THE PREPARATION OF 4A AND 5A CARBON MOLECULAR SIEVES

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The following molecular probes were chosen to evaluate the pore structure of a series of carbons: CO_2 (3·3Å), butane (4·3Å), isobutane (5·0Å), neopentane (6·2Å), benzene (3·7Å, 7·0Å) and cyclohexane (4·8Å, 6·8Å). Phenol–formaldehyde, polydivinylbenzene, polyfurfuryl alcohol and furfuryl alcohol–formaldehyde carbons had a uniform 4Å pore structure. Composite Carbon Molecular Sieves (C.C.M.S.), made by coating commercial activated carbons with partially polymerised furfuryl alcohol, followed by curing and carbonisation of the polymer coating, adsorbed butane and isobutane in the ratio of about 6 : 1. The C.C.M.S. adsorbed more benzene than isobutane, which indicated that the pores were slit-shaped.

Introduction

Molecular sieve materials are widely used today in industry for the separation of hydrocarbons, drying of gases and the removal of trace impurities.[1] The most widely used molecular sieve materials at the moment are the 4A, 5A, 10X and 13X synthetic zeolites made by the Linde Company. These zeolites are crystalline materials having large pore volumes and surface areas, and of prime importance, pores of uniform size. The sizes of the apertures in the above zeolites are estimated to be 3·5, 4·2, 9·0 and 10·0Å, respectively.[2] These zeolite sieves have strongly polar surfaces and have poor acid stability.

Although it is known that some carbons, especially those prepared by the charring of organic polymers,[3] possess both molecular sieve properties (with pores ranging from 3Å to 12Å) and high surface areas, no carbon molecular sieves have been manufactured. This paper outlines our attempts to produce acid stable carbon molecular sieves with sieve properties similar to the Linde 4A and 5A zeolite sieves.

Considerable knowledge regarding the molecular sieve properties of carbons has been obtained from studies designed to elucidate the structure of microporous carbons. These results are reviewed, insofar as they are relevant to our attempts to produce a range of carbon molecular sieves.

Activated carbons have high adsorptive capacities with areas of 1200 $m.^2/g.$ or more being common; but they have no molecular sieve characteristics,[4,5] since the average pore diameter is generally larger than 20Å. On the other hand, the molecular sieve properties of unactivated coals and cokes are well known, but the surface area of these materials is too low to warrant their use as molecular sieves. Values of pore width for coals and cokes lie in the 4—8Å range.[6–10] Bond & Spencer[11] observed that activation of coal chars, to increase the surface area, occurs non-uniformly and leads to the production of activated charcoals whose internal surface area is readily accessible to the largest molecular probes. Lamond & Marsh[12] observed the development of funnel-shaped transitional pores on the surface as a result of activating polyfurfuryl alcohol and polyvinylidene chloride carbons. They also showed that the increase in adsorptive capacity with activation results from capillary condensation (reversible) taking place in these pores.

Metcalfe *et al.*,[13] in an attempt to activate anthracite uniformly, chose material of very fine particle size (6μ) and activated in a 90% carbon dioxide–10% carbon monoxide stream. A 34·8% wt-loss sample was evaluated by measuring the adsorption of butane, isobutane and neopentane at 30°. Retention of partial molecular sieve characteristics, coupled with a significant increase in pore volume accessible from 4·9Å to 5·6Å dia. pores was observed. However, because of the difficulties encountered in the activation of this fine particle size material and in the reproducibility of the results, the method has not been further pursued.

