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Normally, activated carbon is used as a catalyst support for metals. The preparation of activated carbon and some of its typical properties are considered. There are at least two additional approaches which can be used to produce carbon supports exhibiting interesting properties. They are termed glassy carbon and carbon black composite supports. Preparative techniques and properties of these supports are also considered.

#### INTRODUCTION

As the field of heterogeneous catalysis grows, so does the use of carbon as a support for metal catalysts. Of particular interest is the use of carbon supported precious metals (platinum, palladium, rhodium, and ruthenium) as catalysts for the hydrogenation of olefins and aromatic nitro groups and for reductive alkylation reactions. The carbon support has a relatively low cracking activity to promote, for example, hydrogenolysis. Further, the gasification of the carbon substrate by hydrogen proceeds at negligible rates under typical reaction conditions. Despite the high reactivity of carbon to oxygen (leading to gasification), at sufficiently low temperatures carbon can also be used as a support for metal oxides active in catalyzing the oxidation of organic vapors (1). There is also interest in the use of carbon as a support for metal sulfides which are active in catalyzing the hydrodesulfurization of petroleum residua. This is particularly true for residua high in metals, where catalyst regeneration cannot be accomplished only by the burn-off of deposited carbon.

At this time, as far as the author is aware, only activated carbon is being used commercially as a carbon catalyst support. Other types of carbon supports are thought to show promise. Further, there is still much to learn about optimizing the properties of active carbon as a support. In this paper, the production of porous carbons using different approaches and organic precursors will be reviewed. Three broad types of carbon supports will be considered, that is activated carbon, glassy carbon, and carbon black composites.

#### ACTIVATED CARBON

Large amounts of activated carbon are produced each year, primarily being used for the removal of undesirable constituents from water and air. A broad range of organic precursors are used including coal, coconut hulls, acid sludge petroleum coke and wood. A small fraction of the total tonnage produced is used for catalyst supports. It should be strongly emphasized that a very important property of active carbon, if it is to be used as a catalyst support, is that it have high resistance to breakage and attrition. Further, the inorganic constituents of the active carbon, derived from the mineral matter or organo metallics contained in the original precursor, should not be such as to promote undesirable chemical reactions or to interact with the added metal catalyst, resulting in its deactivation or loss of selectivity.

The organic precursors have in common the important feature that they behave as thermosetting materials. That is when they are heated to elevated temperatures they show little or no plasticity. As a consequence, they lead to the production of chars, which possess poor alignment of the trigonally bonded carbon crystallites and, hence, contain high porosities and surface areas (both open and closed). The magnitude of the pore volume and surface area and the distribution of pore size produced is a function of the structure of the organic precursor, the maximum heat treatment temperature (HTT), and the conditions used for activation (or gasification). All activated carbons contain more or less of their porosity and surface area in

macropores, transitional (meso) pores, and micropores. Judicious selection of the organic precursor can lead to the production of activated carbons containing different pore size distributions. All coals have a significant concentration of micropores (2). Low rank American coals (lignites) also have a large concentration of macropores and transitional pores. By contrast, high rank coals (anthracites) have almost all of their porosity concentrated into micropores, that is, pores less than 12A in diameter (2). Pore size distribution is an important consideration when selecting the appropriate activated carbon to use as a catalyst support. If the reaction to be catalyzed involves small molecules, for example the conversion of CO and H<sub>2</sub> to methane, a carbon containing most of its porosity in the micropores would be selected. Conversely, if the reaction involves large molecules, for example hydrodesulfurization of petroleum residua, micropores would be of little utility; a large concentration of macropores (feeder pores) and transitional pores would be desired.

Kawahata and Walker considered the fundamentals of porosity development upon the activation of an anthracite char in 1 atm of CO<sub>2</sub> (3). The principles of their findings can be applied when using other precursors and activating media. Figures 1-3 summarize changes in densities, specific surface area, and specific pore volume as a function of carbon burn-off. As expected, apparent density of the particles decreases as pore volume within the particle is increased by carbon gasification. All chars, before activation, contain some closed pore volume, that is volume in cavities inaccessible to helium through apertures less than about 4A in thickness (4). Upon activation, carbon atoms are removed from the apertures, leading to large increases in helium density, accessible surface area and pore volume. As expected, the specific surface area and specific pore volume increase monotonically as carbon burn-off is taken to high levels, since both the number of accessible pores and their average size are increasing. The extent of area and porosity development decreases with increasing particle size being activated because the gasification rate is, in part, mass transport limited. Hashimoto and Silveston (5,6) have attempted to model the activation process using the results of Kawahata and Walker.

Commercially, however, activation is not taken to very high burn-offs since there is a balance between specific area and specific volume and the fact that carbon is being removed by gasification. Figure 4, for example, shows the change in surface area starting with 1 g of char. A similar plot is found for pore volume. Hence, the optimum burn-off for this system would be about 50%.

