

CARBON MOLECULAR SIEVE SUPPORTS FOR METAL CATALYSTS—I. PREPARATION OF THE SYSTEM—PLATINUM SUPPORTED ON POLYFURFURYL ALCOHOL CARBON

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Abstract—A shape-selective carbon molecular sieve support-platinum catalyst system has been prepared by carbonizing polyfurfuryl alcohol (PFA) containing small amounts of chloroplatinic acid. Although the resulting coke behaves as a 4A molecular sieve, grinding to a particle size of about 50 μ allows appreciable adsorption of *n*-butane, due to the shortened diffusion distance for gaseous adsorbate molecules. The same effect, that is conversion to a 5A sieve, can be produced by addition of an activated carbon filler to the partially-polymerized PFA, thereby causing the formation of macrocracks during carbonization which serve as diffusion pathways. The most important variable in the preparation is the PFA to filler ratio. Varying this ratio allows materials of different surface area and molecular sieve properties to be prepared.

I. INTRODUCTION

The use of activated carbon as a catalyst support, particularly for the noble metals, is widespread and of considerable industrial importance. Most often carbon is used because it is relatively inexpensive and because it provides a high-surface area support with little intrinsic catalytic activity.

Some twenty years ago, Pierce and co-workers[1], along with a number of others [2,3], showed that when certain polymers, such as Saran, were carbonized, carbons were produced which contained a majority of their micropores in the 5-15A range. Later, Walker and co-workers described the preparation of carbon molecular sieves, not only from polyvinylidene chloride and Saran[4,5] but from other polymers as well [6].

During the same time period, molecular shape-selective reactions were performed using zeolite molecular sieve catalyst supports [7,8]. A shape-selective catalyst support possesses its active surface within a pore system penetrable only by molecules smaller than a certain critical size. Thus only molecules small enough to enter the pores will react, and only product molecules of a similarly small size will appear outside the catalyst support pellet or particle.

Recently, Trimm and Cooper[9,10] have used polyfurfuryl alcohol as a starting material for the preparation of a carbon molecular sieve (CMS)-platinum catalyst system. This preparation involved the polymerization (up to 200°C) and subsequent carbonization (at 640°C) of a furfuryl alcohol-formaldehyde mixture containing a colloidal suspension of platinum. A sample containing 5.72% platinum was used for hydrogenation experi-

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ments. This sample showed negligible uptake of isobutane; *n*-butane sorption at 0°C was about 20% the N₂ sorption at 77°K.

In the work reported here, CMS-Pt catalysts have been prepared by carbonizing polyfurfuryl alcohol, containing a platinum salt, around an activated carbon substrate, thus forming the kind of composite material described previously by Walker *et al.*[6]. The successful use of these catalysts for the selective hydrogenation of olefins will be reported later.

2. EXPERIMENTAL

Furfuryl alcohol was obtained from the Quaker Oats Company. Preliminary studies indicated that the properties of the final carbon were the same whether the amber liquid was vacuum distilled to give the clear, water-white monomer or used without further purification.

The substrate carbon used was Barnebey-Cheney Company's type UU activated carbon. When sieved to 28 × 150 (Tyler) mesh, it had a surface area of 1290 m²/g for both *n*-butane and neopentane as measured by a technique described shortly.

Polymerization of furfuryl alcohol was accomplished by means of either hydrochloric or phosphoric acid catalysts; for example, 10 ml of furfuryl alcohol plus 0.1 ml 1N HCl were mixed and allowed to stand for several hours before curing. Curing was performed in an atmosphere of nitrogen, normally at temperatures of 100–200°C for 14–18 hr. Carbonization, also in a nitrogen atmosphere, was accomplished by heating at 5–10°C/min to various temperatures between 550 and 860°C. The soak time at the maximum temperature was 1 hr, after which the sample was cooled in nitrogen, removed from the furnace and sized for adsorption studies. Complete details are given elsewhere [11].

