ALTERATION OF MOLECULAR SIEVING PROPERTIES OF MICROPOROUS CARBONS BY HEAT TREATMENT AND CARBON GASIFICATION

S. K. Verma† and P. L. Walker, Jr.
Department of Materials Science and Engineering, The Pennsylvania State University,
University Park, PA 16802

Abstract—The effect of thermal treatment on the porosity of microporous carbons, of pore structure ranging between that of a carbon molecular sieve (CMS) and an activated carbon (AC), was investigated by adsorption and diffusion of O_2 and Ar. Sieving behavior was improved in the case of carbons containing molecular sieving pores. Selectivity for separation of O_2 and Ar was enhanced by heat treatment of a CMS at ~1100 K. No useful molecular sieving properties were developed by the thermal treatment of an AC. Pore opening by controlled carbon gasification was also demonstrated as a method to adjust the size of the sieving pores of carbons containing an appropriate pore structure. In some cases, the net effect of carbon gasification was shrinkage of pores in a particular size range, which introduced interesting possibilities for production of highly selective CMS.

Key Words—Carbon molecular sieve, activated carbon, polymer, carbon, adsorption, diffusion, O_2, Ar, heat treatment.

1. INTRODUCTION

Workers have shown that the microporous structure of coals[1–5], active carbons[6–9], and polymer based carbons[10–13] can be altered by thermal treatment. With increasing heat treatment temperature (HTT) up to ~1273 K, the microporous structure of such adsorbents is continually developed resulting in higher adsorption volume. But at higher temperatures, sintering results in rapid loss of adsorption volume. Available surface area of heat treated coals has been shown to reach a maximum level at temperatures of ~1273 K and then to decrease at higher HTT[2,4]. In this process, the microporosity was shifted to pores of smaller diameter, demonstrating that the pore structure of adsorbents containing micropores can be controlled effectively by temperature processing. Toda and coworkers[7] have shown that the relative uptake of adsorbates of different molecular sizes such as CO_2, *n*-butane, isobutane and CCl_4 by coal based carbons could be altered significantly by heat treatment in an inert atmosphere. In the case of polymer carbons, Dubinin[10] found that heat treatment results in development of open pore structure up to ~1273 K and that at higher temperatures the average pore size is diminished due to sintering. These studies indicate that, by thermal treatment of selected carbonaceous precursors, the size of micropores can be controlled sufficiently to produce carbons that show specificity in rendering access to different molecules. It appears that the molecular sieving properties of carbons can be modified by thermal treat-ment for their use in gas separation processes by altering the size of pore entrances to allow selective adsorption of a specific gaseous species.

Carbon molecular sieves are now being used commercially in pressure swing adsorption (PSA) systems for separation of gases, especially O_2 and N_2. Performance of PSA is critically dependent on the adsorption selectivity of a CMS for a specific component in the gaseous mixture. In such carbons, selectivity for uptake is controlled by the rate of diffusion of the adsorbing species into pores having constrictions similar in size to that of the adsorbing molecule. Small changes in the size of these constrictions in the micropore structure can impact the rate of diffusion of a gaseous component to a significant extent. In this study, the effects of thermal treatment and gasification of various carbons was investigated for improving their adsorption selectivity for a gas separation process, such as O_2 from N_2 or Ar. Development of molecular sieving pore structures in various adsorbents was followed by measuring adsorption of O_2 and Ar.

2. EXPERIMENTAL

Carbons with microporous structures varying between a system of narrow pores of a CMS and wide-open pores of an AC were studied. Various carbons used include a pelletized CMS, designated in this study as CMS-A; granulated carbons CMS-B and AC-A; and a polymer based carbon (designated as PFA). The pelletized CMS-A is a commercial carbon molecular sieve adsorbent derived from coal and used for separation of O_2 and N_2 in air. Due to its ability to separate these two gases, it can be classified as a

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Table 1. Physical properties of carbons

Carbon	Size	Mercury density g/cc	Surface area (m²/g) CO₂ (298 K)	N₂ (77 K)
CMS-A	4 mm × 1.5 mm	1.356	575	<1
CMS-B	14 × 40 mesh	1.207	680	345
AC-A	4 × 10 mesh	0.886	714	772
PFA	30 × 40 mesh	1.377	957	95

3-4 A CMS. CMS-B is a coal based carbon with a narrow pore size distribution around a pore diameter of 5 A. AC-A is a coal based commercial AC possessing a wide-open pore structure with the micropore volume in pores of 15 to 20 A in size and a system of macropores >1000 A. PFA carbon was made from polyfurfuryl alcohol following the method described by Walker et al.[14] using phosphoric acid as a polymerizing catalyst and by carbonizing at 1023 K for 4 h in N_2. The physical properties of these carbons are presented in Table 1. Surface areas, from CO_2 adsorption at 298 K, were calculated using the Dubinin–Radushkevich (D-R) equation. Surface areas, from N_2 adsorption at 77 K, were calculated using the BET equation.

Molecular sieving characteristics of the pore structure of these carbons, before and after treatment, were evaluated by measuring adsorption of O_2 and Ar under ambient conditions. Gas adsorption experiments were carried out in a volumetric adsorption apparatus using about 1 g carbon. Adsorption was measured by recording, continuously, the change in pressure in the system with help of a sensitive pressure transducer attached near the carbon sample holder. Gas equilibrium was quickly achieved in <5 s after exposing the carbon to the adsorbate. Pressure change due to adsorption could be measured at times as small as 10 s. As received carbons were outgassed at 383 K under vacuum (10^{-4} Pa) for 1 h.

Thermal treatment of carbons at temperatures up to 1323 K under vacuum and in an inert or a reactive gas atmosphere was carried out in the sample holder attached to the main adsorption apparatus. Treatment at higher temperatures was done under a N_2 atmosphere in a separate tube furnace. Carbons were then transferred to the adsorption system under an inert atmosphere for subsequent measurements.

3. RESULTS AND DISCUSSION

3.1 Effect of thermal treatment of carbons on absolute uptake of O_2 and Ar

Let us examine the effect of heat treatment on the pore structure of a CMS. Generally, for manufacturing these carbons, the inherent pore structure of the precursor is initially fixed into a suitable pore range by a controlled thermal treatment followed by a final tailoring of pore apertures either by carbon deposition from cracking of a hydrocarbon[16,17] or by impregnation with an organic compound[18]. Mo-

lecular sieve carbons are known to possess a narrow pore size distribution with pores largely of bottle neck shape [14–16]. These pores have openings or constrictions similar in diameter to that of the adsorbing molecules. Therefore, the carbon offers a kinetic selectivity to diffusion for a specific component of the gas mixture, depending on the minimum dimension of its molecule. For O_2 and N_2 separation, due to the smaller minimum dimension of the O_2 molecule, pore constrictions in a CMS whose size is similar to the minimum dimension of the O_2 molecule allow faster diffusion of O_2 and its preferential adsorption. It implies that performance of such carbons can be significantly affected by altering the size of constrictions in the adsorption pores.