Thermosetting organic polymer carbons have created widespread interest as molecular sieves because of their uniform, ultra-fine capillary structure and frequent high areas. Kipling[3] measured the adsorption of water, ethyl alcohol, benzene and α-pinene on a wide range of 700° polymer carbons. Marsh & Wynne-Jones[14] reported the nitrogen and carbon dioxide surface area values of comparable polymer carbons, but which had been prepared over a wide range of carbonisation temperatures. Carbons derived from thermosetting polymers (chars) have higher areas than those derived from thermoplastic polymers (cokes) and thus the former are of more

interest in this study. Areas of around 500 m.^{2}/g. and pores of 3—5Å are common for the majority of thermosetting polymer carbons.[14,15] However, chars derived from polyvinylidene chloride have areas greater than 1000 m.^{2}/g. and pore diameters estimated as 10—12Å.[14–17]

In this study, a range of thermosetting organic polymer carbons was chosen for evaluation as molecular sieves. Some of the polymer carbons, either because the area accessible through pores of a particular size is small or because of the high price of the polymer, would not be suitable for use as molecular sieves. A new type of carbon was developed to overcome this problem. Activated granular carbon was coated with a partially polymerised polymer solution, followed by curing and carbonisation of the polymer coating. These new materials, ' Composite Carbon Molecular Sieves (C.C.M.S.) ', consisting of activated carbon covered by a layer of microporous carbon, the latter acting as a molecular sieve, the former supplying the adsorptive capacity of the body, have significant advantages over the polymer carbon sieves (P.C.S.).

The monolayer capacities, calculated from either the Langmuir equation[18] or from the Joyner modification of the B.E.T. equation,[19] for microporous solids are generally very close and sometimes exceed the observed adsorptive capacities at a relative pressure of 1·0.[20] Thus, while it is possible that the adsorption is restricted to the formation of a monolayer on the pore wall, several authors have found evidence that the pores are appreciably wider than would be required by this model and that a reversible capillary condensation process must be occurring.[12,15,17,21–23] Barrer[22] has suggested the term ' monolayer area equivalent ' for use in such cases. Lamond & Marsh[12,15] developed a method, to overcome this capillary condensation problem, based upon the application of the Polanyi Potential Energy (P.E.) Theory, as modified by Dubinin,[24] to the low-pressure carbon dioxide adsorption isotherms; it was considered that this method gave true surface areas for a wide variety of carbons. The P.E. surface area values were substantially lower than the Langmuir-B.E.T. values for activated carbons, where capillary condensation could occur to a significant extent. However, the values agreed within 10% for unactivated polymer chars, indicating that while capillary condensation could be the dominating adsorption process in the B.E.T. relative pressure range, the pores were sufficiently fine so that the excess adsorption in the pore centre was negligible compared to that adsorbed on the pore walls.

In this work, the adsorptive capacities of a range of very fine-pore carbons have been measured at a relative pressure of 0·5. For comparative purposes, the results have been expressed as surface areas (or monolayer area equivalents), the value at 0·5 p/p_s being used as the monolayer capacity. The error in taking this value as the monolayer capacity instead of the Langmuir value was less than 2·5% and insignificant to the 10% difference between different methods of area measurement observed by Lamond & Marsh.[12,15]

Experimental

Preparation of polymers

(1) *Furfuryl alcohol polymerised with zinc chloride*[25]

A mixture of 90 parts of furfuryl alcohol (Quaker Oats Co.) and 5 parts of zinc chloride dissolved in 5 parts of water was stirred, under reflux conditions, for 5 h. at 90°. The reflux condenser was removed and after the water had evaporated, the solution was allowed to cool. The liquid resin was cured by heating at 120° for 6 h. and then for 10 h. at 200°.

(2) *Furfuryl alcohol polymerised with phosphoric acid*

This is a modification of the method given in Quaker Oats Technical Bulletin on furfuryl alcohol.[26] A mixture of furfuryl alcohol 87·3%, water 12·45% and phosphoric acid 0·25% was heated and stirred under reflux conditions for 8 h. at 90°. The reflux condenser was removed and after the water had evaporated, the solution was allowed to cool. The liquid resin was cured by heating at 120° for 6 h. and then for 10 h. at 200°.