Generally, the pore volume distribution for an activated carbon can be depicted conveniently on a log-probability plot (3), as shown in Figure 5. For this sample produced from an anthracite char, about 92% of the total pore volume lies in pores less than 30A in diameter.

There is much interest today to understand how the pore size distribution in activated carbons can be modified by alterations in the over-all activation process. For example, the deliberate addition of metal cations to low rank coals, via ion exchange with hydrogen on carboxyl groups, is reported to affect the structure of the char produced on pyrolysis and the structure of the active carbon then produced. The use of different gasification media such as oxygen at low temperatures followed by steam or CO<sub>2</sub> at higher temperatures produces some interesting effects (7).

Carbon gasification not only leads to the development of surface area and pore volume, but it also leads to an increase in surface heterogeneity. Walker and co-workers have shown recently that an increase in surface heterogeneity can lead to an increase in subsequent metal dispersion on the carbon support (8,9). Ehrburger and Walker (9) used two supports -- one a graphitized furnace black and the other this black burned off to 21.4% in O<sub>2</sub> followed by additional activation in concentrated nitric acid. Oxygen chemisorption has shown that activation sharply increases the active surface area of the carbon (8). One weight percent loadings of platinum supported on the two carbon substrates were accomplished by the impregnation technique, starting with chloroplatinic acid dissolved in a mixture of benzene and absolute ethanol. Reduction of the samples was carried out in flowing H<sub>2</sub> for 10 hr at 500°C. Platinum particle size was measured by high resolution

electron microscopy and by hydrogen chemisorption on the platinum. As shown in Figure 6, the platinum particles on the unactivated carbon substrate have a broad distribution peaking between 20 and 30A, while the particles on the activated substrate have a narrow distribution, with most of the particles less than 20A in diameter. Table 1 summarizes results for the arithmetic mean diameter ( $\bar{d}$ ), surface mean diameter ( $\bar{d}_s$ ), and the mean diameter ( $\bar{d}$ ) calculated from hydrogen chemisorption measurements. Clearly metal dispersion is enhanced by using a carbon substrate exhibiting greater surface heterogeneity.

#### GLASSY CARBON

At the Second Industrial Carbon and Graphite Conference in 1965, Walker reported on the production of molecular sieve carbons from selected thermosetting polymer precursors (10). Walker showed that the nature of the molecular sieving could be altered, depending upon the precursor used, HTT, and the addition of activated carbon to the original mix. The concept of using activated carbon particles involved first coating them with polymer and then converting the polymer coating to a molecular sieve carbon by heat treatment. This carbon coating would act as a gate, any molecules passing through the gate then having accessibility to the large surface area in the activated carbon. However, studies showed that the introduction of the activated carbon modified the molecular sieve character of the carbon produced from various polymers. In effect, it increased the accessibility of molecules into the molecular sieve carbon, presumably by introducing more macropores and transitional pores in the carbon and, hence, decreasing the average diffusion distance in the molecular sized pores. These larger pores are thought, in fact, to be cracks resulting from stresses set up as the polymer (binder) shrinks upon its being charred, at the same time that the filler particles are undergoing normal thermal expansion.

Schmitt and Walker utilized this concept to produce a shape-selective carbon molecular sieve support for platinum (11,12). A recipe of 5 parts partially polymerized polyfurfuryl alcohol (PFA) to one part activated carbon and a water solution of chloroplatinic acid was used. Following further polymerization of the PFA, the sample was charred at 700°C, producing a carbon molecular sieve containing 1 wt% of well dispersed platinum. Schmitt and Walker studied the hydrogenation of straight chain and branched chain olefins using 20x100 mesh particles in a fixed bed. As seen in Figure 7, conversion of 1-butene to n-butane at 150°C was substantial, while negligible hydrogenation of 3-methyl-1-butene occurred. A commercial catalyst, having 1 wt% platinum loading on activated carbon, showed substantial conversion of 3-methyl-1-butene to 2-methyl-butane.

Recently, we have been utilizing the Hucke patent (13) to produce monolithic carbon supports in pellet form (14). In the concept of the Hucke patent, a carbon-yielding binder [furfuryl alcohol (FA)], a liquid pore former [diethylene glycol (DEG) or polyethylene glycol (PEG)], a dispersing agent (Triton X-100 or PEG), and a consolidating agent or polymerization catalyst (p-toluene sulfonic acid) have been used. Following partial polymerization of the FA, the liquid pore former is evaporated off, leaving behind a narrow pore size range of larger pores. Table 2 summarizes results for a number of samples produced following heat treatment to 700°C. Surface areas measured using CO<sub>2</sub> at 298°K and N<sub>2</sub> at 77°K show that the samples contain a large number of molecular sized pores of about 5A thickness (4). Superimposed on this presence of molecular sized pores is a pore system of much larger size. The distribution of size in these larger pores has been measured by mercury penetration under pressure; selected results are shown in Figure 8.