Physical data for O_2 and Ar are shown in Table 2. Since these gases have very similar boiling points and critical temperatures, their equilibrium adsorption on a carbon should be essentially the same under identical conditions. Therefore, any chance of separating Ar from O_2 depends on their relative rates of adsorption. Kinetic diameters[19] of Ar and O_2 are also similar. However, the two molecules differ significantly in width, that is, in their minimum dimension[20]. The minimum dimension of O_2 is ~1.0 A smaller than that of Ar. Therefore, for separation of these gases, the critical pore dimensions for which diffusion of Ar becomes activated and that of O_2 remains unactivated may be designated as <3.8 A and >2.8 A, respectively.* Rao et al.[22] have suggested that in addition to the energy barrier at the entrance of pores of critical dimension, diffusion is also dependent upon the energy barrier for diffusion within the pore. However, it is indicated that the largest energy barrier for diffusion through the pores occurs at the entrance of the pore of critical dimension and that the relative rate of diffusion of various species depends on the relative magnitude of this energy barrier. For the CMS-A which contains pores with entrances 3-4 A in size, it is expected that at a given temperature and pressure the rate of O_2 diffusion should be higher than Ar due to the smaller minimum dimension of the O_2 molecule.

Volume uptake-time plots of O_2 and Ar on CMS-A heated to various temperatures under vacuum,

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* As discussed previously[21], the critical pore dimension is larger than the kinetic diameter of the molecule (about 1.6 A); but for simplicity and because of precedence, kinetic diameters will be used in this paper.

Table 2. Physical data for O_2 and Ar

Gas	Boiling point (°K)	Critical temperature (°K)	Pauling dimensions		Kinetic diameter A
			Length A	Width A	
O_2	90	155	3.9	2.8	3.46
Ar	87	151	3.84		3.40

for 30 min at each temperature, are shown in Fig. 1. The diffusion rate of each gas is significantly increased on heating up to ~973 K. This increase in adsorption is thought to result primarily from partial desorption of the surface carbon—oxygen complex and, to some extent, to the decomposition of the organic impregnant, if any, present on the as-received carbon. The increase in rate of Ar adsorption indicates that, due to the heat treatment, some pore entrances are enlarged to a size >3.8 A and some

additional pore volume is also created, as will be discussed later. At a HTT of ~1073 K, a breakpoint was noted for this carbon, as the uptake rate of Ar is significantly diminished. At a HTT of 1098 K, Ar uptake is reduced to a level similar to the uptake on the virgin carbon (outgassed at 383 K). However, uptake of O_2 at 8 min remains high, though some decrease in initial diffusion rate on the sample heated to 1098 K is noted. Reduction of Ar diffusion in the 8 min period indicated that the size of some pore
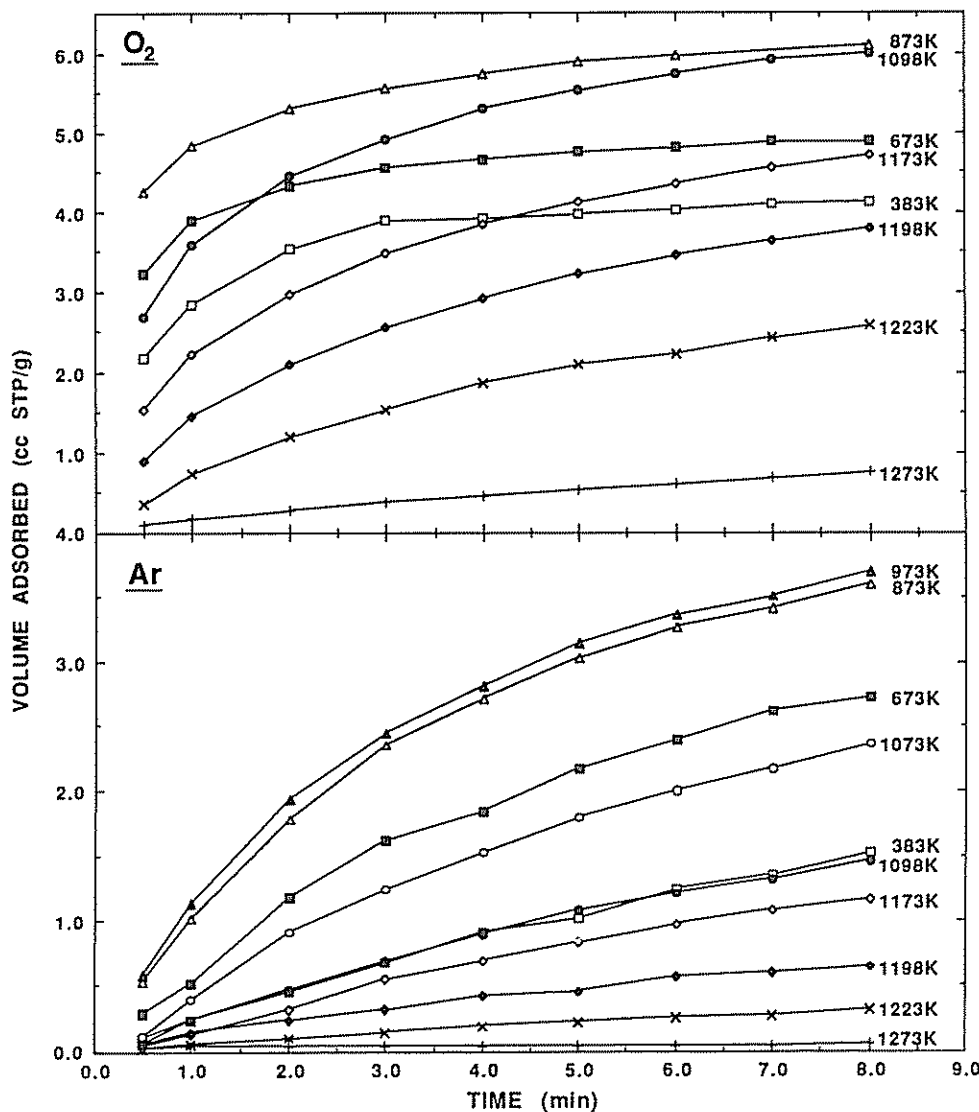

