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NOTE

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INTRODUCTION

Naturally occurring and synthetic zeolites (*1*, *2*) find wide application in industry as molecular sieves. Some carbonaceous materials also show molecular sieve properties; however, their efficiencies and capacities are considerably lower compared with those of zeolites. Molecular sieve carbons can be obtained by coating activated carbons with thermosetting resins (*3*). Composite molecular sieves were obtained by heating precarbonized polyvinylidene chloride with certain binders (*4*). It has been found that the adsorption capacities of charcoals (*4*, *5*) depend on the accessibility of sorbate molecules, indicating molecular sieve action. Youssef (*6*, *7*) has produced molecular-sieve carbons by carbonizing date pits and bagasse, in the presence and absence of zinc chloride, under controlled conditions. Carbon molecular sieves are used extensively in gas chromatography for the separation of permanent gases and light hydrocarbons. Carbon molecular sieves also find commercial application for the manufacture of pure hydrogen from hydrogen-rich gases such as coke-oven gas, and for the separation of air by the pressure-swing adsorption technique.

The objective of this investigation was to prepare carbons from Maghara coal, recently available on the commercial market. Coal-based carbons, if they possess molecular sieve properties, are superior to molecular sieve carbons from agricultural by-products because they have more satisfactory mechanical properties.

EXPERIMENTAL

A nonactivated Maghara coal sample, M, was obtained by the destructive distillation of the original Maghara coal at 600°C in a limited supply of air. MZ1, MZ2, and MZ3 are zinc chloride activated carbons which were obtained by carbonizing Maghara coal at 600°C with 25, 50, and 100 wt% zinc chloride, respectively.

The adsorption of nitrogen at −196°C and of carbon dioxide at 25°C was measured by using a conventional volumetric apparatus. The adsorption of benzene, *n*-butane, isobutane, carbon tetrachloride, isooctane and α-pinene was measured at 35°C by using quartz spring balances. The adsorbates used were Analar grade. The sample was activated at a pressure of 10^{-6} bar and at a temperature of 200°C before each experiment.

RESULTS AND DISCUSSION

The adsorption isotherms are generally Type I of the BDDT classification, characteristic of microporous sorbents. The molecular diameters of the adsorbates vary. Excluding nitrogen and carbon dioxide, the molecular diameters of the organic vapor adsorbates investigated vary between 3.7 and 8.0 Å. The adsorption of these adsorbates with Type I isotherms indicates that the pores are only a few molecular diameters in width. Figure 1 shows representative adsorption isotherms on MZ1.

Nonactivated Maghara coal M adsorbed an extremely small amount of nitrogen at −196°C. The adsorption of nitrogen in ultrafine pores at this very low temperature is controlled by activated diffusion (*8*). Conse-

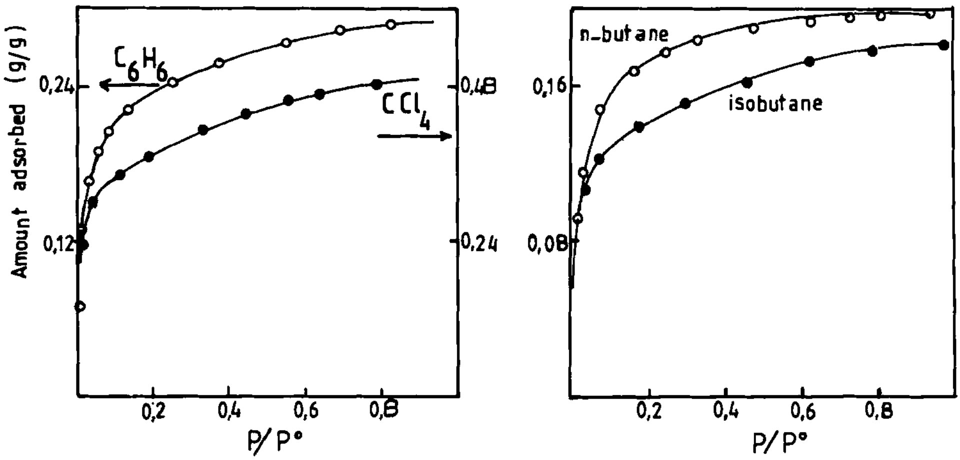

FIG. 1. Representative adsorption isotherms of Sample MZ1.

quently, nitrogen adsorption at −196°C is not a measure of surface area but can be taken as evidence for the existence of ultrafine pores. Carbon dioxide adsorption at 25°C was recommended (*9*) for use as a surface area measure of molecular sieve carbons because of the absence of any diffusion control. The adsorption of carbon dioxide at 25°C was measured in the pressure range 25–800 bar, which is very low compared with the saturation pressure of carbon dioxide at 25°C (48,300 bar). The Dubinin-Polanyi equation (*10*) was applied to interpret the data obtained from carbon dioxide adsorption. M, MZ1, MZ2, and MZ3 had measured carbon dioxide surface areas of 80, 300, 330, and 348 m^2/g, respectively. Sample M also adsorbed small amounts of benzene and *n*-butane but it did not show any measured adsorption of isobutane, carbon tetrachloride, isooctane, or α-pinene. MZ1 has larger pores since it showed fair amounts of nitrogen adsorption and appreciable amounts of even larger and bulky molecules such as isobutane and carbon tetrachloride. However, MZ1 did not exhibit any measurable adsorption of isooctane and α-pinene. The increase in the nitrogen adsorption capacity of MZ1 compared to M indicates that zinc chloride removes the constrictions between fine pores and/or slightly widens the existing ultrafine pores, making them accessible to nitrogen adsorption at −196°C. Light hydrocarbons may be absorbed during carbonization and cause partial blocking of the pores forming. Thus, some constrictions occur in the pore structure of carbonaceous material. In zinc chloride activation, hydrogen is removed from the carbonaceous material as HCl rather than as methane and lower hydrocarbons (*11*) which may deposit and form pore constrictions. The evidence that refers to the slight pore widening brought about by zinc chloride activation is that MZ1 showed isobutane and carbon tetrachloride adsorption while M did not.