Subsequent heat treatment at temperatures above 700°C allows us to modify the nature of the pore system in these samples, as seen in Table 3. The surface area in the molecular sized pores is progressively eliminated at HTT about 900°C, such that upon heat treating to 1500°C the CO<sub>2</sub> and N<sub>2</sub> areas are in close agreement. These areas are contained in the transitional and/or macropore pore systems. Heat treatment to 1500°C has little effect on pellet density, pore volume in the larger pores, and average pore size in these pores.

At this time, we are investigating the addition of iron to these samples using two techniques, that is addition of iron nitrate or ferrocene into the original mix or impregnation of the 700°C pellets using an iron nitrate solution. We have an interest in evaluating these supported catalysts for their activity and selectivity in converting CO and H<sub>2</sub> to hydrocarbons.

Glassy carbon supports are of additional interest since they are very hard and resistant to abrasion. For example, equivalent weights of pellets of carbon and commercial aluminas were tumbled in a micro-strength grinder (15) for 2 hr. For the two samples of alumina tested, 67.2% and 89.2% of the starting weight passed through a 200 mesh sieve following this exposure. This is to be compared to only 37.8% and 46.6% of the two carbon pellets tested passing through the 200 mesh sieve.

#### CARBON BLACK COMPOSITES

The impetus behind the development of carbon black composites as catalyst supports was two-fold. It was desired to obtain a porous carbon artifact with (i) a large volume of transitional pores (20-200A in diameter) and (ii) a negligible volume of micropores. A large volume of transitional pores is necessary if mass transport limitations are to be minimized in catalytic reactions involving large molecules. For these reactions, micropores are of little utility. Yet during impregnation of a carbon support containing micropores, the metal catalyst will deposit in them and, in effect, be wasted.

Activated carbons do not offer the desired pore size distribution. They always contain a significant micropore volume. The ratio of volume in transitional pores to micropores can be increased by going to larger carbon burn-offs during preparation but only at the sacrifice of a decrease in mechanical strength of the carbon. Monolithic glassy carbon supports containing a significant transitional pore volume and a negligible open micropore volume can be produced, as just discussed. Another approach can now be considered.

The approach, as outlined in a recent patent by Schmitt et al (16), consists of using carbon blacks as the filler in the production of composites. Carbon blacks are available commercially which have arithmetic mean diameters ranging from about 80 to 2000A. Pores in the carbon artifact are formed by the packing together of carbon black particles (spheres) and holding the particles together with a suitable binder. The arithmetic mean diameter of the pore size will be a function of the arithmetic mean diameter of the carbon black selected as the filler. The breadth of the pore size distribution will be determined by the breadth of the particle size distribution of the carbon black selected. Obviously bimodal and trimodal distributions of pore sizes can be obtained, if desired, by the mixing of carbon blacks having different arithmetic mean diameters.

The preparation of a carbon black composite can be considered, as discussed elsewhere (16). In 75 cc of acetone were dissolved 7.5 g of polyfurfuryl alcohol. To this solution were added 30 g of carbon black having an arithmetic mean diameter of 120A. After thorough mixing, the resulting composition was extruded. The extrudates were heated overnight at 110°C to volatilize off the acetone present, prior to heating under flowing N<sub>2</sub> to 600°C in 1 hr and holding at this temperature for an additional hour. Cylindrical pellets of about 1/16 in in diameter were obtained.

Figure 9 presents pore size distributions for the carbon black composite and for a commercial activated carbon, as determined by mercury penetration (16). The total pore volumes in these two samples were comparable, that is 0.92 and 0.86 cc/g, respectively. However, the carbon black composite has its pore volume primarily centered in pores between 40 and 100A radius whereas the pore volume in the activated carbon primarily exists in pores less than 10A in radius.

To these two samples were added 2 wt% Pd using conventional impregnation techniques as described in detail elsewhere (16). The samples, in a particle size of 40x60 mesh, were then evaluated as to their activity to catalyze the reduction of 2,4-dinitrotoluene. In a mixture of 10 cc of water and 60 cc of isopropanol in a 500 cc

Parr bottle, 0.91 g of 2,4-dinitrotoluene was dissolved. Enough catalyst in a 50% water-wet state was added to provide 0.2 g of catalyst on a dry basis. The bottle was attached to the Parr hydrogenator and pressurized with H<sub>2</sub> to 40 psig and then isolated. Shaking of the bottle was carried out and the extent of reaction was followed by noting the decrease in H<sub>2</sub> pressure with time. The reaction bottle was maintained at 35 ± 0.5°C, using a thermostated water jacket. Results are shown in Figure 10. Reaction was complete in approximately 45 min when the Pd-supported on the carbon black composite was used. For Pd supported on the activated carbon, a reaction time of about 115 min was required. It is thought that superior results obtained when using the carbon black composite can be attributed primarily to the existence of a large transitional pore volume in this support and thus the smaller mass transport limitations imposed thereby.