Fig. 1. Effect of HTT on diffusion of O_2 and Ar in CMS-A at 298 K.

constrictions has been reduced to <3.8 A. On increasing the HTT further up to 1273 K, the diffusion rates of both O_2 and Ar are sharply diminished. These results suggest that with increasing HTT above ~973 K, the size of the pore entrances is gradually decreased to <3.8 A and ultimately even <2.8 A. Although some surface-oxygen complex may still be desorbing at temperatures >973 K, pore sintering becomes predominant. Koresh and Soffer[23], in their work on a fibrous CMS, have also shown that for HTT up to 973 K pore enlargement is predominant due to elimination of CO_2 and CO. At somewhat higher temperatures, reduction in pore size becomes predominant, in agreement with our studies.

The effect of heat treatment on another potential carbon sieve material, CMS-B, presents a different picture. Diffusion plots of O_2 and Ar on this carbon are shown in Fig. 2. Following heating to only 383 K, this carbon does not show any useful sieving be-

havior for separation of O_2 and Ar. Obviously, the pore constrictions in this carbon are larger than th minimum dimension of the Ar molecule. The adsorbing pores offer no kinetic resistance; and, therefore, both gases show similar rates of diffusion. Diffusion plots of O_2 and Ar on CMS-B heat treated to higher temperatures are also included in Fig. 2. Heat treating this carbon at temperatures between 1123–1273 K in vacuum and 1373–1673 K in N_2 for 1 h produces significant changes in the pore structure and uptake rates. Uptake rates of O_2 are significantly increased upon heating up to 1123 K. On the other hand, there is only a small change in Ar uptake rates upon heating above 383 K up to 1123 K. It indicates that up to 1123 K mainly pores with constrictions of size <2.8 A are enlarged to a size between 2.8–3.8 A. The 1123 K-heat treated carbon shows some favorable selectivity for uptake of O_2. Upon heat treatment to higher temperatures, diffusion rates for both
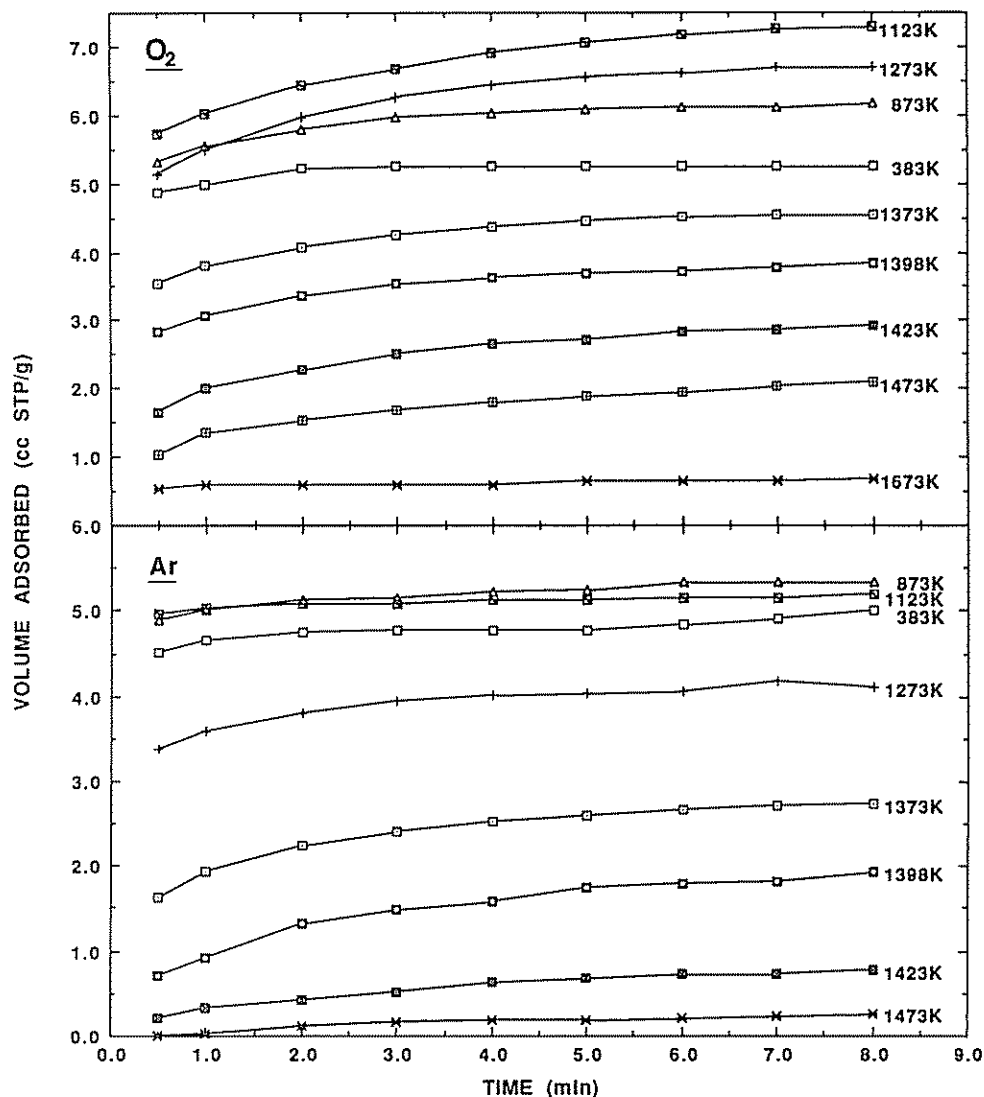

Fig. 2. Effect of HTT on diffusion of O_2 and Ar in CMS-B at 298 K.

Table 3. Effect of heat-treatment on surface areas of
selected carbons

Carbon	Pretreatment	Surface area (m²/g)	
		CO₂ (298 K)	N₂ (77 K)
CMS-B	383 K, 1 h, vac	680	345
	1123 K, 1 h, vac	717	315
	1273 K, 1 h, vac	680	—
	1673 K, 1 h, N₂	37	46
PFA	383 K, 1 h, vac	952	95
	1173 K, 1 h, vac	966	51

gases decrease gradually due to pore sintering. However, differences in rates of diffusion of O_2 and Ar are maintained for all carbons heat treated above 1123 K. The CMS-B carbon heated at 1273 K or 1373 K shows some useful differences in diffusion rates of O_2 and Ar (even up to a 30 min adsorption period). At HTT >1373 K adsorption volumes are reduced significantly. As received CMS-B clearly has pores of a larger average aperture size than does CMS-A. Therefore, as expected, a higher HTT is found for CMS-B before uptake rates of O_2 and Ar pass through a maximum.