Addition of platinum to the samples was in all cases accomplished by pipetting the required volume of an aqueous chloroplatinic acid solution into the mixture before the

curing step. Since the rate of polymerization of furfuryl alcohol is dependent on pH [12], aqueous NaOH was sometimes added to the H₂PtCl₆ solution before contact was made with the monomer. In this way violent spattering due to rapid polymerization was avoided.

Static adsorption results were obtained with conventional McBain spring balances having a sensitivity of 0.18 mm/mg. Samples were degassed at 200°C to a vacuum of at least 10⁻³ Torr. Adsorption was then carried out using various adsorbates at a relative pressure of 0.5 and with an equilibration time of 1 hr. Table 1 summarizes the gases and conditions used.

3. RESULTS AND DISCUSSION

Although much has been written about the validity of stating 'surface areas' for microporous solids, in many cases such values are useful, particularly as a basis for comparison with other published data. Although no claim is made that the values given here represent equilibrium values, in nearly all cases adsorption was rapid, with 70–80 per cent of the 1 hr amount being taken up within 15 min. One case in which slow diffusional effects were evident was in carbonized polyfurfuryl alcohol (PFA) containing no substrate activated carbon. When PFA containing about 1 wt% (final weight) platinum was carbonized at 600°C and the resulting coke ground with mortar and pestle, the adsorption results shown in Table 2 were obtained. Similar

Table 1. Conditions for static adsorption

Gas	Adsorption temp., °C	Minimum cross-section*, Å	Molecular area, Å ²
CO ₂	-77	3.3	17 ¹
<i>n</i> -Butane	0	4.3	47 ¹³
Isobutane	0	5.0	51 ¹³
Neopentane	0	6.2	62 ¹³

*Data supplied by D. W. Breck.

samples prepared without platinum gave essentially the same adsorption values.

It can be seen that larger particles of this material effectively behave as a 4A molecular sieve—that is, one which will adsorb appreciable amounts of carbon dioxide but very little *n*-butane. That many of the pores are somewhat larger than would be expected on the basis of this result is shown by values obtained with the smaller particles. Here a shortening of the gaseous diffusion distance, as previously shown for coals [14], results in a material which will adsorb *n*-butane but not isobutane—that is, it is a 5A molecular sieve.

The production of a composite material is attractive since a considerable portion of the final product would be relatively inexpensive activated carbon. The carbonized polymer would function as a molecular 'gate' while the substrate carbon, with its high surface area, would provide most of the adsorptive capacity of the material. The use of a small particle size substrate introduces difficulties, however, since to be effective the polymer carbon shell should be thin (to minimize diffusion distances) yet complete—containing no large breaks which would destroy molecular sieve properties. With small substrate particles, adequate draining of excess polymer becomes extremely difficult, even when the viscosity of the polymer is lowered by solution in acetone.

Preliminary experiments indicated that when furfuryl alcohol was partially polymerized, as described previously [6], it could still be readily dissolved in acetone. Further, when the acetone was evaporated and the resulting PFA carbonized, the coke had adsorption properties identical to those of carbonized PFA which had not been dissolved. Thus a PFA-acetone solution could be added to substrate carbon in any desired ratio. Some results of such a technique are shown in Fig. 1. As can be seen, molecular sieving is pronounced; most samples adsorb about twice as much *n*-butane as isobutane. In addition, two general trends are apparent.