#### ACKNOWLEDGMENTS

Production of the glassy carbon samples and measurement of their physical properties were performed by Drs. O. P. Mahajan and A. Oya. The author appreciates having fruitful discussions with Dr. Mahajan.

#### REFERENCES

1. Nwankwo, J. N. and Turk, A., *Env. Sci. Tech.*, 9, 846 (1975).
2. Gan, H., Nandi, S. P. and Walker, P. L., Jr., *Fuel*, 51, 272 (1972).
3. Kawahata, M. and Walker, P. L., Jr., *Proceedings Fifth Carbon Conference*, Pergamon Press, New York, Vol. 2, 1963, pp. 251-263.
4. Walker, P. L., Jr., Austin, L. G., and Nandi, S. P., *Chemistry and Physics of Carbon* (Editor, P. L. Walker, Jr.) Marcel Dekker, New York, Vol. 2, 1966, pp. 257-371.
5. Hashimoto, K. and Silveston, P. L., *A.I.Ch.E. Journal*, 19, 259 (1973).
6. Hashimoto, K. and Silveston, P. L., *A.I.Ch.E. Journal*, 19, 268 (1973).
7. Tomkow, K., Siemieniewska, T., Jankowska, A., and Czechowski, F., *Fuel*, 56, 266 (1977).
8. Ehrburger, P., Mahajan, O. P., and Walker, P. L., Jr., *J. Catalysis*, 43, 61 (1976).
9. Ehrburger, P. and Walker, P. L., Jr., "Carbon as a Support for Catalysts", *J. Catalysis*, in press.
10. Walker, P. L., Jr., Lamond, T. C., and Metcalfe, J. E., III, *Second Industrial Carbon and Graphite Conference*, S.C.I., London, 1966, pp. 7-14.
11. Schmitt, J. L., Jr. and Walker, P. L., Jr., *Carbon*, 9, 791 (1971).
12. Schmitt, J. L., Jr. and Walker, P. L., Jr., *Carbon*, 10, 87 (1972).
13. Hucke, E. E., U. S. Patent 3,859,421, Jan. 7, 1975.
14. Walker, P. L., Jr., Oya, A., and Mahajan, O. P., *Abstracts, Thirteenth Biennial Conference on Carbon*, American Carbon Society, 1977, pp. 382-383.
15. Clendenin, J. D., Barclay, K. M., and Wright, C. C., *Trans. Amer. Soc. Mech. Engr.*, 67, 405 (1945).
16. Schmitt, J. L., Jr., Walker, P. L., Jr., and Castellion, G. A., U. S. Patent 3,978,000, August 31, 1976.

TABLE 1  
 MEAN DIAMETERS OF SUPPORTED PLATINUM FROM  
 ELECTRON MICROSCOPY AND CHEMISORPTION MEASUREMENTS (9)

<u>Substrate</u>	<u>Diameters, A</u>		
	$\bar{d}_a$	$\bar{d}_s$	$\bar{d}$
Unactivated	36	73	66
Activated	16	25	17

TABLE 3  
 EFFECT OF HEAT TREATMENT ON PROPERTIES OF  
 SELECTED GLASSY CARBON SUPPORTS

<u>HTT, °C</u>	<u>Surface Area, m<sup>2</sup>/g</u>		<u>Pellet Density</u> (g/cm <sup>3</sup> )	<u>Pore Volume</u> (cm <sup>3</sup> /g)
	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub></u>		
	<u>Sample 3</u>			
700	830	420	1.185	0.159
900	994	282	1.192	0.162
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

TABLE 2

## PROPERTIES OF GLASSY CARBON SUPPORTS PREPARED AT 700°C

Sample	Recipes for Production of Samples					Properties of Carbons				
	FA cm <sup>3</sup>	DEG/PEG cm <sup>3</sup>	Triton X-100 cm <sup>3</sup>	PTSA g	Surface area, m <sup>2</sup> /g N <sub>2</sub>	Surface area, m <sup>2</sup> /g CO <sub>2</sub>	Pellet density (g/cm <sup>3</sup> )	D <sub>m</sub> (Å)	Pore Volume (cm <sup>3</sup> /g)	
1	100	57	50	11.3	712	442	1.114	110	0.173	
2	100	57	100	11.3	932	39	1.375	<60	0.022	
3	100	25	75	11.3	830	420	1.185	105	0.159	
4	100	15	85	11.3	781	454	1.125	105	0.181	
5	100	50	0	17	934	539	0.983	13500	0.306	
6	100	100	0	17	856	520	0.840	50000	0.503	
7	100	150	0	17	904	548	0.867	2350	0.460	
8	100	200	0	17	850	248	0.886	580	0.446	
9	100	200	0	25	687	-	0.842	730	0.491	
10	100	85	15	17	922	307	0.949	23350	0.340	
11	100	75	25	17	919	554	0.970	32000	0.285	
12	100	65	35	17	748	34	0.920	<60	0.070	
13	100	50	50	17	872	470	1.091	210	0.221	
14	100	25	75	17	930	400	1.107	150	0.228	
15	100	15	85	17	843	418	1.061	135	0.256	
16	100	75	75	21.4	816	180	1.159	90	0.156	
17	100	0	100	17	888	453	1.023	270	0.295	