Not only does thermal treatment of CMS affect their rate of uptake of gases, but it also can affect their surface areas, as seen in Table 3. Heat treatment of CMS-B carbon up to 1273 K has little effect on its surface area as measured by CO_2 uptake at 298 K. More severe heat treatment to 1673 K effectively removes access of CO_2 to most of the micropores which may remain. As expected, under these conditions, the surface areas accessible to CO_2 and N_2 are essentially equal.

Taking the area occupied by a physically adsorbed molecule of O_2 at 298 K as 27 A^2, it is estimated that O_2 covers ~39 m²/g of the surface of the CMS-B sample pretreated at 383 K. This represents a fractional coverage of 0.06, based on the CO_2 surface
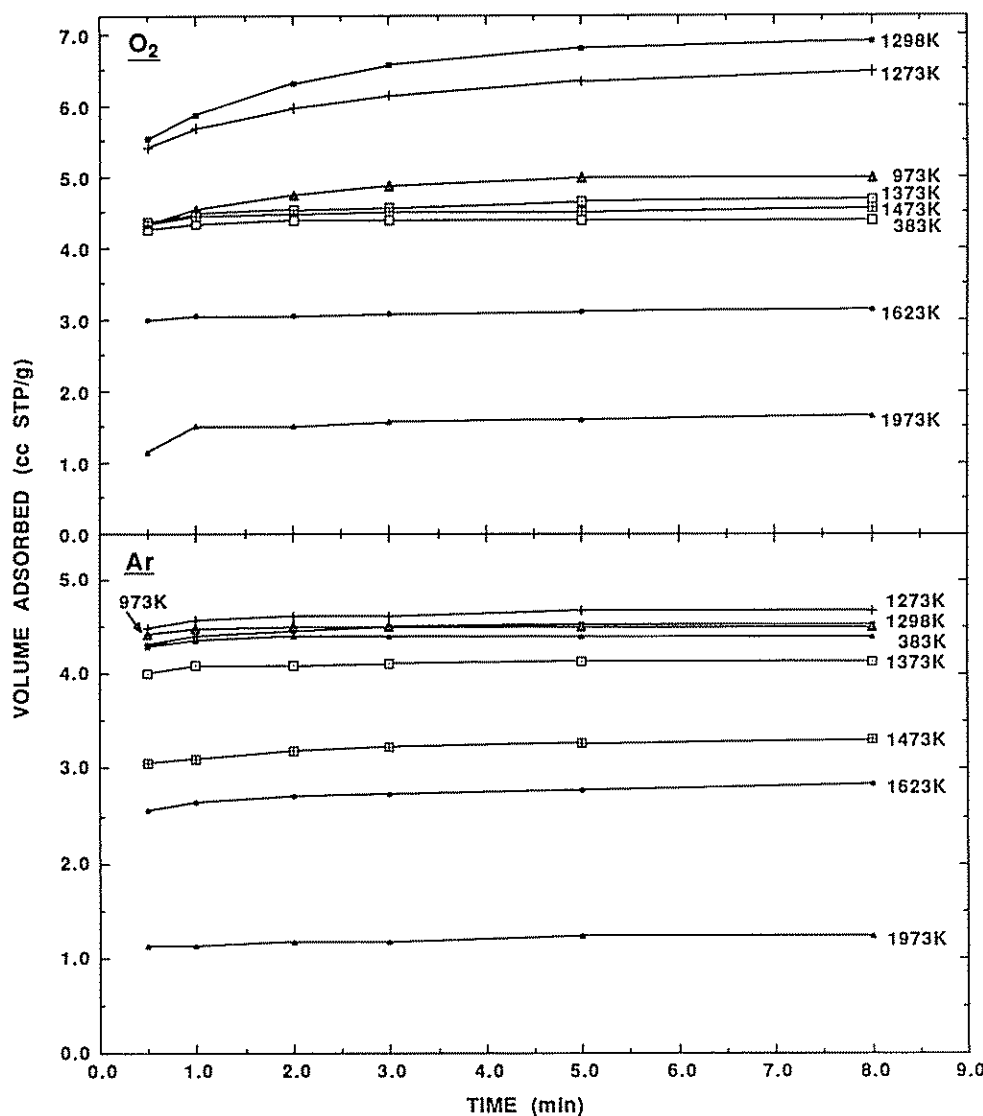
Fig. 3. Effect of HTT on diffusion of O_2 and Ar in AC-A at 298 K.

area, after 8 min adsorption time. Following pre-treatment of CMS-B to 1673 K, it is estimated that O_2 covers ~5 m^2/g of its surface after 8 min adsorption time, or a fractional coverage of 0.14.

In contrast to the above narrow-pore carbons, AC-A carbon has a wide open pore structure. It possesses high adsorptive capacity due to a large available surface area. Such carbons show negligible molecular sieving characteristics because they contain large micropores with an average pore size of ~20 A. Therefore, most of this microporosity is easily accessible not only to smaller gas molecules but also to quite large molecules such as long chain hydrocarbons. The pore structure of such carbons can be significantly changed upon heat treatment[7]. In this study, AC-A was subjected to thermal treatment in an attempt to modify its pore structure into a system of pores of entrances <3.8 A to be useful in separation of O_2 and Ar. Diffusion plots of O_2 and Ar on AC-A after heat treatment at temperatures up to 1973