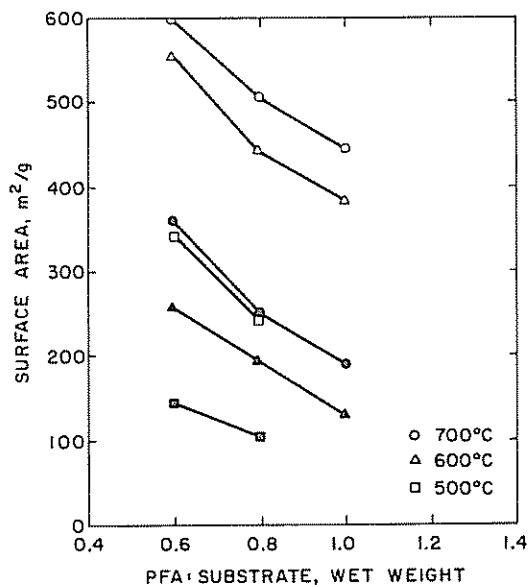


Fig. 1. Surface areas of composite carbon molecular sieves as a function of carbonization temperature and relative amount of polymer carbon. Open symbols, *n*-butane. Closed symbols, isobutane.

Surface area values decrease with decreasing carbonization temperatures (below 700°C) and with increasing amounts of PFA (as compared with substrate carbon) in composite samples.

Holding the PFA:substrate carbon ratio constant and varying carbonization temperature gave the results shown in Fig. 2. Increasing carbonization temperature up to 800°C results in higher surface areas, probably due to the enlargement of pores in the polymer carbon as volatile carbonization products are released. Since the surface area of carbonized PFA reaches a maximum at a carbonization temperature of 700°C [15], an effect due to the presence of substrate carbon is indicated. Finally, as shown by the values at 850°C, pore shrinkage begins and surface areas decline.

As the relative amount of polymer carbon is increased with respect to the substrate, a point is reached when it is difficult to visualize

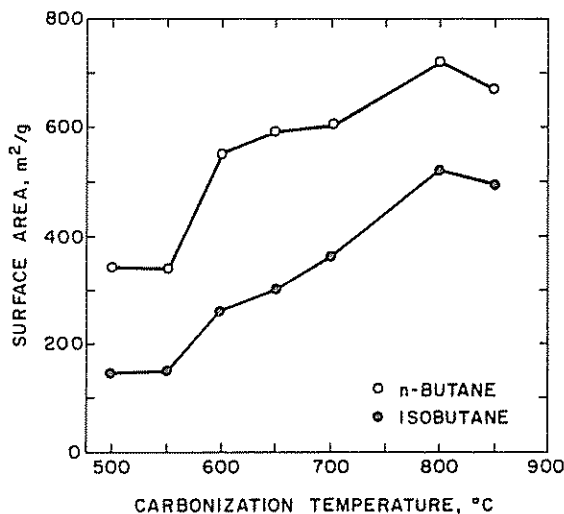


Fig. 2. Surface areas of 0.6 PFA: substrate composite carbon molecular sieves with varying carbonization temperature.

the composite as a particle of activated carbon with a polymer carbon 'skin'. Instead, the product would seem to be activated carbon particles in a polymer carbon matrix. The adsorption properties of the composite, therefore, would be those of the polymer carbon, as modified by the substrate, instead of the reverse. This effect is shown in Fig. 3.

When high PFA:substrate ratios are desired, partially polymerized PFA can be weighed directly and the acetone solution step by-passed. The results shown in Fig. 3 were obtained for 20×100 (Tyler) mesh particles. Since PFA carbonized at 700°C was found to give about a 50% weight yield, a PFA:substrate ratio of 2.8 (wet) would result in a final material consisting of about 60% polymer carbon and 40% substrate carbon. As seen from Fig. 3, this material exhibits surface areas of about $290 \text{ m}^2/\text{g}$ for *n*-butane and $50 \text{ m}^2/\text{g}$ for isobutane.