(3) *Furfuryl alcohol–formaldehyde*

A mixture of 66·2% of furfuryl alcohol, 33·1% of formalin (37·2% formaldehyde) and 0·7% of a solution of phosphoric acid (1 vol. of 85% H_3PO_4 + 2 vol. of water) was heated under reflux conditions for 90 min. at 90°.[27] The resin was partially neutralised (pH 4—5) with aqueous sodium hydroxide, cooled to 70° and dehydrated in vacuum. The resin was cured by heating with 1% maleic acid for 6 h. at 120° and then for 10 h. at 200°.

(4) *Polydivinylbenzene*

Divinylbenzene (45% ethyl-vinylbenzene, Dow Chemical Co.) was purified by distillation.

One ml. of a 10% solution of benzoyl peroxide in divinylbenzene was added to 100 ml. of divinylbenzene and the mixture was cured by heating for 18 h. at 120° in covered dishes.[14]

(5) *Phenol–formaldehyde*

Liquid resin obtained from Catalin Corporation of America, No. 194, was cured by heating at 180° for 4 h.

Activated carbon coating procedure

The activated carbon was allowed to soak in a bath of resin maintained at 90° for 3 h. The coated carbon was separated from the excess resin by pouring the mixture onto a wire screen. It was then allowed to drain at 90° for 1 h. The polymer coating was cured as for the polymer itself and the coated carbon then separated from the screen for carbonisation. The granulated (4 × 10 or 4 × 6 mesh size) commercial activated carbons (see Table I) were used as fillers to produce C.C.M.S.

Table I

Activated carbons used in preparation of C.C.M.S.

Fillers	Surface Areas, $m^2/g.$	
	Butane, 0°C	Neopentane, 0°C
(A) Barnebey-Cheney Co. low-activated coconut shell charcoal	1030	930
(B) Barnebey-Cheney Co. medium-activated coconut shell charcoal	1420	1430
(C) Pittsburgh Activated Carbon Co. (BPL)	1080	1060
(D) Columbia Co. (CXC)	1490	1490

Carbonisation

The polymer or polymer-coated activated carbon was carbonised in a stream of oxygen-free nitrogen. During the carbonisation step, the rate of heating, the carbonisation temperature, and the time the carbon was held at the maximum temperature (soak-time) were varied to determine the effect of carbonisation conditions on the pore structure. The carbonised polymers were ground, with either the 30 × 60 mesh fraction or the −100 mesh fraction (only used for the char from the polydivinylbenzene) used for adsorption studies. The C.C.M.S. had a particle size closely approaching the particle size of the activated carbon fillers used.

Molecular probe studies

The adsorptive capacities, at a relative pressure of 0·5, towards the gases listed in Table II,

Table II

Gases used in molecular probe studies

Gas	Adsorption temperature, °C	Minimum cross-section, Å	Molecular area, $Å^2$
Carbon dioxide	−77	3·3[2]	17[14]
Butane	0	4·3[2]	47[4]
Isobutane	0	5·0[2]	51[4]
Neopentane	0	6·2[2]	62[4]
Benzene	40	3·7, 7·0[3]	—
Cyclohexane	40	4·8, 6·8[3]	—

were measured gravimetrically. Prior to adsorption the carbon was outgassed at 250° to a pressure of 10^{-3} torr for 6 h. The sample was suspended in a small aluminium bucket from a silica spring, having a sensitivity of 18 cm./g. A cathetometer was used to measure the extension, which could be read to ± 0·003 cm. The diffusion of molecules into pores slightly smaller than the diameter

of the adsorbate molecule is an activated process, and the rate of attainment of equilibrium is extremely slow. The extent of adsorption was measured after 1 h. and thus the adsorptive capacities are not necessarily equilibrium values. For comparative purposes, adsorptive capacities at a relative pressure of 0·5 were determined for the Linde 4A and 5A $\frac{1}{8}$ in. cylindrical pellets.