K are shown in Fig. 3. As seen, the virgin carbon, outgassed at 383 K for 1 h, shows no selectivity between O_2 and Ar uptake. However, heating to 129 K under vacuum for 1 h yields a significant increase in O_2 diffusion rate over that for Ar. Some pores with entrances <2.8 A are enlarged to a size between 2.8 and 3.8 A to allow unactivated diffusion of O_2 to occur. Active carbons do contain some ultrafine pores that are not accessible to even He. Upon heating to a moderate temperature, entrances to such pores may be enlarged due to elimination of some surface oxygen functional groups. On heat treating to 1373 K in N_2 for 1 h, the carbon shows little selectivity. It appears that the fine sieving pores generated initially by HTT of 1298 K are reduced in size due to pore sintering. Upon further heating in steps up to 1973 K in N_2, adsorption capacity is continuously diminished for both gases and no specificity in adsorption is observed.
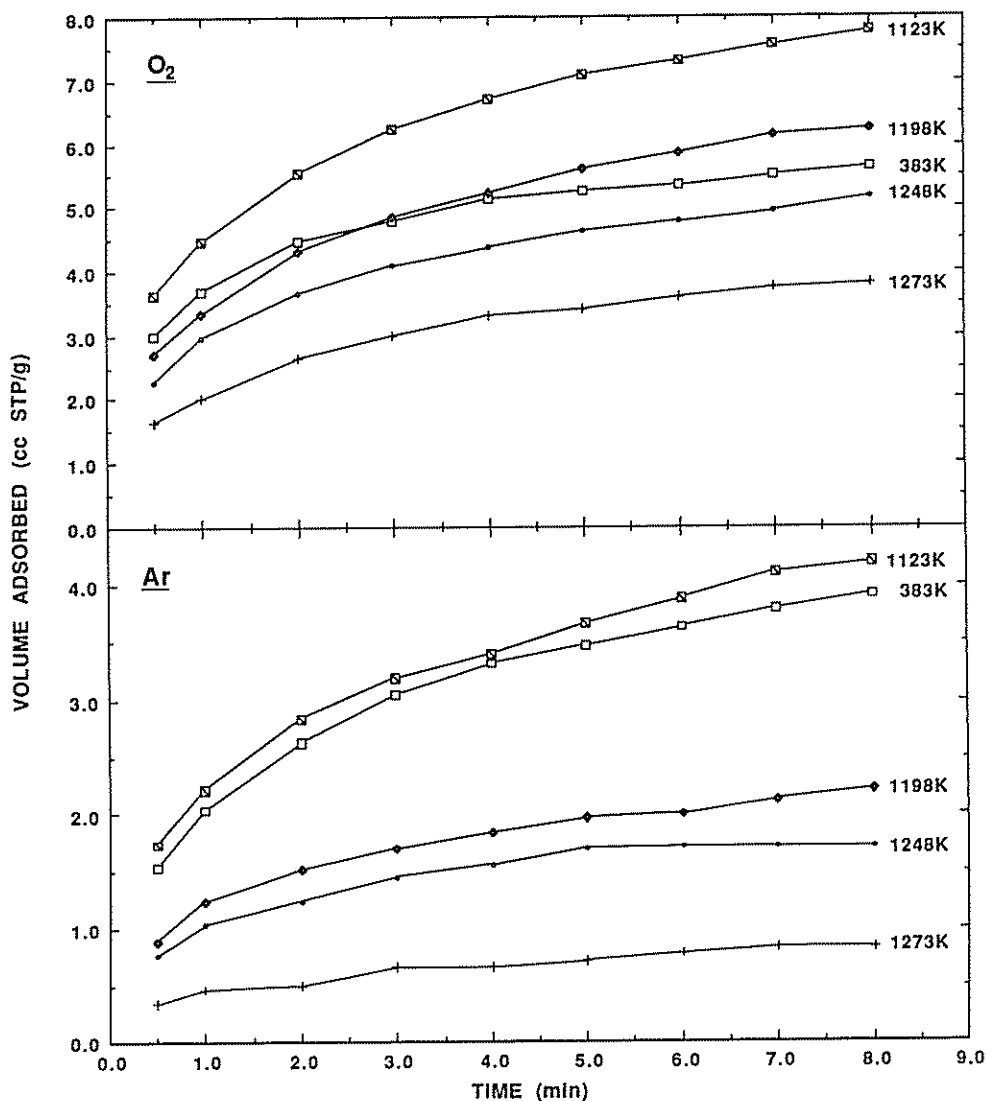
The effect of thermal treatment of the AC-A at

Fig. 4. Effect of HTT on diffusion of O_2 and Ar in PFA at 298 K.

the highest temperatures on O_2 and Ar uptake is different than that found for the heat treated CMS. In the case of the CMS, heat treatment to the highest temperatures resulted in a continuous decrease in uptake of both gases, but uptake of O_2 was always significantly higher than that found for Ar. For the AC-A, heating to the highest temperatures also resulted in a continuous decrease in uptake; but uptake of O_2 and Ar was more closely the same. This is the result of the open microporosity in the original AC-A having a considerably broader distribution in pore size than that existing in the original CMS samples. As the micropores are reduced in size upon heat treatment of AC, a much smaller number passes into the size range 3.8 to 2.8 A at any HTT as a result of sintering than is the case for the CMS samples. Thus, it is unlikely that an AC can be converted to a superior CMS simply by thermal treatment.

The effect of heat treatment on a polymer based carbon derived from polyfurfuryl alcohol (PFA) was also investigated. Polymer based carbons are known to exhibit shape selectivity by preferential adsorption of flat molecules. Lamond et al.[12] have concluded in their study of polymer carbons that molecular sieve effects observed in these carbons are due to the presence of slit-shaped pore constrictions. The as-received PFA carbon used in this study shows a significant selectivity for CO_2 over N_2 (Table 1), which suggests that it should also show selectivity for O_2 over Ar.

Diffusion plots of O_2 and Ar on PFA carbon, before and after heat treatment, are shown in Fig. 4. The virgin carbon shows some selectivity for O_2 adsorption. Upon heating to 1123 K, O_2 uptake is significantly enhanced to a level almost double the amount of Ar adsorbed. Argon adsorption shows no appreciable change upon heating to 1123 K. Upon further heat treatment in increments up to 1273 K, diffusion rates of both gases are continuously diminished. These results suggest that upon increasing the HTT up to 1123 K, the majority of the new open void volume in this carbon is created in pores with constrictions <3.8 A in size. At higher temperatures, sintering primarily occurs. The decrease in Ar diffusion indicates that an increasing number of pore constrictions are reduced to a size <3.8 A. Concurrent loss in O_2 diffusion suggests that some pore constrictions are also reduced to a size <2.8 A. Those reduced in size below 2.8 A exceed those reduced in size below 3.8 A.