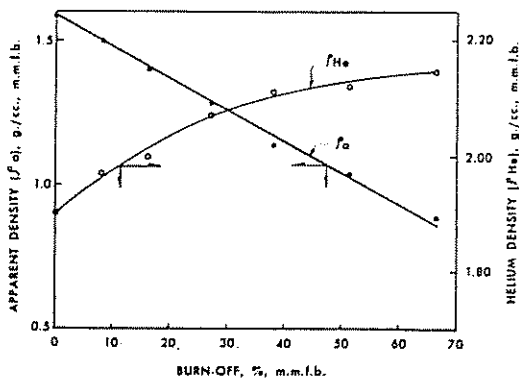


Figure 1 - Variation of apparent and helium densities with burn-off for 42x65 mesh anthracite activated at 850°C (3).

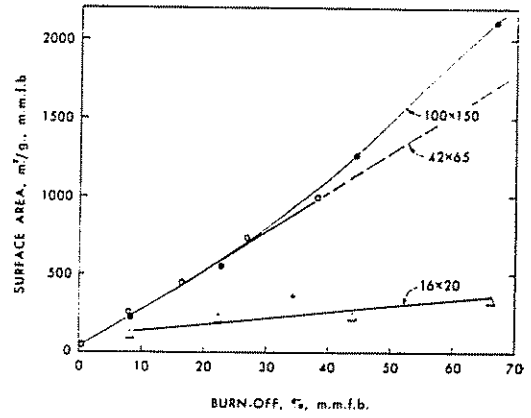


Figure 2 - Variation of specific surface area with burn-off for three particle sizes of anthracite at 900°C (3).

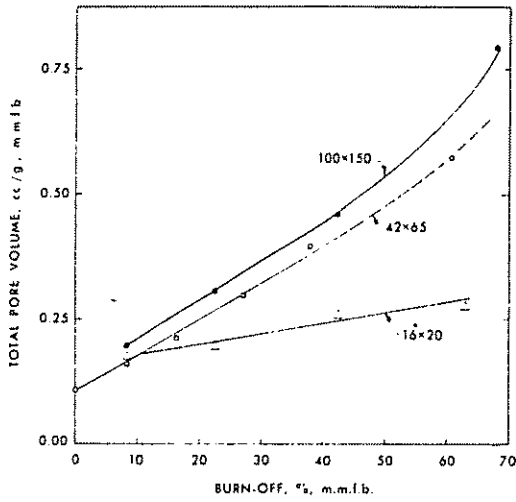


Figure 3 - Variation of specific total pore volume with burn-off for three particle sizes of anthracite activated at 900°C (3).

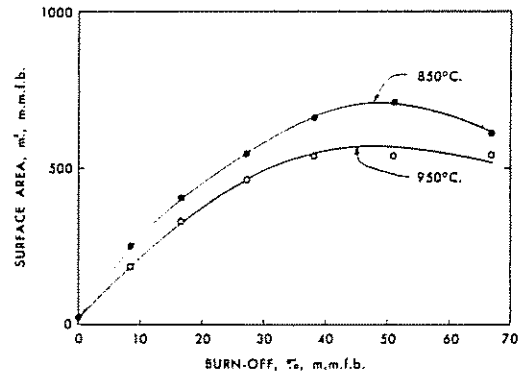


Figure 4 - Variation of surface area with burn-off for 42x65 mesh anthracite activated at 850 and 950°C -- basis 1 g of devolatilized anthracite (3).

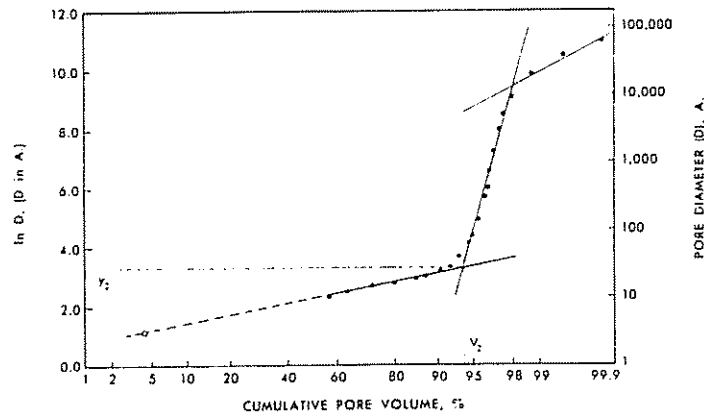


Figure 5 - Pore volume distribution in 42x65 mesh anthracite activated at 850°C to 38% burn-off (3).



