PREPARATION OF CARBON MOLECULAR SIEVES BY PROPYLENE PYROLYSIS OVER MICROPOROUS CARBONS

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Abstract—Modification of the pore structure of microporous carbons by depositing carbon from pyrolysis of C_3H_6 between 973–1123 K was investigated in regard to development of molecular sieving properties for separation of O_2 and Ar. Excellent adsorption kinetics and selectivity for separation of O_2 and Ar were achieved by depositing carbon on a substrate carbon that contains pores of a narrow size distribution. Activated carbons showed no useful development of molecular sieving characteristics after carbon deposition. This is attributed, primarily, to their containing too wide a size distribution of micropores.

Key Words—Carbon molecular sieves, activated carbon, propylene, pyrolysis, carbon, adsorption, diffusion, O_2, Ar.

1. INTRODUCTION

Separation of gases, such as O_2 and N_2, by using a carbon molecular sieve (CMS) adsorbent and a pressure swing adsorption (PSA) technique has been constantly growing among other separation technologies. A CMS contains a pore system formed of micropores with extensive adsorption volume and pore entrances of size equivalent to that of an adsorbing molecule[1–3]. Such proximity of pore walls at the pore entrance allows rapid diffusion of molecules of kinetic diameter smaller than the size of the pore opening, while restricting entry of larger molecules. In this manner, due to the difference in relative rates of diffusion of gas molecules of different sizes into CMS-type adsorbents, components of gas mixtures can be efficiently separated. For some gases, the rate of diffusion into a CMS may vary up to several orders of magnitude, depending on the size of pore entrances, or so-called "constrictions or apertures" available in the adsorbent, relative to those of adsorbing molecules.

Generally, for manufacturing CMS adsorbents, the inherent pore structure of the carbonaceous precursor is initially fixed into a suitable pore range by controlled thermal treatment followed by final tailoring of the pore apertures, either by carbon deposition from cracking of hydrocarbons[4,5] or by impregnating with an organic compound[6]. Moore and Trimm[7] reported development of molecular sieving characteristics, suitable for separating O_2 and N_2, in a carbon with pores of average diameter of 0.50–0.55 nm by cracking benzene vapor at 1085–1240 K. On the other hand, Chihara and Suzuki[8], who followed pyrolysis of ethylbenzene and styrene vapor at 673 K on a similar carbon, observed that the diffusivities of both O_2 and N_2 diminished due to pore blocking without any increase in selectivity. These reports suggest that the organic used for cracking and the conditions of its pyrolysis should be carefully chosen to produce sufficient and selective deposition of carbon at the pore apertures, so that the adsorption selectivity is enhanced with minimum reduction in adsorption capacity.

In a previous publication[9], it was reported that the pore structure of microporous carbons can be altered to varying degrees by heat treatment or mild gasification. These treatments demonstrated the potential of improving molecular sieving characteristics of certain starting microporous carbons, specially those with a narrow pore size distribution. In another paper[10], development of sieving properties in a microporous carbon with a narrow pore structure was demonstrated by chemisorbing propylene at 573–873 K followed by its cracking at a higher temperature. Deposition of a suitable level of pyrolytic carbon was achieved through several cycles of chemisorption of propylene, followed by its cracking at an elevated temperature. The number of such cycles required to achieve desired selectivity varied with the width of pore apertures present in the starting material. Such a treated carbon showed suitably high kinetic selectivity for O_2.

In this study, CMS adsorbents have been prepared by the concurrent chemisorption and cracking of propylene at temperatures of 973 K and higher over microporous carbon. Propylene was selected as the preferred organic source of pyrolytic carbon since its ΔH for cracking is very low, and it is easy to handle under ambient conditions. Molecular sieving properties of various carbons were studied by measuring rates of O_2 and Ar uptake under ambient conditions as before[9,10].

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Table 1. Physical properties of carbons

| Carbon | Size (mesh) | Density (g/cc) | | V_T(cc/g) | Surface area (m²/g) | |
		Hg	CH₃OH		CO₂	N₂
CMS-B	14 × 40	1.207	1.888	0.299	680	345
AC-A	4 × 10	0.886	2.048	0.641	714	772
AC-B	4 × 10	0.845	2.019	0.688	1367	1706
AC-C	4 × 10	0.486	2.433	1.647	1258	2118

2. EXPERIMENTAL

Total pore volumes (V_T) potentially available to propylene at the commencement of its cracking were estimated from densities of the carbons measured in liquid mercury (ρ_{Hg}) and liquid methanol (ρ_{CH3OH}) at room temperature. That is,

$$V_T = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{CH3OH}} \qquad (1)$$

The (ρ_{CH3OH}) was used instead of (ρ_{He}) to calculate V_T since it was thought to give a better estimate of pore volume available to propylene. That is, the minimum dimension of methanol approaches the minimum dimension of propylene more closely than does the dimension of He.

