

GLASSY CARBON AS A CATALYST SUPPORT
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Introduction

Noble metal catalysts supported on activated carbons are used in several industrial chemical processes. However, these carbons are invariably associated with mineral impurities which may act in some cases as dissociating centers for reactant molecules and/or may act as catalyst poisons. Further, activated carbons usually have a polymodal distribution of pores whose diameters vary from a few angstroms to several thousand angstroms. Depending upon the sizes of the reactant and product molecules involved in catalytic reactions, a part of the area contained in smaller pores and, hence, the catalyst contained in such pores may not be accessible for the reactions. There is thus interest in the production of relatively pure carbons with desired shape (configuration), porosity, pore size distribution and surface area. We believe that such carbons can be prepared by judiciously choosing and/or modifying the experimental conditions and procedures outlined by Hucke (1) for the preparation of glassy carbons. The present study describes the results of such an attempt.

Experimental

The basic ingredients for preparing glassy carbons with controlled porosity are: a carbon-yielding binder, a liquid pore former, a dispersing agent and a consolidating agent (1). The pore forming liquid helps escape of gases during pyrolysis of the binder. The function of the dispersing agent is to produce a uniform distribution of the various ingredients. The consolidating agent promotes catalytic polymerization of the binder. In the present study we have used furfuryl alcohol (FA) as the binder, diethylene glycol (DEG) as the pore former, Triton X-100 (iso-octyl phenoxy polyethoxy ethanol) as the dispersing agent and p-toluene sulfonic acid (PTSA) as the consolidating agent. We have also used polyethylene glycol (PEG) both as a pore former and as a dispersing agent.

The following procedure was used to prepare carbons. The consolidating agent was added to the mixture of the dispersing agent and pore former at about 75-95°C. After cooling the resultant solution to about 15°C, the binder was added in small amounts with constant stirring; the temperature during the addition was kept between 20 and 25°C. The mix was then allowed to polymerize at 20-25°C for 2.5 hr, after which it was put into molds (glass tubing, 6mm O.D. and 25cm long). For thermal setting, the following cycle was generally used: 24 hr in cooling water at 15-20°C, 24 hr at room temperature (20-25°C), 24 hr at 45°C, 2 days at 70°C (after 12 hr at 70°C, samples were removed from the molds) and 3 days at 95°C. The polymerized sample 'rod' was cut into pellets of about 2cm in length. The pellets were then pyrolyzed in a N₂ flow using the following heating cycle: 100-300°C at 4°C/hr, 300-325°C at 2°C/hr, 325-425°C at 5-6°C/hr and 425-

700°C at 10°C/min. Soak time at 700°C was 2 hr. Two samples were further heated in an Ar flow to different temperatures, up to a maximum of 1500°C, using a heating rate of 10°C/min. Soak time at each selected maximum heat treatment temperature (HTT) was 2 hr.

Surface areas of carbons were determined from N₂ adsorption at 77°K using the BET equation and from CO₂ adsorption at 298°K using the Polanyi-Dubinin equation. Pellet density was determined by mercury displacement. Pore size distribution was determined from mercury porosimetry data obtained up to a maximum pressure of 30,000 psi. For a given carbon, the cumulative volume of mercury intrusion (up to 30,000 psi) has been referred to as its pore volume in the text.

Results and Discussion

Recipes for the production of samples are given in Table 1. Surface areas, pellet densities and pore volumes of various carbons heat treated at 700°C are given in Table 2. The volumes of mercury intrusion into pores as a function of pressure for different samples are plotted in Figure 1. Pore diameters corresponding to maxima in pore size distribution curves are referred to as D_m in the text and are listed in Table 2. For each sample, the CO₂ area is significantly higher than the N₂ area. This indicates the presence of micropores in which adsorption of N₂ at 77°K is restricted due to activated diffusion. For various samples, pore volumes vary from 0.022 to 0.493 cm³/g, pellet densities vary from 0.840 to 1.375 g/cm³ and D_m values vary from < 60 to 50,000Å.

Samples 1 and 2 differ markedly in their properties, particularly N₂ areas, pore volumes and D_m values. The two samples differ only in the proportion of the dispersing agent in the starting mix used for their preparation. Thus, by varying the proportion of the dispersing agent in the starting mix it should be possible to prepare carbons with different properties.