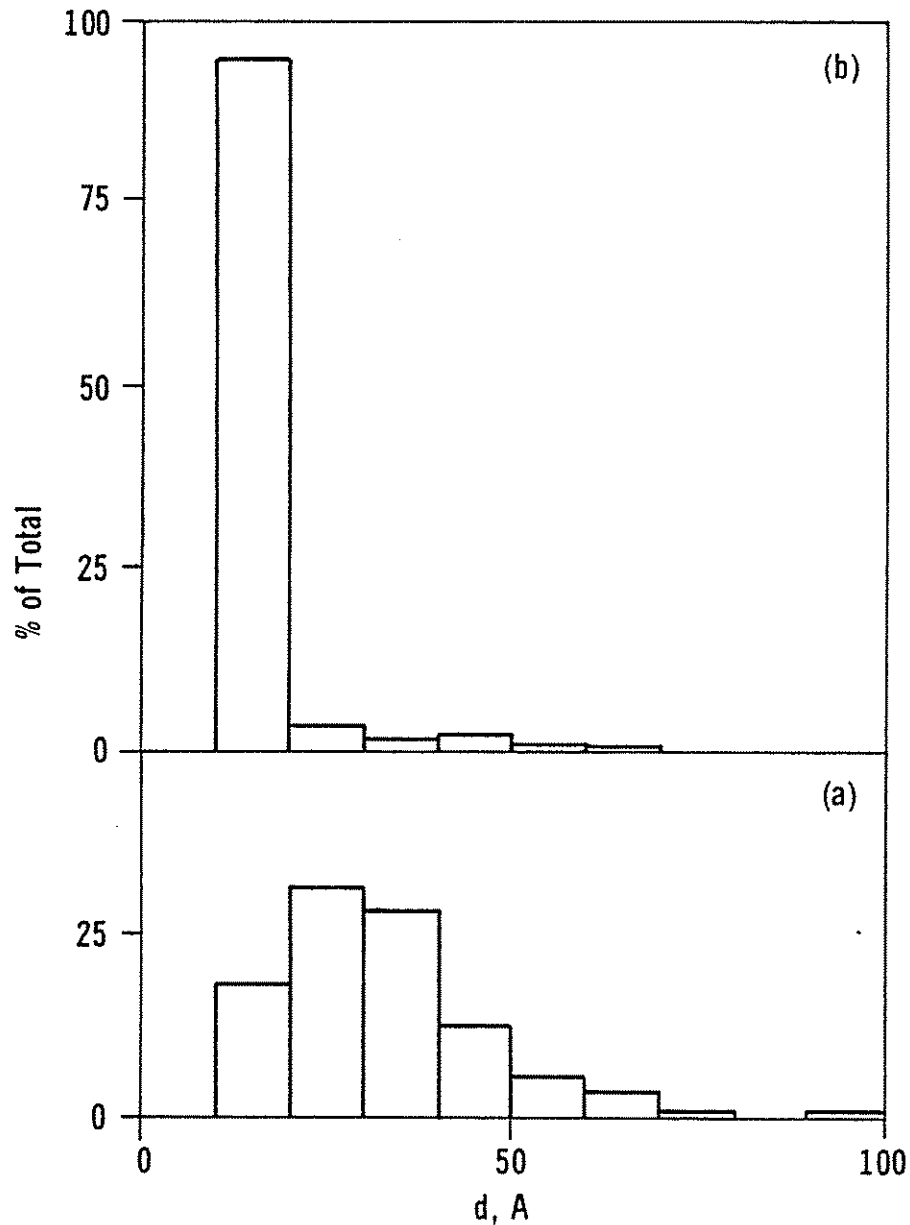


Figure 6 - Histograms of platinum particle size distribution following preparations at 500°C a) on unactivated support and b) on activated support (9).

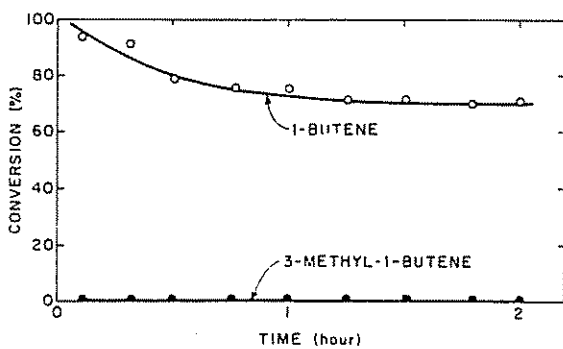


Figure 7 - Competitive hydrogenation of 1-butene and 3-methyl-1-butene over 1% platinum-glassy carbon catalyst at 150°C. Residence time, 1.8 sec (12).