Surface areas, from CO_2 adsorption at 298 K, were calculated using the DR equation. Surface areas, from N_2 adsorption at 77 K, were calculated using the BET equation.

Physical characteristics of various microporous carbons used in the study are presented in Table 1. The nature of their micropore structure and their physical properties are discussed elsewhere[9,10]. The CMS-B sample has essentially all of its porosity and surface area in a narrow range of pore size in the ultramicropore region. Consequently, some sieving between CO_2 and N_2 is noted[2]. The AC samples are activated carbons, which have significant fractions of their total pore volume in micropores, transitional pore, and macropores. The AC samples have broader distributions of pore size in the micropores than does the CMS-B sample. Further, the peak in the micropore size distribution occurs at a larger pore size for the AC samples. Surface areas, calculated from N_2 uptake, are larger than those calculated from CO_2 uptake, due to some capillary condensation of N_2 in the larger micropores.

All carbons were first degassed under vacuum at either 1123 K or 1223 K and then held isothermally at a desired temperature before exposure to propylene. Treatment in propylene was carried out by flowing a stream of 100% propylene or a propylene/N_2 mixture through the carbon bed at 0.1 MPa total pressure and flow rate of 100 cc/min for a specified period. Following this treatment, the carbon was degassed at the same temperature or at 1123 K. Molecular sieving properties of various carbons were measured, before and after treatment, by adsorption

of O_2 and Ar, volumetrically, under ambient conditions as discussed elsewhere[9].

The rate of pyrolysis of propylene on these carbons was measured by using a Cahn Electrobalance. The carbon sample held in a quartz boat was suspended in a quartz reactor tube. The system could be connected either to the desired gas stream or to vacuum for degassing the carbon to 10^{-4}MPa. Change in weight of the carbon was recorded as a function of time on a continuous chart recorder.

3. RESULTS AND DISCUSSION

Results for diffusion of O_2 and Ar on the as-received CMS-B were reported earlier[9,10]. As seen in Fig. 1 A, this carbon shows no significant difference in rates of uptake of these gases. However, degassing
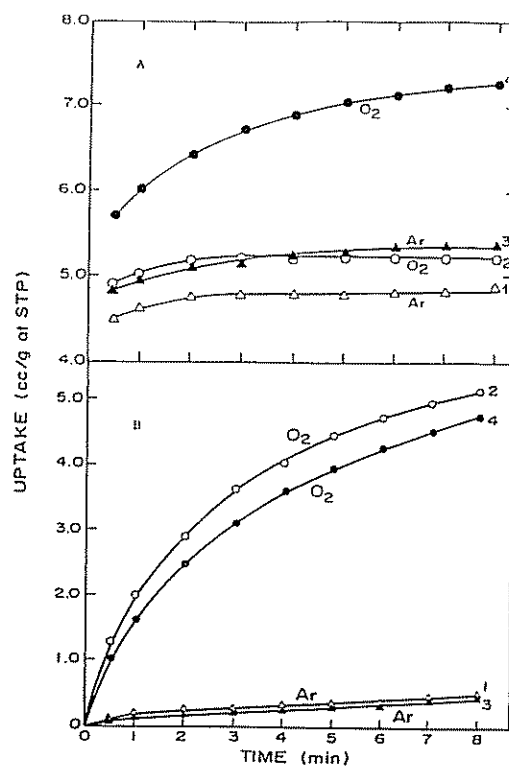

Fig. 1. Uptake of O_2 and Ar in CMS-B at 298 K: A)–(1,2)–degassed at 383 K, 1 hour: (3,4)–degassed at 1123 K, 1 hour after run 2. B)–(1,2)–degassed at 1123 K, 0.5 hours; exposed to C_3H_6 at 973 K, 3 minutes: (3,4)–HTT in vacuum at 1123 K, 1 hour after run 2.

of this carbon at an elevated temperature (1123 K) provides additional adsorption capacity, as also seen in Fig. 1 A. It was suggested that in the degassed carbon additional pores of size originally smaller than the minimum dimension of O_2 (0.28 nm) become accessible to O_2 and in part Ar (0.38 nm) due to enlargement of pore apertures caused by the removal of surface-oxygen complex[9,10]. Such high adsorption capacity for O_2 is desirable in the precursor carbon for also producing a CMS of high adsorption capacity. Thus, carbon deposition from pyrolysis of propylene was carried out on preheated carbons in this study.