All the adsorbates were better than 99·5% pure. A Linde molecular sieve 5A trap was used to remove n-hydrocarbon impurities in some of the adsorbates. The chosen series of molecular probes allowed good comparison of the carbon molecular sieves with the Linde product: carbon dioxide is adsorbed on both the 4A and 5A sieve, butane is adsorbed on the 5A sieve, isobutane and neopentane are adsorbed on neither. Benzene and cyclohexane, which are planar molecules, were useful in that they gave some indication of the pore geometry of the carbon molecular sieves.

Results and discussions

Polymer carbon sieves

The equivalent monolayer areas of five polymer carbon sieves are given in Table III.

Table III

Carbonisation temperature, °C	Surface area, m.²/g.			
	CO_2	Butane	Isobutane	Neopentane
Polyfurfuryl alcohol (zinc chloride) carbons				
500	310	120	30	10
600	330	140	35	10
700	380	225	60	10
750	385	260	50	10
800	400	150	30	10
Polyfurfuryl alcohol (phosphoric acid) carbons				
500	415	30	0	0
600	430	30	0	10
700	460	30	0	0
800	445	10	0	0
Furfuryl alcohol–formaldehyde carbons				
400	380	44	0	0
500	428	64	0	0
600	390	15	0	0
700	414	10	0	0
Divinylbenzene carbons				
625	325	10	0	0
700	443	5	0	0
775	378	5	0	0
850	394	5	0	0
Phenol–formaldehyde carbons				
400	380	45	0	0
500	428	65	0	0
600	390	14	0	0
700	414	10	0	0
800	490	0	0	0

Although not shown in the Table, varying either the carbonisation soak time from 2 to 12 h. or the rate of heating from 5 to 20°/min. did not alter significantly the measured areas. For the results shown in the Table, a heating rate of 7·5°/min. and a soak time of 4 h. were used. The sieve properties of the phenol–formaldehyde, polydivinylbenzene, phosphoric acid polymerised furfuryl alcohol, and the furfuryl alcohol–formaldehyde carbons compared favourably with the Linde 4A sieve (CO_2 area, 530 m.²/g.; butane, 10 m.²/g.). The 700 and 800° carbons exhibited the sharpest separations, since the butane area had reached a maximum below these temperatures while the CO_2 area increased or stayed constant. Heating the carbons above 800° would result in extensive pore shrinkage and a loss of CO_2 adsorptive capacity.[14] As expected, the adsorption of isobutane and neopentane on these chars could not be detected.

The carbon prepared from the pyrolysis of zinc chloride-polymerised furfuryl alcohol (Table III) had slightly wider pores than the other carbons, possibly caused by the zinc salt acting as an activating agent during carbonisation of the polymer.

Composite carbon molecular sieves

The monolayer equivalent surface areas of four C.C.M.S. (four different activated carbons coated with a layer of phosphoric acid polymerised furfuryl alcohol polymer carbon) are shown in Table IV (a—d), for a heating rate of 7·5°/min., Table IV (a, c and d) with a 4 h. soak time at

Table IV

Carbonisation temperature, °C	Surface Area, m.²/g.			
	CO_2	Butane	Isobutane	Neopentane
	(a) *C.C.M.S. formed using filler (A)*			
500	455	225	30	0
600	480	320	30	0
700	640	240	40	0
750	640	320	70	15
800	750	270	30	0
850	505	365	40	0
	(b) *C.C.M.S. formed using filler (B)*			
500	430	110	10	0
600	465	190	40	0
650	515	240	10	0
700	525	335	70	0
750	550	330	50	15
750	560	345	80	30
750	545	175	10	0
800	470	167	10	0
850	465	115	10	0
	(c) *C.C.M.S. formed using filler (C)*			
500	195	165	100	30
600	335	280	145	60
700	445	415	295	100
750	490	430	315	125
800	635	480	340	135
850	500	360	255	105
	(d) *C.C.M.S. formed using filler (D)*			
500	470	350	105	10
600	510	450	159	30
700	540	405	90	20
800	407	270	43	15