3.2 *Effect of thermal treatment of carbon on uptake selectivity of O_2 and Ar*

The preferential adsorption of molecular species on CMS can be expressed, more explicitly, by using the term kinetic selectivity or selectivity which can be expressed as the ratio of O_2 to Ar uptake (O_2/Ar) for specific adsorption times. A PSA adsorption cycle for separation of such gases may range up to 5 min. Therefore, the selectivity of various heat treated carbons for 30 s and 5 min adsorption periods has

been considered and plotted against HTT in Fig. 5. For the CMS-A carbon the ratio at 30 s decreases with HTT up to 873 K. At HTT >873 K, the ratio increases sharply. It goes through a maximum at ~1098 K and then falls off rapidly with heat treatment at higher temperatures.

Heat treatment also has a marked effect on the O_2/Ar ratio for the other two starting molecular sieve carbons CMS-B and PFA. The HTT at which the maximum O_2/Ar ratio is found is a function of the starting carbon. For the 30 s adsorption cycle, the maximum in O_2/Ar ratio occurs as HTT increases in going from CMS-A to PFA to CMS-B. The temperature at which the maximum O_2/Ar ratio occurs is expected to depend upon a balance between the stablity of oxygen complex on the carbon and the resistance of each carbon to sintering. The stability of oxygen complexes, as to their release as CO and CO_2, is expected to depend upon the nature of their bonding with edge carbon sites. Resistance to sintering, or reduction in aperture size in carbons, is expected to depend upon a balance between the ease of removal of interstitial carbon atoms from between layer planes[24] of defective crystallites (and the accompanying dewrinkling of these basal planes) and the ease of breaking of crosslinks between poorly aligned crystallites (allowing improved crystallite alignment). The former process would be expected to increase aperture size created by crystallite packing; the latter process would be expected to reduce aperture size.

3.3 *Effect of extensive carbon gasification on uptake of O_2 and Ar*

So far it has been assumed that removal of carbon atoms by desorption of oxygen complex as CO and CO_2 (carbon gasification) will result only in enlargement of aperture size. However, it has recently been shown by Easler[25] and Hurt et al.[26] that carbon gasification of disordered carbons (chars) can also lead to particle shrinkage as a result of gasification-induced atomic rearrangement. This can result in reduction in aperture size and loss of volume in open micropores. It is believed that gasification of low-temperature, disordered carbons results, in part, in removal of cross-linking atoms allowing somewhat better alignment of small trigonally bonded carbon crystallites to occur. It accelerates the normal sintering process which can occur at higher temperatures (thermally) in the absence of carbon gasification. Thus, the overall effect of carbon gasification on aperture size in molecular sieve carbons will depend upon a balance between removal of carbon atoms around apertures (aperture enlargement), and crystallite rearrangement enhancing sintering (aperture shrinkage).

Gasification of the virgin carbon samples has been limited, up to this point, to that produced as a result of removal of oxygen complexes upon their initial heat treatment in an inert gas or vacuum. It was of interest to see what effect additional gasification would
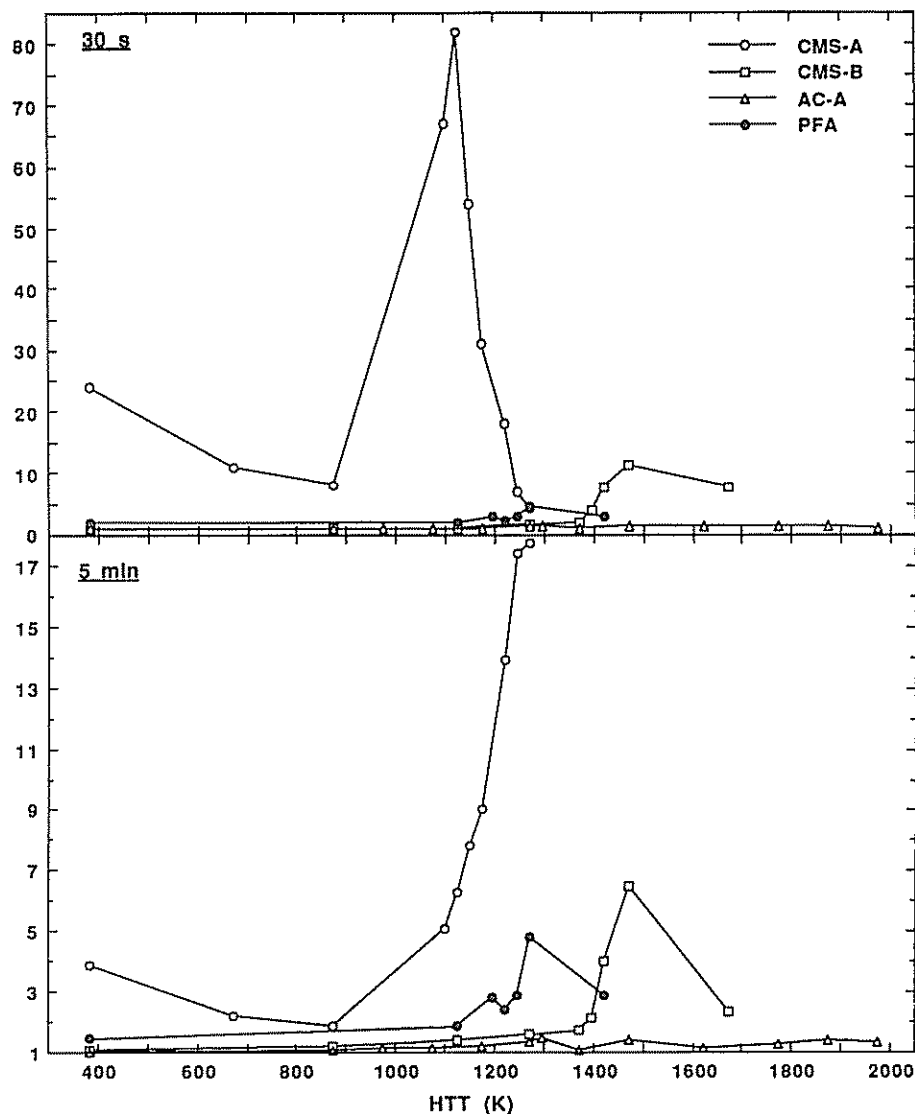
Fig. 5. Effect of HTT of carbons on ratio of O_2 to Ar uptake after 30 s and 5 min.

have on carbons originally heat treated to sufficiently high temperatures such that sintering essentially reduced most aperture sizes below 2.8 A. Despite the loss of most of their capacity for O_2 and Ar uptake, it is expected that an adsorption volume of significant potential still exists in closed off cavities. Small angle X-ray scattering studies in our laboratory on PFA carbons, for example, have shown that whereas accessible surface area to CO_2 is reduced to <1 m²/g upon heat treatment to 2273 K, 380 m²/g of area still exists in the carbon[27]. The question to be answered then was could further gasification of the carbons enlarge aperture sizes sufficiently to restore significant capacity for O_2 uptake and sieving between O_2 and Ar. The carbons selected for this study were CMS-A heat treated to 1273 K under vacuum and AC-A heat treated to 2273 K in N_2.