For carbon deposition, a sample of CMS-B degassed at 1123 K was exposed to a stream of 100% propylene at 973 K for a period of 3 minutes. Only about 1% of pyrolytic carbon was deposited during this period. Assuming that the ρ_{Hg} of the carbon deposited from propylene equals 1.64 g/cc[11], this carbon would occupy ~2% of the total pore volume of CMS-B. The period of 3 minutes for the exposure to propylene was optimized in our system for CMS-B after several test runs on this carbon followed by measurements of O_2 and Ar diffusion. After exposure to propylene, the carbon was degassed at 973 K for 1 hour to eliminate excess propylene and gaseous products of its cracking, if any, from the carbon surface. The treated carbon was then cooled to 298 K under vacuum and subjected to adsorption of Ar for a 30-minute period. Then the carbon was degassed at 373 K for 1 hour followed by adsorption of O_2 at 298 K.

Diffusion plots of the volume uptake of these gases on the modified CMS-B are shown in Fig. 1 B. It is seen that due to deposition of the pyrolytic carbon, O_2 uptake is reduced somewhat from run 4 of Fig. 1 A to run 2 of Fig. 1 B. On the other hand, Ar uptake is drastically reduced from run 3 of Fig. 1 A to run 1 of Fig. 1 B. The uptake at 8 minutes for O_2 is reduced by about 29%, while that of Ar is reduced by over 90%. Due to carbon deposition, selectivity, described earlier[9] as the ratio of O_2 uptake to Ar uptake, is increased from 1.2 to 11.2 at 30 s and 1.3 to 11.1 at 5-minute adsorption periods. For this modified carbon, the difference in volume uptakes for O_2 and Ar is similar to that reported earlier for a commercial CMS[9,10]. Upon further heat treatment of the modified CMS-B carbon at 1123 K for 1 hour under vacuum, the rate of diffusion for both gases is slightly diminished (as in runs 3 and 4, Fig. 1 B). The effect is somewhat greater in the case of O_2. It is thought that upon heat treatment at 1123 K, cracking of polymerized-chemisorbed propylene complex, remaining on the surface following treatment at 973 K, occurs. This results in additional deposition of carbon, reducing further the size of some pores below 0.28 nm and thus diminishing O_2 uptake. Heat treatment to 1123 K may also induce some sintering of pores, reducing their size below that of O_2. Some pore entrances that did allow rapid diffusion of Ar are also reduced to a size below 0.38 nm, reducing the Ar adsorption rate.

The rate and amount of propylene cracking over microporous carbons will depend upon cracking conditions (temperature, pressure, and time) as well as the active surface area of the carbon. Thus the conditions selected will be of paramount importance in determining the success in converting microporous carbons to useful CMS. Selected runs were made measuring the effect of variables on propylene cracking rates. The effect of propylene concentration in the gas phase upon the rate of product deposition was investigated by exposing AC-C to varying concentrations of propylene, that is, 10% and 24% propylene in He and 100% propylene, at 973 K. Prior to each run, the carbon surface was cleaned by heating it under vacuum at 1273 K for 1 hour. The rate of deposition is depicted in Fig. 2. At lower concentrations of propylene in the gas stream, deposition is slower for the first 30 minutes of exposure. The rate of deposition is seen to increase with propylene concentration, as expected. Over 85% carbon loading is achieved in 100% propylene in just 20 minutes. Hoffman, *et al.*[12] have reported earlier that the rate of propylene pyrolysis over a carbon surface is first-order in propylene pressure. In addition, the rate was also shown to be proportional to active surface area of the substrate carbon. The maximum rates of deposition are found to also be first-order in propylene pressure in this study, within experimental error. Following the attainment of maximum rates, the rates fall rapidly and sharply to very low rates, suggesting that the infiltration of the pore system of AC-C is essentially complete. A weight loading of 90% is equivalent to a volume loading of the pore system of AC-C of ~34%.