maximum temperature was used. The C.C.M.S. appeared at first to have a range of pore sizes from 4Å to 6Å. The butane/isobutane separation ratio ranged from 4 to 7 : 1; the butane/neopentane ratio was around 15 : 1. The C.C.M.S. formed using filler (C) was the exception in that the sieve adsorbed appreciably more isobutane and neopentane than the other sieves. These results, which were quite reproducible, are of interest. The mixing of the activated carbon fillers with the polymer carbon binder could have had two extreme effects. One, the binder could have charred as it did when carbonised alone. In this case, the C.C.M.S. would have been expected to have had negligible capacity for the adsorption of butane, isobutane and neopentane. Second, the binder upon carbonising could have undergone such serious shrinkage that coupled with the normal thermal expansion of the filler, extensive macrocracks in the binder would have resulted.[28] In this case, the C.C.M.S. would have been expected to have adsorption characteristics similar to the activated carbon fillers; that is, large and essentially equal adsorption of butane and neopentane. In fact, neither of these two extreme cases was found. Instead, the capacity of the C.C.M.S. for butane was substantial, while the capacity for neopentane was, in most cases, small. Obviously, however, some interaction between the filler carbons and the binder has occurred.

Comparable surface areas for the Linde 5A sieve are CO_2, 560 m.²/g.; butane, 520 m.²/g.; isobutane and neopentane, 30 m.²/g. The C.C.M.S. did not produce as sharp a separation between butane and isobutane as did the Linde 5A sieve. The reason for this will become clear shortly.

The adsorptive capacities towards benzene and cyclohexane were measured for the 700° C.C.M.S. (Table V). For the three C.C.M.S., which had appreciable butane/isobutane separation,

Table V

Adsorptive capacities (ml./g.) of 700°-C.C.M.S.

Filler	*Butane*	*Isobutane*	*Neopentane*	*Benzene*	*Cyclohexane*
A	0·110	0·021	0·004	0·051	0·006
B	0·145	0·022	0·005	0·061	0·024
C	0·141	0·093	0·032	0·127	0·046
D	0·138	0·030	0·005	0·056	0·022

the benzene adsorption was approximately 50% of the butane value and approximately twice the isobutane value. The adsorptive capacities of these carbons towards cyclohexane was much lower and lay between the values for isobutane and neopentane. These results demonstrate that the pores are slit-shaped, with a minimum dimension of ~ 5Å and a maximum dimension greater than ~ 7Å. Whether or not the slit-like character of the pores is due to the pore geometry of activated carbon or is solely due to the structure of the carbon coating has not been determined. It is apparent why butane/isobutane separation ratios much above 6 to 1 were not observed. By rotation, an isobutane molecule can present the same minimum cross-sectional diameter to a 5Å slit as can a butane molecule. It would be interesting to determine whether the difference in the adsorptive capacities of the C.C.M.S. towards the two gases could be related to the amount of entropy decrease required to align the isobutane molecule with a 5Å slit.

Further experimental work is being conducted in this laboratory on C.C.M.S. in the expectation of improving their gas separation ability, increasing the surface area of one 5Å (slit) sieve described, and in preparing sieves with other pore sizes. Separation ratios of two components are also being measured dynamically in a flow system.

Conclusions

Carbons exhibiting molecular sieve properties can be prepared from various thermosetting organic polymers and also from mixtures of activated carbons (used as the filler) and thermosetting organic polymers (used as the binder). The extent of uptake of various molecules by molecular sieve carbons is complicated by their pore shape, which appears to be slit-like instead of essentially circular as in zeolite molecular sieves.