Since it is difficult to think of a polymer carbon 'skin' comprising nearly two-thirds of the particle and since the obvious molecular sieving would not occur if the unselective substrate carbon was exposed to the adsor-

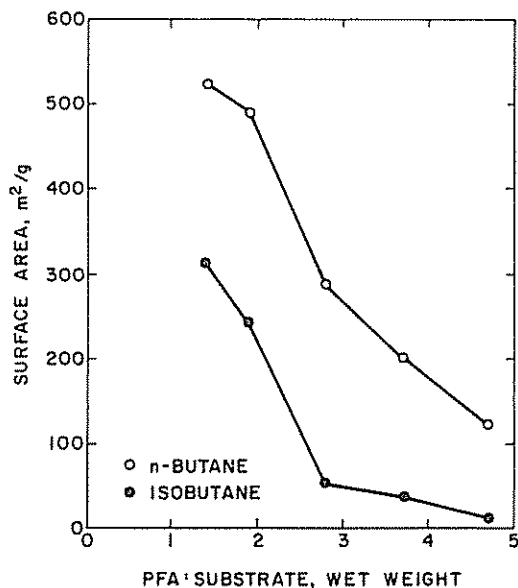


Fig. 3. Effect of changing relative amount of polymer carbon on surface areas of composite samples carbonized at 700°C .

bate gases, the question arises as to how the polymer carbon can exhibit such high surface areas. Pure carbonized PFA would be expected to show little if any adsorption for particle sizes in the 20×100 mesh range (Table 2).

We believe that for these composite samples, the internal surface of the polymer carbon becomes available in the same way as for the samples containing no substrate carbon—through a shortening of the gaseous diffusion distance. In the latter case, the

Table 2. Surface areas of PFA-Pt carbonized at 600°C

Particle size (Tyler mesh)	Surface area (m^2/g)		
	CO_2	<i>n</i> -Butane	Isobutane
10×28	375	0	0
28×150	415	35	0
150×270	—	170	0
270×400	400	365	20
— 400	390	375	50

particles themselves are ground smaller but this is not possible with the composite material since it would cause unwanted exposure of the substrate carbon. When the polymer is carbonized, however, it shrinks due to the loss of volatile decomposition products. This shrinkage occurs against the rigid substrate particles with the result that macrocracks are formed in the polymer carbon. These macrocracks serve as diffusion pathways for adsorbate molecules, thus increasing the rate at which adsorption equilibrium is attained.

If the above hypothesis is valid, the pore structure of the substrate carbon should be important since it would affect the extent of thermal expansion of the substrate particle during carbonization of the PFA. In addition, the distribution of pore sizes could determine how much polymer would be able to penetrate into the substrate. The exact result of these effects is difficult to predict, but some differences in adsorption properties would be expected between samples prepared with different substrate carbons. This has in fact been shown by Walker, *et al.*[6].

In order to further illustrate the importance of the pore structure of the substrate in composite materials, additional samples were prepared under identical conditions except that in two cases the substrate carbon had been subjected to a heat treatment temperature of 2000°C. This treatment lowered the *n*-butane area from 1290 m²/g to

35 m²/g. In the other two cases the same substrate, but not heat-treated, was used. PFA:substrate ratios were 5.0 in each case. Table 3 shows the adsorption results on 20 × 100 mesh (Tyler) material.

As Table 3 shows, samples made with the heat-treated substrate gave lower adsorption values for all three adsorbates. However, these results supply additional proof that the measured surface area is due to the polymer carbon, since the values for those samples prepared with the heat-treated substrate are still many times larger than for the substrate alone.

In conclusion, the adsorption properties of carbonized polyfurfuryl alcohol can be modified by the additional of various substrate or filler materials. Effective 5A carbon molecular sieve catalyst supports can be produced by using an activated carbon substrate, although it is not necessary for the substrate itself to possess a high surface area. Thus, since the adsorptive capacity of the composite is almost entirely due to the carbonized PFA, the catalytically active species (platinum) is placed in this portion of the sample. Selective catalysis performed using these materials in a continuous flow system will be fully described in a forthcoming publication.

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Table 3. Surface areas of composite samples prepared with heat-treated (HT) and non-heat-treated (NHT) substrate carbon

Substrate temp. °C	Carbon-ization	Surface area (m ² /g)		
		CO ₂	<i>n</i> -Butane	Isobutane
NHT	700	505	210	75
HT	700	320	80	25
NHT	550	470	195	35
HT	550	335	180	20

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