Four additional carbon samples were prepared from the same starting mix as was used for preparing sample 3, but the heat treatment conditions between the polymerization and carbonization steps were different in each case. It was found that with the exception of N₂ areas, thermal history used has some effect on other properties studied.

The results obtained with samples 5 and 6 are very significant. For preparing sample 5, PEG is used both as a pore former and as a dispersing agent. If instead of PEG, a 1:1 mixture of PEG and Triton X-100 is used, marked changes in properties of the carbon produced (sample 6) are observed. For instance, D_m values for samples 5 and 6 are 50,000 and 210Å, respectively. These results

suggest that by varying the proportion of PEG and Triton X-100 in the starting mix it should be possible to prepare carbons having D_m values over a wide range of pore diameters.

It is well known that the structure of porous carbons can be modified by suitable heat treatment. Effect of HTT in the 700-1500°C range on the properties of samples 3 and 4 is shown in Table 3. Pore volumes and D_m values (not shown) are essentially independent of HTT. Pellet densities show some variation upon heating. Both the N_2 and CO_2 areas decrease sharply above 1000°C. For $HTT \geq 1400^\circ C$, the N_2 and CO_2 areas are about the same.

In conclusion, results of the present investigation strongly suggest the possibility of preparing glassy carbons with desired porosity, pore size distribution and surface area as catalyst supports.

References

- Hucke, E. E., U.S. Patent 3,859,421, Jan. 7, 1975.

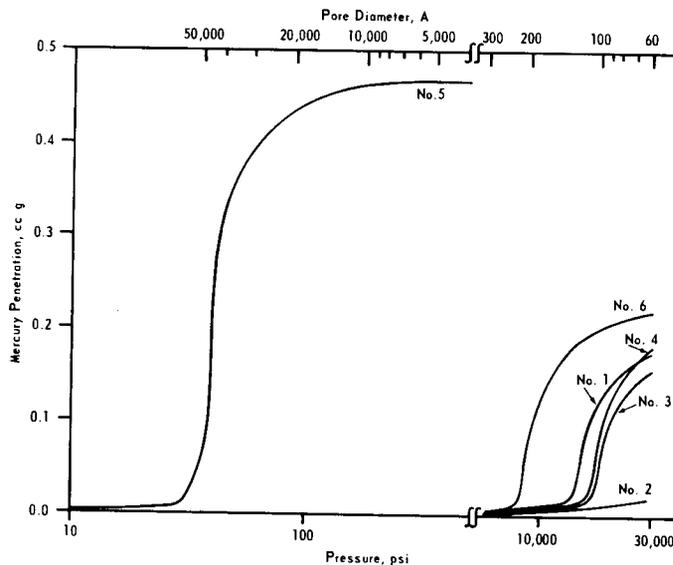


Figure 1. Pore Size Distributions in Carbon Pellets

TABLE 1

RECIPES FOR PRODUCTION OF SAMPLES

Sample	FA	DEG/PEG	Triton X-100	PTSA
1	100 cm ³	57 cm ³ DEG	50 cm ³	11.3 g
2	100	57	100	11.3
3	100	25	75	11.3
4	100	15	85	11.3
5	100	100 PEG	0	17
6	100	50	50	17

TABLE 2

PROPERTIES OF CARBONS

Sample	Surface area, m ² /g		Pellet density (g/cm ³)	D_m (A)	Pore Volume (cm ³ /g)
	CO ₂	N ₂			
1	712	442	1.114	108	0.173
2	932	39	1.375	<60	0.022
3	830	420	1.185	103	0.159
4	781	454	1.125	103	0.181
5	856	520	0.840	50,000	0.493
6	872	470	1.091	210	0.221

TABLE 3

EFFECT OF HEAT TREATMENT ON PROPERTIES OF CARBONS

HTT, °C	Surface area, m ² /g		Pellet Density (g/cm ³)	Pore Volume (cm ³ /g)
	CO ₂	N ₂		
	<u>Sample 3</u>			
700	830	420	1.185	0.159
900	994	282	1.192	0.162
1000	972	126	-	-
1100	513	92	1.217	0.161
1300	154	81	1.211	0.164
1400	72	72	-	-
1500	52	67	1.206	0.163
	<u>Sample 4</u>			
700	781	454	1.125	0.181
900	846	384	1.178	0.181
1100	377	97	1.183	0.179
1300	156	87	1.171	0.180
1500	72	90	1.154	0.180