Since the rate of carbon deposition is very high in 100% propylene at 973 K, it may be difficult to control the deposition of carbon. Therefore, in another
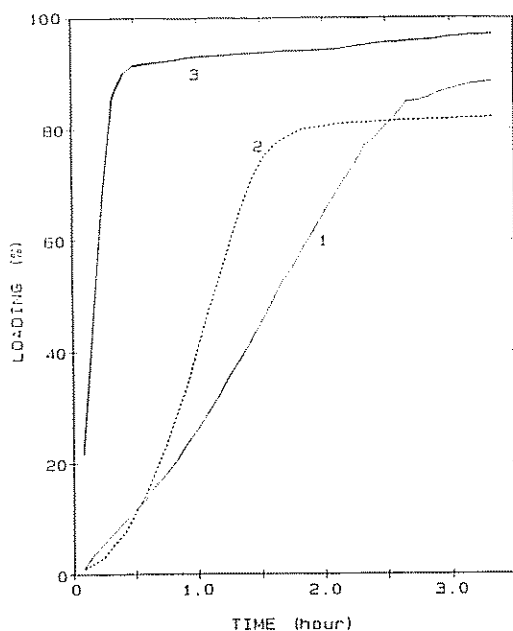

Fig. 2. Propylene pyrolysis on AC-C (degassed, 1273 K, 1 hour) at 973 K: (1)–10% C_3H_6 in He; (2)–24% C_3H_6 in He and (3)–100% C_3H_6.

set of tests, carbon deposition on several batches of CMS-B (degassed at 1123 K, 1 hour) was carried out from diluted streams of propylene of 10%, 30%, and 50% concentration in N_2 at temperatures from 973 to 1123 K. After cracking propylene for a specified period, the carbon was degassed at the cracking temperature and then tested for Ar and O_2 adsorption. Several propylene pyrolysis runs were made for carbon deposition required to achieve a certain level of sieving for O_2 and Ar. Table 2 depicts the history of propylene pyrolysis runs and the adsorption runs of Ar and O_2 carried out on the modified samples of CMS-B. Selectivity between runs f and g of batch-II of CMS-B reacted with 30% propylene shows a small increase as compared to that of runs d and e of batch-I that was reacted with a 10% propylene stream. Diffusion plots of Ar and O_2 for these adsorption runs are shown in Fig. 3. It is seen that after the exposure of the carbon of batch-I to 10% propylene for a much longer period (a total time of 225 minutes), the Ar uptake is diminished only moderately, compared to a more significant reduction in the case of batch-II that was exposed to a 30% propylene stream for only a total of 70 minutes. The latter sample also exhibits some reduction in O_2 uptake rate.

The rate of propylene pyrolysis is also affected by temperature. Results for the pyrolysis of propylene on AC-C (preheated at 1273 K, 1 hour in N_2) at temperatures between 923 and 1023 K using a stream of 10% propylene in He are presented in Fig. 4. The change of maximum deposition rates with temperature can be expressed by the Arrhenius equation, giving an activation energy of 38 kcal/mole. Pyrolysis of propylene at 923 K is slow; less than 40% weight increase is registered in 4.5 hours. As the temperature is raised to 973 K or 1023 K, the rate of pyrolysis increased several fold. Loading of 80%–90% is achieved in 3 hours at 973 K and 1 hour at 1023 K. After this loading, further weight uptake is slow and insignificant. It is interesting to note that the rate of pyrolysis is much higher at 1023 K, but total loading is nearly the same as that observed at 973 K.

The effect of pyrolysis of propylene at 1023 K from 30% propylene and 1123 K from 50% propylene streams on modification of sieving properties of CMS-B carbon was also investigated. Volume uptake of O_2 and Ar for the modified carbons are shown in Fig. 5. The order of various treatments and selectivity of the modified carbons is presented in Table 2. Compared to runs f and g of batch-II, the modified sample of batch-III of CMS-B shows somewhat better sieving properties after only 30 minutes exposure to propylene. At 1123 K, the modified carbon of batch-IV (exposed to a 50% propylene stream for only 2 minutes) exhibits better sieving properties, though a somewhat lower rate of O_2 uptake than batch-III (as in Fig. 5).