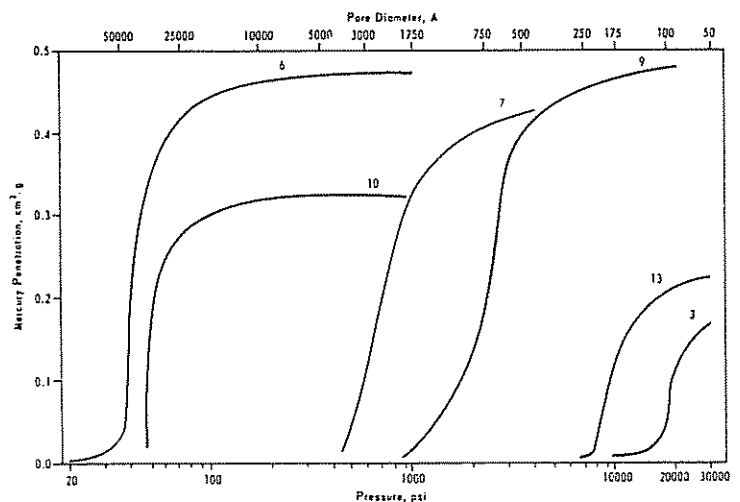


Figure 8 - Pore size distributions in selected glassy carbon catalyst supports.