Following heat treatment at 1273 K, CMS-A shows negligible diffusion of Ar and has a limited number of apertures that allow adsorption of O_2, as seen in Table 4. A sample of this carbon was exposed to a stream of O_2 (50 cc/min) at temperatures between 373–523 K for different periods. Initially this carbon was given a number of exposures to O_2 at 373 K for 24 h. Each exposure resulted in some O_2 chemisorption. After each exposure, the carbon was outgassed at 1198 K for 1 h to eliminate the carbon—oxygen complex formed during reaction with O_2. As a result, some carbon atoms were removed during each exposure (cycle). After selected exposures to O_2 and subsequent outgassing at 1198 K, the carbon was cooled to ambient temperature followed by measurement of O_2 and Ar uptake. Results are shown in Table 4.

As the cumulative number of gasification cycles at 373 K increases, rates of uptake of both O_2 and Ar increase. This means that not only are apertures being enlarged in the size range from 2.8 to 3.8 A

Table 4. Effect of gasification of heat treated CMS-A carbon on subsequent O_2 and Ar uptake

Cumulative cycles	Treatment	O_2(Ar) Uptake (cc/g STP) in min			O_2/Ar ratio in min		
		0.5	8	30	1	5	30
1	1273 K, 1 h, vac	0.08 (nil)	0.95 (nil)	1.82 (nil)	∞	∞	∞
	Treatment in O_2						
2–4	O_2-373 K, 24 h	0.30 (nil)	1.76 (0.12)	3.10 (0.24)	57	20	13
5–8	O_2-373 K, 24 h	0.89 (0.11)	3.25 (0.49)	4.38 (0.89)	9.9	8.5	4.9
9–11	O_2-373 K, 24 h	1.36 (0.13)	3.69 (0.79)	4.75 (1.45)	11	5.4	3.3
12	O_2-398 K, 24 h	1.81 (0.32)	3.89 (1.46)	4.81 (2.11)	4.4	2.7	2.3
13	O_2-473 K, 24 h	3.79 (3.15)	5.15 (3.92)	5.58 (4.13)	1.2	1.3	1.4
14	O_2-523 K, 24 h	5.52 (4.11)	7.26 (4.36)	7.77 (4.46)	1.4	1.6	1.7
	Treatment in H_2						
2	H_2-873 K, 2 h	0.54 (0.01)	3.10 (0.16)	4.46 (0.50)	97	20	8.9
3	H_2-873 K, 2 h	0.56 (0.05)	3.21 (0.34)	4.63 (0.89)	14	11	5.2
4	H_2-873 K, 2 h	0.69 (0.03)	3.61 (0.43)	4.74 (0.93)	13	9.1	5.1

After each cycle in O_2, carbon was outgassed at 1198 K for 1 h.

but also a significant number are being enlarged to a size greater than 3.8 A. The result is that the selectivity O_2/Ar ratio continuously decreases with increasing extent of carbon gasification. This means that there will be an optimum number of gasification cycles where the rate of O_2 uptake has been increased to a satisfactory level while the selectivity O_2/Ar ratio has not been reduced too much. Additional cycles of exposure to O_2 at temperatures between 398 K and 523 K result in continued increases in rates of O_2 and Ar uptake but in decreasing selectivity.

Carbon can also be gasified by reaction with H_2. The reactivity of a sample of the fresh CMS-A carbon with H_2 was studied in a TGA at 873 K. The carbon was first heated to 873 K in N_2 and held at this temperature for 2.5 h prior to replacing N_2 with flowing H_2 at 873 K. Weight loss was 0.65% over a 2 h period.

Table 4 presents results for the effect of gasification in H_2 on subsequent rates of uptake of O_2 and Ar. After each treatment cycle in H_2, the carbon was not outgassed at 1273 K as was done after treatment in O_2. Rather, the sample was simply cooled to 383 K and held at this temperature for 1 h under vacuum. Uptake of O_2 and Ar was then measured at ambient conditions. As with gasification in O_2, increasing extents of gasification in H_2 result in both increasing rates of O_2 and Ar uptake and a decreasing selectivity O_2/Ar ratio. At comparable uptake rates of O_2, however, selectivity is better when treatment is carried out in H_2 rather than O_2. Naturally, results are dependent upon the treatment temperature and time used; but treatment in H_2 does have a bonus. That is, it passivates the surface to some extent, by the formation of some C-H surface complex, thus reducing oxygen chemisorption when the carbon is exposed to air at room temperature. This,

Table 5. Effect of gasification of heat-treated AC-A carbon on subsequent O_2 and Ar uptake

Cumulative cycles	Treatment	O_2(Ar) uptake (cc/g STP) in min			O_2/Ar ratio in min		
		0.5	8	30	1	5	30
1	N_2-2273 K, 1 h	nil (nil)	nil (nil)	0.04 (0.02)	—	—	2.0
	Treatment in H_2						
2	H_2-873 K, 2 h	0.01 (0.05)	0.01 (0.07)	0.05 (0.10)	0.1	0.1	0.5
3	H_2-1023 K, 2 h	0.08 (nil)	0.08 (0.03)	0.10 (0.09)	40	2.7	1.1
	Treatment in O_2						
4	O_2-423 K, 24 h	0.14 (0.10)	0.20 (0.15)	1.40 (0.15)	1.4	1.4	1.4
5	O_2-523 K, 24 h	0.75 (0.60)	0.87 (0.64)	0.87 (0.71)	1.2	1.2	1.2
6	O_2-573 K, 24 h	1.04 (0.01)	1.21 (0.01)	1.32 (0.01)	178	198	132
7	O_2-623 K, 72 h	1.91 (1.09)	2.43 (1.09)	2.65 (1.13)	1.9	2.1	2.3
8	O_2-673 K, 24 h	1.85 (0.97)	2.41 (1.03)	2.62 (1.03)	2.1	2.3	2.5
9	O_2-773 K, 24 h	2.12 (0.92)	2.71 (0.95)	2.91 (0.99)	2.5	2.8	2.9
10	O_2-823 K, 24 h	2.77 (1.82)	3.34 (1.87)	3.54 (1.87)	1.6	1.7	1.9

After each cycle in O_2, carbon was outgassed at 1223 K for 30 min.

in turn, reduces water pick-up on the carbon sieve and leads to a more reproducible sieving performance. These results will be presented in a future publication.

