molecules varying in size from water (3.2 Å) to CCl_4 (6.0 Å). We attempted to use water to get better definition of 3-Å pores and used CS_2 to discriminate between pores less than 4.0 Å. However, for several experiments at 0.5 partial pressure the water uptake was always less than the CS_2 adsorption. It is known that water adsorption on carbon is influenced by hydrogen bonding and surface interactions. Therefore water adsorption is usually less than the expected uptake based on the micropore volume. We attribute our low results to these factors. To overcome the factors responsible for the low uptake, we increased the water partial pressure to 0.9 and studied three representative carbons. The results of these studies are summarized in Table 4.

Increasing the partial pressure of water in all cases increased the uptake to the amount of CS_2 adsorbed. This shows that under high vapor pressure water can also be an effective probe of micropores below 3.7 Å.

We found that higher outgassing temperatures influenced the kinetic selectivity for some of these carbons. Since we wanted to measure the effective micropore size which controls this rate, we only desired to remove any physisorbed surface species

TABLE 4

Water adsorption on carbon adsorbents

Sample	Water uptake at 28°C (ml STP/g)	
	$P/P_0=0.5$	$P/P_0=0.9$
CMS-3A	0.120	0.159
CMS-4A	0.128	0.161
CSS	N.A.[a]	0.283

[a] N.A. = not available.

and found that outgasing under vacuum or helium flow at 110°C was sufficient and did not alter the relative rates of gas uptake.

One might question the validity of this molecular probe method since in certain cases the adsorption after 24 h of exposure may not reach equilibrium. To determine the magnitude of this effect, we measured uptake curves for each vapor sorbed on some selected carbons ranging from "3A-like" to CSS type. In five out of the six cases all vapors were at least 95% of their equilibrium value after 8 h of exposure. For one sample after 100 h, the CH_2Cl_2 uptake was still slowly increasing and was nearly twice the value recorded at 24 h. The smaller CS_2 had achieved an equilibrium value after 8 h. This clearly indicates that the pore volume measured under these conditions is significantly lower than that actually present. This is due to the close match in size of the pore mouth and probe molecule. It is therefore possible to have pore distributions which are skewed 0.3 Å or less toward smaller pores or a narrower distribution. However, by carrying out the molecular probe studies in a consistent manner and taking all adsorption data 24 h after exposure, it has been possible to assess the "effective" pore distribution which is important for identifying suitable carbon precursors for further modification. This method enables us to define and understand the importance of micropore size distribution for separation of permanent gases and small hydrocarbons.

Duplicate studies for three of the carbons showed the method is reliable with the largest difference in uptake being 0.01 ml/g for *n*-butane on CMS-4A. In addition, for many samples the total micropore volume from pycnometry and porosimetry measurements are in excellent agreement with CS_2 uptakes.

McEnaney [22] has expressed concern that in certain cases molecular probe studies on carbons were complicated by the micropores swelling when contacted with a hydrocarbon vapor. To see if this was a factor in our studies we measured the N_2 uptake at a $P/P_0 = 0.5$ after 24 h for CMS-4A and -5A. N_2 and CH_2Cl_2 have the same minimum Van der Waals diameter (4.0 Å) and should give similar uptake at the same partial pressure if there is no change in pore size and surface interactions are negligible. The results from this study are given in Table 5. The uptakes for CH_2Cl_2 and N_2 are in good agreement. This suggests that the CMS adsorbents used for this study do not swell significantly and also that the functionality or polarizability of the organic molecules is not strongly influencing the uptake of these sorbates.

It should be noted that carbons having a significant amount of porosity between 10 to 25 Å will give pore volumes which are significantly larger than that calculated from the difference in mercury and helium densities. This is due to some multilayer adsorption of the molecular probes in the larger micropores at the high relative pressure. Fig. 2 gives the incremental pore size distribution obtained using mercury intrusion (to 60 000 p.s.i.) for the carbons of interest. In all cases there is not significant mesopore (30–1000 Å) content, and in combination with the molecular probe results, indicates there are very few pores below 1000 Å until you access the molecularly sieving porosity around 5 Å. Therefore this method is most applicable to carbon samples having this unusual bimodal pore distribution (*i.e.* no pores between 6 and

TABLE 5

N_2 and CH_2Cl_2 uptakes at $P/P_0 = 0.5$ after 24 h

Adsorbent	CH_2Cl_2 (ml liquid/g)	N_2 (ml liquid/g)
CMS-4A	0.16	0.15
CMS-5A	0.24	0.22

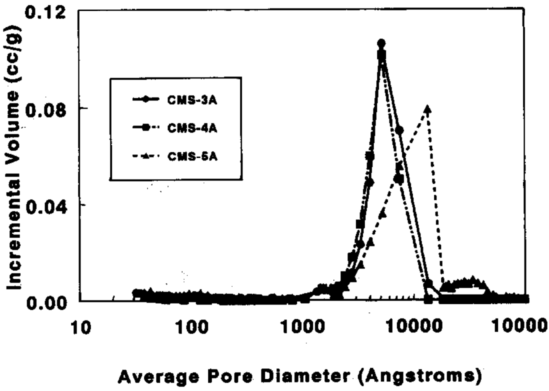

Fig. 2. Incremental pore size distribution of carbon molecular sieves from mercury porosimetry to 60 000 p.s.i.

1000 Å). However, to obtain the relative pore volumes for differently sized molecules, the method has general utility for a wide range of carbons.