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Discussion

Prof. P. L. Walker, jun.: I want to call your attention to molecular sieve carbon pellets ($\frac{3}{16}$ in. dia.) made from carbonised Saran as the filler and lignite pitch as the tinder. In order to test the ability of the material to separate hydrocarbon mixtures, a dynamic adsorption apparatus was employed. The performance of this material to separate a mixture of n-heptane and iso-octane was compared with that of a Linde 5A molecular sieve and a granular activated carbon. Equal weights of solid were used in each test. In the dynamic test, helium, at a fixed flow rate, was passed through a bubbler containing a mixture of the two hydrocarbons, and the concentration of the hydrocarbons was monitored before and after passage through a bed of adsorbent. For the granular activated carbon, neither of the hydrocarbons broke through the bed for 78 min. Then each hydrocarbon broke through at the same time; following ~ 120 min. the split hydrocarbon concentrations equal their entering concentrations. For the 5A sieve, iso-octane broke through the bed after 2 min. and reached its inlet concentration after 6 min., n-heptane broke through after 39 min. and reached its inlet concentration after ~ 80 min. This is clearly molecular sieve action. For the molecular sieve carbon, iso-octane broke through after 4 min. and reached its inlet concentration after 12 min. n-Heptane did not break through the bed until 63 min., reaching its inlet concentration after 110 min. There is much to be done on developing carbon molecular sieves, but certainly the fact that they show promise is clear.

Dr. J. J. Kipling: The adsorption measurements were carried out at $p/p_0 = 0{\cdot}5$. Has the author any information on the adsorption of vapours by the coated carbons at high relative pressures? The isotherms for activated charcoals and for zeolitic materials are often alike at low p/p_0, but differ at high p/p_0, because the former may rise rapidly as capillary condensation occurs, whereas the latter tend to a constant value. This might be a basis for discovering whether the coating material is usefully filling the large pores in the original charcoal which would otherwise remain of little use for molecular sieve purposes.

Mr. A. J. Groszek: Graphite has one interesting surface property, namely, some parts of its surface have an exceptionally strong affinity for methylene groups, which are, of course, building blocks of hydrocarbon molecules. Because of this, the strength of adsorption of hydrocarbons on graphite depends very much on the number of contacts they can make with the graphite surfaces; thus normal paraffins are adsorbed more strongly than branched molecules and graphite adsorbs preferentially normal paraffins from their mixtures with branched molecules, this applies to both gaseous and liquid mixtures. A further interesting fact is that the same sites that have a strong affinity for methylene groups, have a relatively very weak affinity for polar molecules, such as water, and the preferential adsorption of normal paraffins occurs readily on graphite in the presence of water. In view of this I wonder whether there is an element of this specific surface property of graphite in the action of carbon molecular sieves described by Prof. Walker. One crucial test for this would be to find out whether the adsorption of n-butane can take place in the pressure of water or methanol. We know that this is not taking place readily on Linde molecular sieves. In general measurements of competitive adsorption can, in my opinion, shed a lot of light on the specific surface properties of various solids, which may not necessarily reside in the molecular sieve effects.

Prof. Walker: One of the most interesting aspects of the properties of carbon molecular sieves relative to zeolitic sieves is a difference in behaviour to water uptake. For zeolitic sieves, water is strongly held and adsorbed preferentially to hydrocarbons. On the other hand, on a carbon sieve, low in oxygen, hydrocarbons are taken up preferentially to water.

Mr. H. W. Davidson: The polymer-coated absorbent carbons may be looked on as absorbent reservoirs controlled by coating orifices. This would affect the kinetics of absorption. In particular I doubt if activated absorption is applicable.

Prof. Walker: Of course, activated diffusion is the basis of molecular sieve action. If the kinetic diameter of a molecule closely approaches the aperture size in the solid, diffusion becomes activated. The activation energy increases sharply with further decrease in aperture size or increase in the size of the diffusing species. For the most efficient utilisation of a molecular sieve material, the diffusion distance should be as small as possible. This is why the CCMS

material discussed in this paper is of particular interest. The molecular sieve phase, the binder, is in a relatively thin coating around the activated carbon filler particles. Thus the diffusion distance, before the sorbing species reaches the high capacity filler, is small.

Mr. J. van Aken: Which mechanism do you suppose the binding between the outer charcoal surface and the carbonised resin is achieved?

Prof. Walker: As indicated in the paper, we calculated surface areas on the basis of sorbate uptake at a relative pressure of 0·5. Very little uptake was found at higher relative pressures.