Table 2. Effect of depositing carbon on CMS-B from different propylene/N_2 mixtures on sieving properties

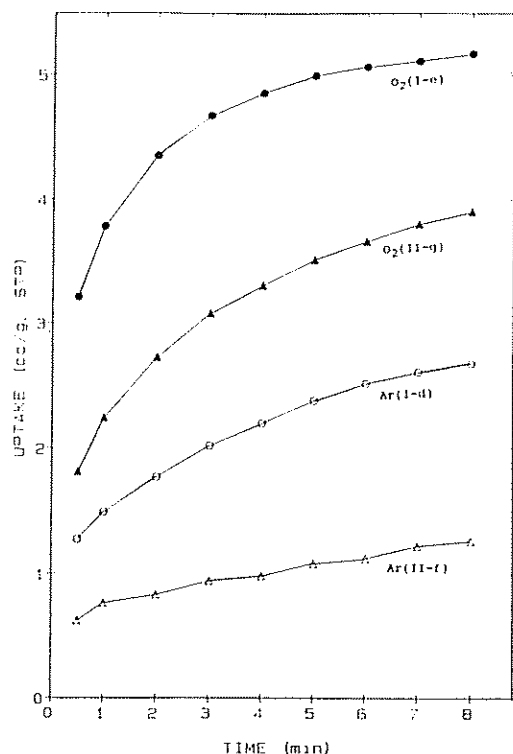| Run	Adsorbate	Temp (°K)	Time (hours)	Pretreatment	Uptake at 30 min (cc/g)	O_2/Ar ratio at (min) 0.5	O_2/Ar ratio at (min) 5
BATCH-I							
a	Ar	973	1	10% C_3H_6 at 973 K, 60 min	5.15	—	—
b	Ar	973	1	10% C_3H_6 at 973 K, 45 min	4.90		
c	O_2	383	1		6.61	1.7	1.4
d	Ar	973	1	10% C_3H_6 at 973 K, 120 min	3.91		
e	O_2	383	1		5.17	2.5	2.1
BATCH-II							
a	Ar	973	1	30% C_3H_6 at 973 K, 20 min	5.01	—	—
b	Ar	973	1	30% C_3H_6 at 973 K, 20 min	4.36		
c	O_2	383	1		6.34	1.5	1.6
d	Ar	973	1	30% C_3H_6 at 973 K, 20 min	3.01		
e	O_2	383	1		5.80	2.4	2.1
f	Ar	973	1	30% C_3H_6 at 973 K, 10 min	2.07		
g	O_2	383	1		4.93	2.9	3.2
BATCH-III							
a	Ar	1023	1	30% C_3H_6 at 1023 K, 30 min	2.95		
b	O_2	383	1		7.00	2.4	3.9
BATCH-IV							
a	Ar	1123	1	50% C_3H_6 at 1125 K, 2 min	3.35		
b	O_2	383	1		6.59	∞	3.8

Fig. 3. Uptake of O_2 and Ar in modified CMS-B at 298 K: (I-d,e)-Carbon deposited from 10% C_3H_6 at 973 K, 225 minutes; (II-f,g)-Carbon deposited from 30% C_3H_6 at 973 K, 70 minutes.
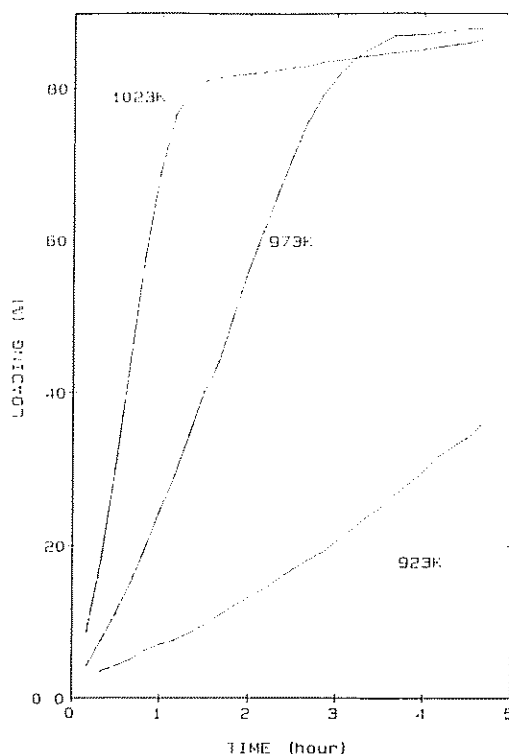

Fig. 4. Propylene pyrolysis on AC-C (degassed at 1273 K) at 923–1023 K from 10% C_3H_6 in He.