MZ2 and MZ3, on the other hand, have larger pore sizes; they showed appreciable adsorption of isooctane and α-pinene. This may indicate that increasing of the amount of zinc chloride increases the adsorption capacity and the accessibility of carbon. The adsorption of adsorbates to varying extents and the absence of adsorption of others in some carbons indicates that different carbons have pores of different diameters associated with them.

The surface area is a useful parameter frequently used as a measure of the adsorption capacity of solids. But for microporous solids this should be taken with much reserve because the forces of adsorption on the opposite walls of the micropore enhance adsorption. Also, in micropores of molecular size, capillary condensation (micropore filling) rather than surface coverage may take place, and therefore the concept of surface area loses its significance.

In order to compare the sorption capacities and pore accessibilities, the total pore volumes of the organic vapor adsorbates were compared. These apparent pore volumes were taken at a relative pressure of 0.95, and they are expressed as volume of liquid, assuming the adsorbates have a normal liquid density. The apparent pore volumes determined are recorded in Table 1.

It is evident from Table 1 that:

1) For zinc-chloride-activated carbons, the adsorption capacity of any adsorbate increases with an increase in the amount of zinc chloride used in the activation.

2) The apparent pore volumes for a given sample of carbon, as measured by adsorbates of molecular diameters ≤5.2 Å, are very close. A considerably lower apparent pore volume for a certain sample is obtained by adsorbates of larger molecular diameter. Thus, for MZ, apparent pore volumes between 0.30 and 0.35 cm^3/g were calculated, i.e.,

$$\text{Range of difference} = \frac{0.05}{(0.35 + 0.30)/2} = 15\%$$

The same is also true for MZ2 and MZ3.

3) Much smaller values of apparent pore volumes for the same sample are calculated from the adsorption of adsorbates with larger molecular diameters, i.e., >5.2 Å (isooctane and α-pinene). This phenomenon may be referred to as a screening effect.

4) It seems that with an increasing quantity of zinc chloride, the screening effect becomes less pronounced. Thus, MZ1 did not show any adsorption for isooctane and α-pinene, while MZ2 and MZ3 had appreciable adsorption of these adsorbates.

Figure 2 shows the apparent pore volume plotted versus the molecular diameter. It is evident that a decrease of pore volume with molecular diameter is slow up to a diameter of 5.2 Å (for carbon tetrachloride). With

TABLE 1

Pore Volume (cm^3/g) of Various Carbons Calculated by Adsorption at $P/P^\circ = 0.95$

Sample	Benzene	*n*-Butane	Isobutane	Carbon tetrachloride	Iso-octane	α-Pinene
M	0.12	0.09	—	—	—	—
MZ1	0.35	0.32	0.30	0.30	—	—
MZ2	0.42	0.42	0.39	0.37	0.10	0.06
MZ3	0.48	0.45	0.45	0.44	0.28	0.23

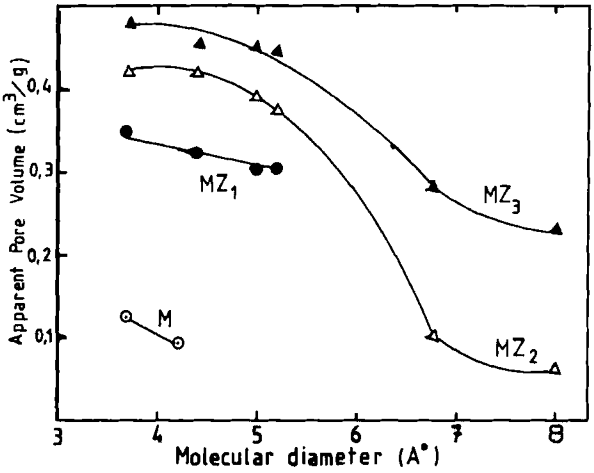

FIG. 2. Apparent pore volume (cm³/g) versus molecular diameter.

a further increase in molecular diameter, the decrease in apparent pore volume becomes rapid. Comparison of the plots for MZ2 and MZ3 shows that the decrease is less sudden for MZ3, which indicates that the screening effect reduces with increasing zinc chloride.

We feel that molecular sieve carbons could be prepared from Maghara coal (subbituminous coking coal). The adsorption capacity of coal-based molecular sieve carbons increases upon activation with zinc chloride. However, an increase in the amount of zinc chloride above a certain limit reduces the screening effect of the carbon.

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