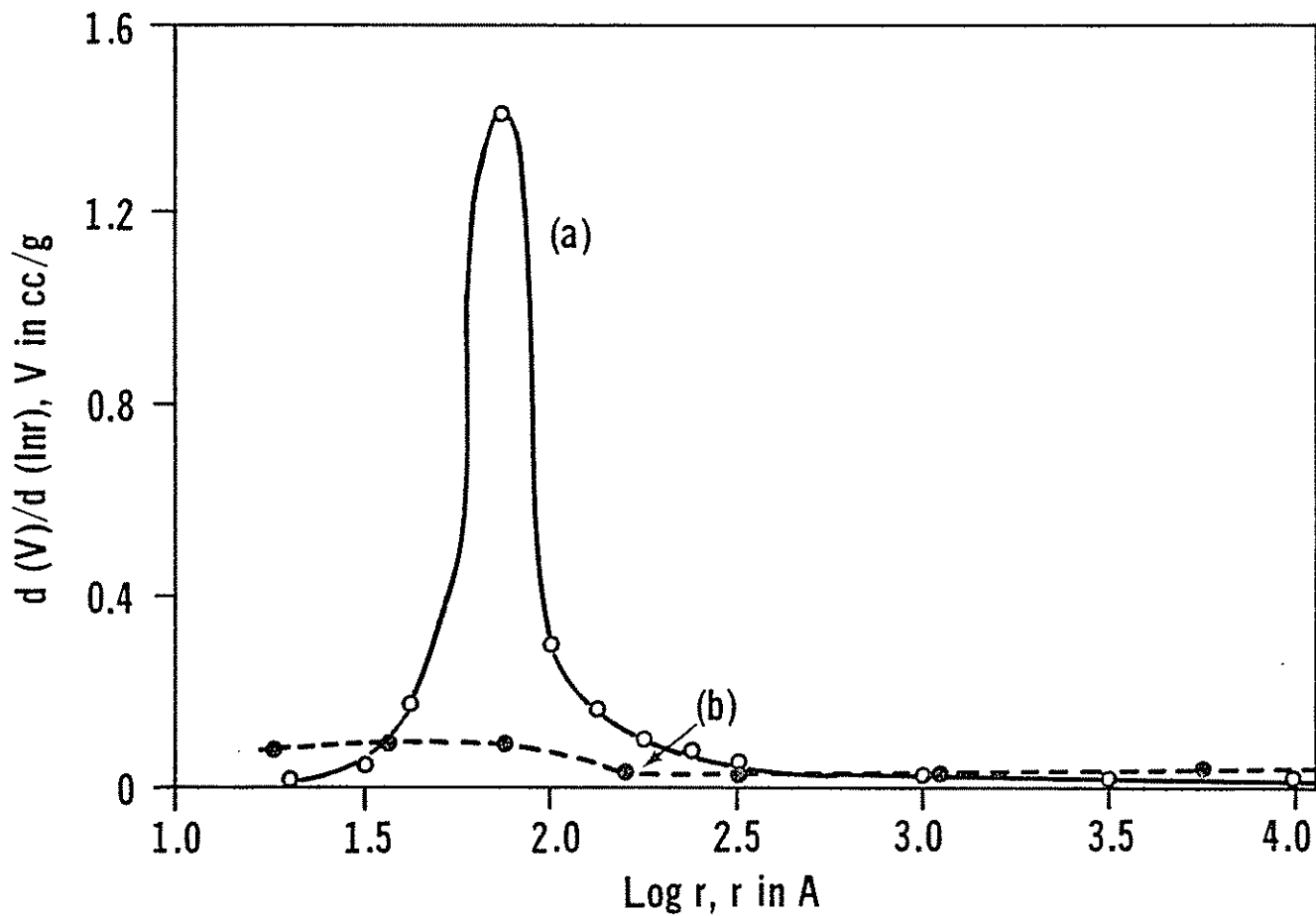


Figure 9 - Pore size distributions in a) carbon black composite and b) activated carbon (16).

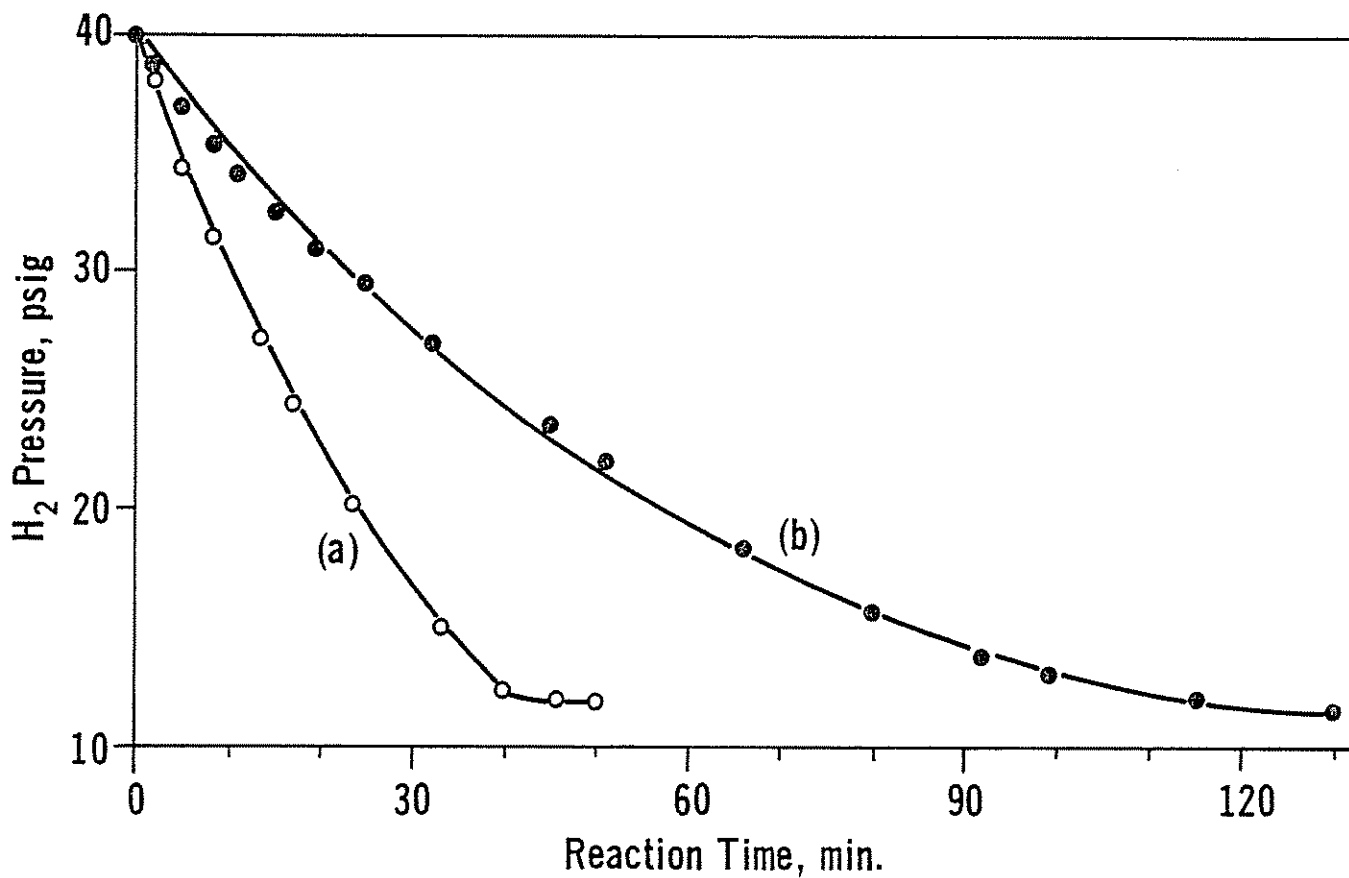


Figure 10 - Decrease in hydrogen pressure during the reduction of 2,4-dinitrotoluene over 2% palladium-carbon at 35°C (16).