Interestingly, the CMS of batch-IV shows no measurable access to Ar for the first minute of exposure.

Production of CMS by hydrocarbon pyrolysis at elevated temperatures offers some interesting implications for achieving the optimum sieve. As pyrolysis temperature increases, the description of the process changes from Zone I to Zone II kinetics[13]. If pyrolysis temperature is sufficiently low, deposition rate is controlled solely by the rate of cracking of propylene over carbon active sites. Deposition is uniform throughout the artifact and the desired sieving behavior is only achieved with a maximum amount of carbon deposited. As pyrolysis temperature is increased, the rate of propylene cracking increases rapidly—much more rapidly than the initial rate of propylene diffusion into the artifact. Deposition becomes increasingly more non-uniform, the amount of carbon deposited being maximum close to the exterior surface of the artifact and minimum at its center. Progressively less carbon need be deposited in the artifact before the desired sieving behavior is achieved. In the limit, deposition of carbon is restricted to a narrow shell close to the exterior surface of the artifact. The "gate" principle has been achieved, whereby any molecule able to pass through the gate in the selected diffusion time has access to the total pore volume originally present in the starting sample, since no carbon has been deposited within it. One must be careful not to go to too high a deposition temperature, how-

ever. In this case, Zone III will be reached, where deposition from the homogeneous, gas-phase cracking of propylene becomes very rapid. Carbon will be deposited only on the exterior surface of the artifact. This carbon is expected to lack sieving properties and also to be susceptible to abrasion as the artifact is handled. Comparing adsorption results of various carbon batches -I (run e), -II (run g), -III (run b) and -IV (run b) from Table 2, it is seen that the adsorption capacity of O_2 remains high after carbon deposition. However,
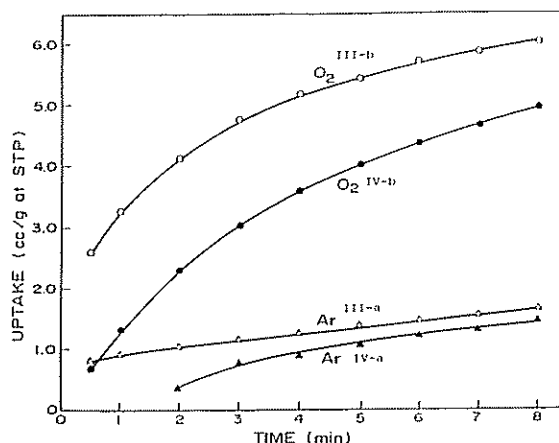

Fig. 5. Uptake of O_2 and Ar in modified CMS-B at 298 K: (III-a,b)-Carbon deposited from 30% C_3H_6 at 1023 K, 30 minutes; (IV-a,b)-Carbon deposited from 50% C_3H_6 at 1123 K, 2 minutes.
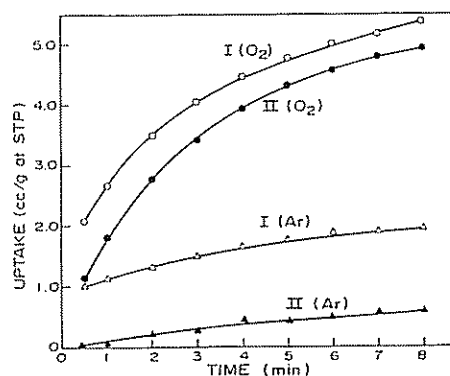
Fig. 6. Uptake of O_2 and Ar at 298 K in modified CMS-B produced in bulk in a fluid bed. Propylene pyrolysis at 973 K. Open symbols, 3 minutes; closed symbols, 4 minutes.

probability is high that optimum conditions are not represented by any of the runs listed in Table 2.