A sample of the AC-A, heat treated in N_2 at 2273 K for 1 h, was reacted first with H_2 and then with O_2. Results for uptake of O_2 and Ar are summarized in Table 5. Heat treatment of AC-A at 2273 K is seen to essentially eliminate subsequent uptake of both O_2 and Ar at ambient temperature. Treatment cycles in H_2 up to 1023 K results in little increase in either O_2 or Ar uptake rates. This is in contrast to treatment of the CMS-A carbon in H_2 at 873 K where significant pore volume accessible to O_2 was opened up.

Cycles 4 and 5 for the first treatments in O_2 produce significant increases in uptake rates of both O_2 and Ar but result in little selectivity. Most of the pore volume which has been opened up is accessible through apertures >3.8 A in size. The next sample which underwent six cycles, with the final cycle being treatment in O_2 at 573 K for 24 h, produced particularly interesting results. The uptake rate of O_2 on this sample was increased significantly but that for Ar was decreased to essentially nil. The result is the generation of very high selectivity O_2/Ar ratios. It suggests that for cycle six the dominant effect of carbon gasification was attack of crosslinks, permitting in turn some carbon crystallite building blocks to move more closely together. The result, as discussed previously, was to shrink essentially all apertures below 3.8 A in size. This run demonstrates an important principle (potentially) for producing CMS of very high selectivity. Unfortunately, at present, it is not possible to select the conditions under which this principle can be optimized. The next run, cycle seven, consists of exposure to O_2 at 623 K for 72 h. It produces large increases in both O_2 and Ar uptake rates, resulting in the removal of most of the selectivity achieved for the preceding sample. The next sample, which underwent eight cycles, is also noteworthy. Treatment of this sample in O_2 at 673 K for 24 h resulted in some decrease in uptake rates of both O_2 and Ar. Clearly, again, the dominant effect of gasification in cycle eight was sample sintering. The following sample, which underwent exposure to O_2 at 773 K for 24 h in its ninth cycle, again showed the effect of sintering, with the O_2 uptake rate increasing and that for Ar decreasing. Finally, in the last sample treatment in O_2 at 823 K for 24 h in the tenth cycle resulted in significant increases in both the rates of O_2 and Ar uptake. Since the increase in rate of Ar uptake was more substantial, on a fractional basis, the resulting selectivity O_2/Ar ratio further decreased.

4. CONCLUSIONS

Molecular sieving of O_2 and Ar in microporous carbons can be modified by their heat treatment in vacuum or inert gas and/or gasification in O_2 and H_2. Such treatments modify the number and fraction of pore apertures <2.8 A in thickness, those between 2.8 A and 3.8 A, and those >3.8 A. For good selectivity in separating O_2 from Ar, one wants to maximize the number and fraction of pores between 2.8 A and 3.8 A.

REFERENCES

1. P. L. Walker, Jr. and I. Geller, *Nature* **178**, 1001 (1956).
2. S. P. Nandi, V. Ramadass, and P. L. Walker, Jr., *Carbon* **2**, 199 (1964).
3. H. Marsh and T. Siemieniewska, *Fuel* **46**, 441 (1967).
4. P. Chiche, S. Durif and S. Pregermain, *Fuel* **44**, 5 (1965).
5. Y. Toda, M. Hatami, Y. Yoshida, and H. Honda, *Carbon* **8**, 565 (1970).
6. H. G. Vesterdal, U.S. Patent No. 2,556,859, June 12, (1951).
7. Y. Toda, N. Yuki and S. Toyoda, *Carbon* **10**, 13 (1972).
8. A. J. Groszek, R. Howes, and S. R. Tennison, Abstracts 14th Biennial Conf. on Carbon, p. 14 (1979).
9. K. J. Masters and B. McEnaney, Abstracts 14th Biennial Conf. on Carbon, p. 16 (1979).
10. M. M. Dubinin, Proc. 5th Carbon Conf., Pergamon Press, Oxford, Vol. 1, p. 81 (1962).
11. H. Marsh and W. F. K. Wynne-Jones, *Carbon* **1**, 269 (1964).
12. T. G. Lamond, J. E. Metcalfe, III, and P. L. Walker, Jr., *Carbon* **3**, 59 (1965).
13. P. L. Walker, Jr., A. Oya, and O. P. Mahajan, *Carbon* **18**, 378 (1980).
14. P. L. Walker, Jr., T. G. Lamond, and J. E. Metcalfe, III, Proc. 2nd Conf. on Industrial Carbon and Graphite, Society for Chemical Industry, London, p. 380 (1966).
15. H. Juntgen, *Carbon* **15**, 273 (1977).
16. H. Juntgen, K. Knoblauch, and K. Harder, *Fuel* **60**, 817 (1981).
17. H. Munzner, H. Heimbach, W. Korbacher, W. Peters, H. Juntgen, K. Knoblauch, and D. Zundrof, U.S. Patent, 3,960,769 (1976).
18. H. Munzner, H. Heimbach, W. Korbacher, W. Peters, H. Juntgen, K. Knoblauch, D. Zundrof, and H. Horbel, U.S. Patent 3,962,129 (1976).
19. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley and Sons, New York (1954).
20. L. Pauling, *Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York (1948).
21. P. L. Walker, Jr., L. G. Austin, and S. P. Nandi, In *Chemistry and Physics of Carbon* (Edited by P. L. Walker, Jr.), Vol. 2, pp. 257–371. Marcel Dekker, New York (1966).
22. M. B. Rao, R. G. Jenkins, and W. A. Steele, *Langmuir* **1**, 137 (1985).
23. J. Koresh and A. Soffer, *J.C.S. Faraday 1* **76**, 2457 (1980).
24. J. Maire and J. Mering, In *Chemistry and Physics of Carbon* (Edited by P. L. Walker, Jr.), Vol. 6, pp. 125–190. Marcel Dekker, New York, (1970).
25. T. E. Easler, Ph.D. Thesis, The Pennsylvania State University, 1983.
26. R. H. Hurt, D. R. Dudek, J. P. Longwell, and A. F. Sarofim, *Carbon* **26**, 433 (1988).
27. R. G. Jenkins and P. L. Walker, Jr., *Carbon* **14**, 7 (1976).