Hydrocarbon cracking

There have been extensive efforts to reduce the size of the microporosity using hydrocarbon cracking on source carbons which have porosity larger than 4 Å. An extensive amount of synthetic work using these molecular probe studies and competitive adsorption studies showed that in order to produce an effective O_2-selective CMS there must be the proper match between the hydrocarbon size and the carbon support. By controlling this size match, we demonstrated that facile O_2 selectivity can be imparted using isobutylene on 4A, and 1,1-dimethylcyclohexane or preferably 1,3,5-trimethylcyclohexane on 5A [12,13]. The effect on micropore distribution for hydrocarbon cracking on 4A is shown in Fig. 3. Cracking isobutylene on CMS-4A gives an O_2-selective carbon which has the same selectivity as a CMS-3A carbon [14]. This is not surprising since the micropore distributions are indistinguishable. In contrast, the CMS-4A sample treated with cyclohexane appears to be plugged and have little microporosity at 3.7A. O_2 uptake on this adsorbent is very slow. These adsorption results are totally consistent with the micropore distribution found using the molecular probe method.

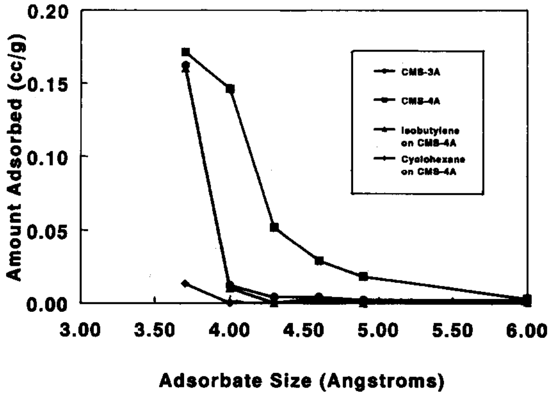

Fig. 3. Micropore distributions for hydrocarbon deposition on CMS-4A.

Equilibrium adsorption studies

We also measured O_2 and N_2 isotherms for the O_2-selective CMS-3A at 87 and 77 K, respectively, to see what fraction of the microporosity was accessible to both N_2 and O_2. No appreciable N_2 adsorption occurred over two days; however, a large amount of oxygen (155 ml STP per g near saturation) slowly adsorbed. The O_2 isotherm is type I and required two days to measure 40 data points to a relative pressure of 0.95. The absence of appreciable N_2 adsorption indicates that the O_2-selective carbon has a bimodal pore distribution with an insignificant amount of accessible porosity between 4 and 30 Å. Attempts to adsorb Xe (4.4 Å), which is spherical in shape at 298 K, produced a similar result. The O_2-selective carbons appear to have an unusual micropore distribution with only micropores less than 4 Å. Only 6.5 ml N_2 STP per g was adsorbed on CMS-3A at a $P/P_0 = 0.989$. This translates to a total pore volume accessible to N_2 of 0.01 ml/g for pores up to 1750 Å. This is very small compared to the helium- and O_2-accessible micropore volumes which are about 0.2 ml/g. The results from N_2 adsorption are in complete agreement with the previously discussed porosimetry results for CMS-3A and confirm its unusual bimodal pore distribution.

Attempts to determine the micropore distribution for CMS-3A using a *t*-plot analysis were unsuccessful. This was due to the very slow N_2 adsorption at 77 K due to the activated diffusion. Despite repeated attempts it was not possible to obtain closure of the N_2 isotherm upon desorption. Using oxygen at liquid argon temperature the adsorption and desorption isotherms were totally indistinguishable. This confirms that differences observed in the adsorption–desorption branches of the N_2 isotherm were due to non-equilibrium effects. The lack of hysteresis in the O_2 isotherm upon desorption indicates a total absence of mesoporosity from CMS-3A.

In an attempt to assess the microporosity from the oxygen isotherm, we applied the Dubinin–Radushkevich (DR) equation. The DR plot exhibits negative deviation from linearity at low relative pressure. One possible explanation for this is activated diffusion [23]. The long analysis time required to measure the isotherm supports this conclusion. We therefore could not use the DR equation on oxygen isotherms as a means of measuring the microporosity of these materials.

CMS adsorbents and activated carbons consist of a random distribution of voids between distorted graphitic particles consisting of three or four carbon layers [5]. Discussions of the bulk structure of activated carbon can be found in refs. 5 and 7. The constrictions or selective barrier to the micropores give rise to the kinetic selectivity observed in CMS. Modifying these constrictions by heating, hydrocarbon deposition and the like have a minor influence on the overall micropore volume but can greatly affect the molecular sieving properties of the adsorbent. Since the overall accessible pore volume is marginally effected, the size discriminating constrictions or "gates" must be close to the surface of the carbon particle. Similar behavior was observed by Koresh and Soffer [10] in their study of carbon cloth.

Conclusion

We found that O_2-selective carbons have an unusual bimodal pore distribution with an insignificant amount of accessible porosity between 4 and 1000 Å. The molecular probe method reported here is an effective and efficient way to monitor small changes in the effective micropore size distribution of CMS adsorbents having <6 Å pores which greatly alter their kinetic selectivity for O_2 from air in a time domain which is useful for a practical application such as air separation. The method establishes the relative size and amounts of micropores which are O_2-selective. This approach provides a suitable nanoscale ruler to effectively measure relative micropore size to within 0.3 Å. Controlled studies on small-pore zeolites confirmed that the minimum effective diameter of the molecular probes gave the best correlation to known micropore sizes. The molecular probe method facilitates the proper selection of hydrocarbon needed for converting a non-selective activated carbon precursor into an effective air separation adsorbent.

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