Two larger samples of modified CMS-B were also prepared using 20-g batches of this carbon in a fluidized bed reactor. In each case, virgin carbon was degassed at 1123 K for 1 hour. The temperature was then lowered to 973 K and the carbon maintained at this temperature under N_2. Propylene was passed through the carbon bed at a rate of 2.5 L/min for 3 minutes in the case of batch-I and 4 minutes for batch-II. The flow rate of 100% propylene was determined to match the condition used in the smaller (1-g) reactor. After carbon deposition, each batch was degassed at 973 K for 1 hour and then cooled to ambient temperature under vacuum. These samples of modified CMS-B were stored under N_2. Diffusion plots for Ar and O_2 uptake on the two CMS samples are presented in Fig. 6. Both modified carbons show improved sieving properties for separation of Ar and O_2. Batch-II carbon exhibits a significantly lower adsorption rate for Ar, apparently due to higher carbon deposition. These results demonstrate the scale-up

potential of this process to produce CMS of desired sieving characteristics from a carbon of narrow micropore size distribution, such as CMS-B.

Activated carbons typically exhibit no molecular sieving properties for the separation of gas mixtures like O_2 and Ar or N_2. Rates of uptake of O_2 and Ar on AC-A, for example, are essentially the same[9]. Their average micropore size is quite large (2 nm) as compared to the size of these molecules; therefore, their pores are equally accessible to both molecules. Walker, et al.[1] have suggested that the pore structure of these carbons can be converted into a CMS type by coating them with a thermosetting polymer. Such modified carbons may exhibit potentially high adsorption capacity. In a previous publication[9] it was shown that the pore structure of these carbons can be varied by thermal treatment or mild gasification. Attempts were also made to convert their pore structure into a CMS type by chemisorbing propylene or depositing carbon by cracking the sorbed propylene[10]. Both these treatments exhibited little improvement in the sieving properties of these carbons for the separation of O_2 from Ar.

In this study, rapid pyrolysis of propylene over activated carbons, resulting in deposition of pyrolytic carbon near the external surface was investigated. Deposition of carbon in this manner may create constrictions of suitable size in the transport pores, thus keeping the adsorption volume intact. Results of propylene pyrolysis on AC-A and AC-B, and the order in which various adsorption runs were made after deposition of carbon are presented in Table 3. As-received carbons, degassed at 1123 K for 1 hour, were exposed to 100% propylene at 973 K for specified periods. Following each exposure, the carbon was degassed at 973 K and then cooled to ambient temperature under vacuum. Before each adsorption run, the carbon was degassed at 373 K for 1 hour. Volume uptake of O_2 and Ar is shown in Fig. 7. It is seen that for both activated carbons, increasing carbon deposition

Table 3. Effect of depositing carbon from propylene on activated carbons on sieving properties

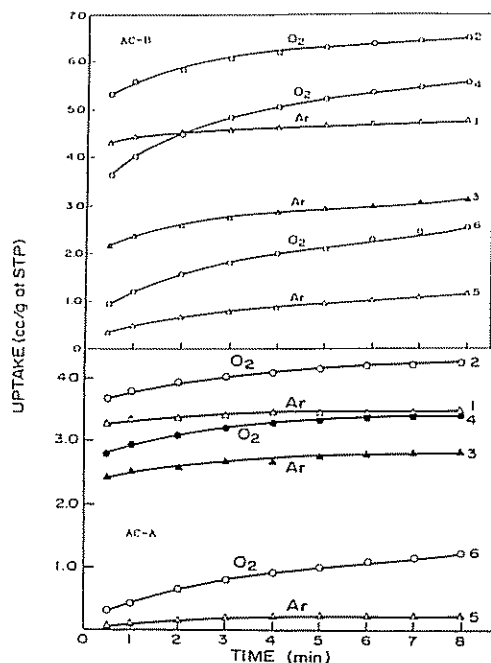| Run	Adsorbate	Temp. (°K)	Time (hours)	Pretreatment	Uptake at 30 min (cc/g)	O_2/Ar ratio at (min.)	
						0.5	5
CARBON AC-A							
1	Ar	973	1	973 K, 10 min.	3.70		
2	O_2	383	1		4.57	1.7	1.4
3	Ar	973	1	973 K, 5 min.	3.02		
4	O_2	383	1		3.84	1.2	1.2
5	Ar	973	1	973 K, 10 min.	0.49		
6	O_2	383	1		2.08	7.2	4.4
CARBON AC-B							
1	Ar	973	1	973 K, 3 min.	4.89		
2	O_2	383	1		6.97	1.2	1.3
3	Ar	973	1	973 K, 5 min.	3.70		
4	O_2	383	1		6.62	1.7	1.8
5	Ar	973	1	973 K, 5 min.	1.88		
6	O_2	383	1		3.80	2.4	2.2

Fig. 7. Diffusion of O_2 and Ar in AC-A and AC-B at 298 K after modification by carbon deposition from C_3H_6 (see Table 3 for conditions used).

lowers the diffusion of both O_2 and Ar to nearly similar extents. The adsorption capacity for each gas is continuously diminished without, usually, any significant improvement in selectivity being achieved. Selectivity is reasonable for modified carbon AC-A in runs 5 and 6 but only at the sacrifice of most of its capacity for O_2.

