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Carbon Vol. 18, pp. 377–378

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Carbon as a support for catalysts—IV. Modification of molecular sieve character of glassy carbons by varying heat treatment temperature

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In a recent publication it was shown that glassy carbons having different molecular sieve characteristics can be produced by changing the proportions of carbon-yielding binder (furfuryl alcohol, FA), liquid pore former (diethylene glycol, DEG), dispersing agent (Triton X-100), and polymerization catalyst (*p*-toluene sulfonic acid, PTSA) in the original mix[1]. It will be shown in this letter that molecular sieve character can also be altered by varying the heat treatment temperature (HTT) of the glassy carbon.

Formulations for the production of the two samples used in this study are given in Table 1. The procedure used to prepare the 973°K glassy carbon samples is fully described in a recent publication[1]. Further heating of the samples to different temperatures up to 1773 K was conducted in an Ar flow using a heating rate of 10°K/min and a soak time at maximum temperature of 2 hr.

As discussed, when a liquid pore former is included in the formulation it is possible to not only produce a 973°K glassy carbon containing super micropores exhibiting molecular sieving but to also superimpose a pore system of larger size exhibiting a narrow distribution[1, 2]. For samples 1 and 2 the 973°K carbons had an average pore diameter (D_m) in the large pores of about 10 nm. These D_m values, as measured by mercury porosimetry, were essentially unchanged upon heating the glassy carbons to temperatures up to 1773°K. Also, as seen in Table 2, heat treatment has little effect on the pellet density and pore volume in the pores larger than 6 nm in diameter, as measured by mercury porosimetry. On the other hand, as seen in Table 2, heat treatment above 973°K results in major changes in surface areas measured by CO_2 adsorption at 298°K and N_2 adsorption at 77°K. The CO_2 surface area increases upon heat treatment from 973 to 1173°K and then decreases upon heat treatment to higher temperatures. The N_2 surface area monotonically decreases with increasing HTT above 973°K. The ratio of CO_2 area to N_2 area is indicative of the extent of molecular sieving in pores of about 0.5 nm in thickness in carbons, as previously discussed[3]. Thus, by varying HTT it is possible to alter the extent of molecular sieving in the glassy carbons over a wide range.

At HTT around 1673–1773°K the CO_2 and N_2 areas closely approach each other. This means that the thickness of the slits in the super micropores has been reduced to an extent that CO_2 at 298°K can no longer diffuse through them at a measurable rate. The N_2 surface areas for the 1773°K samples agree closely with the areas predicted for the large pore system from the equation

Table 1. Formulations for production of samples

Sample	FA, cm³	DEG, cm³	Triton X-100, cm³	PTSA, g
1	100	25	75	11.3
2	100	25	85	11.3

Table 2. Effect of heat treatment on properties of carbons

HTT, K	Surface area, m²/g		CO_2 Area / N_2 Area	Pellet density g/cm³	Volume in large pores cm³/g
	CO_2	N_2			
			Sample 1		
973	830	420	1.98	1.185	0.159
1173	994	282	3.52	1.192	0.162
1273	972	126	7.71	—	—
1373	513	92	5.57	1.217	0.161
1573	154	81	1.90	1.211	0.164
1673	72	72	1.00	—	—
1773	52	67	0.78	1.206	0.163
			Sample 2		
973	781	454	1.72	1.125	0.181
1173	846	384	2.20	1.178	0.181
1373	377	97	3.88	1.183	0.179
1573	156	87	1.79	1.171	0.180
1773	72	90	0.80	1.154	0.180

for cylindrical pores, that is area = (4) (volume in large pores)/(D_m). This is expected following the disappearance of the open super micropores.

This study thus shows that great flexibility exists in the preparation of glassy carbons as catalyst supports. If desired, samples can be prepared which have a system of large pores superimposed on an open super micropore system. On the other hand, samples can also be prepared which only have an open system of large pores. The choice of support will depend upon the size of the reactant and product molecules for the reaction to be catalyzed. If the reaction involves large molecules, such as in the hydrodesulfurization of heavy oils or liquefaction of coal, a glassy carbon having pores of only a large size will be chosen. If on the other hand, a selective catalysis reaction is of interest, such as selective hydrogenation of CO to low molecular weight organics, the presence of a super micropore system will be necessary.

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