4. AFTERTHOUGHTS

It is disappointing that in this study and previous studies[9,10] we were unable to convert a conventional activated carbon (showing no sieving for O_2-Ar) into an excellent sieve for this pair of gases. We were attracted to activated carbons since they have high surface areas. The AC was modified by thermal treatment[9], carbon gasification[9], the two-step process of low-temperature propylene chemisorption followed by higher temperature cracking[10] and, finally, by simultaneous hydrocarbon chemisorption and cracking at the same higher temperatures. In hindsight, we now appreciate that such results could have been predicted. As discussed earlier, the AC samples we selected have a rather wide pore size distribution with the maximum in the distribution around 2 nm. If the carbon is going to be an excellent sieve for O_2-Ar, ideally it will have all of its pore constructions between 0.28 and 0.38 nm. Further, it will have a substantial pore volume (or surface area) in this pore range. The difficulty of starting with an AC of wide pore-size distribution is to obtain a large pore volume in the range of 0.28 to 0.38 nm. In principle, the micropores in the starting AC which are larger

than 0.38 nm (that is, most of the pore volume in our starting samples) can be reduced below 0.38 nm in width using heat treatment or carbon deposition. The problem is that to achieve this, the majority of the pores will also be reduced in size below 0.28 nm, resulting in their being closed not only to Ar but also to O_2. This is the result of starting with a wide pore-size distribution in the original material. That distribution is simply moved downward to a smaller average pore size during processing, leaving a relatively small pore volume (surface area) in pores between 0.28 and 0.38 nm in width.

The question can now be raised, after the fact, in this research—can an AC of broad pore-size distribution, showing initially no sieving for O_2-Ar, be converted to a good sieve? We feel that the answer is maybe. How? Push the "gate" principle, which we discussed earlier, to the limit. Deposit carbon in a thin layer just inside the outer surface of the artifact. Leave the remainder of the interior micropore volume essentially unchanged. Deposit carbon in the outer layer until essentially all of its micropores fall below 0.38 nm. As just discussed, these micropores will have little capacity for O_2, but this is of no concern, since a high capacity remains in the interior, original carbon micropores. If the starting AC contains negligible transitional and macropores, the ratio of the diffusion rates of O_2 to Ar in the outer carbon layer should be high and diffusion of O_2 should be reasonably rapid because of the thinness of this outer layer.

To achieve deposition in a thin outer layer only, one wants to select a temperature where kinetics in the transition region between Zones II and III apply[13]. In fact, one wants to be very close to Zone III. This will mean going to a high temperature for propylene cracking. At least two factors can limit how high a temperature one can reach. First, we cannot go so high as to close out the micropore system as a result of sintering. For example, for AC-A sintering sets in, resulting in loss of O_2 adsorption, at temperatures higher than 1298 K[9]. Second, as temperature increases, the homogeneous cracking of hydrocarbons to yield carbon becomes an increasingly greater contributor to total carbon formation from heterogeneous and homogeneous (gas phase) cracking. Homogeneous cracking is undesirable, but can be minimized by working at low hydrocarbon pressures. Therefore, in retrospect, runs should have been made at ~1300 K and in about a 1% propylene stream.

Results may still not be successful since ACs may have too high an amount of their total pore volume in transitional and macropores. This would negate the "gate" principle.

5. CONCLUSION

Carbons that possess a narrow pore-size distribution in micropores, such as CMS-B, can be modified for molecular sieving of Ar (0.38 nm) from O_2 (0.28 nm) by carbon deposition from pyrolysis of propyl-

ene at temperatures between 973 and 1123 K. Carbon deposition permits the maximization of the number and fraction of pores between 0.28 and 0.38 nm. Precursor carbons that possesss a fairly wide pore-size distribution, such as activated carbons, are not found suitable for producing CMS using the approaches described in this paper.

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