

CHEMISORPTION OF HYDROCARBONS ON GRAPHITIZED CARBON BLACKS AT 300°C*

W. P. Hoffman, F. J. Vastola and P. L. Walker, Jr.

Department of Material Sciences
The Pennsylvania State University
University Park, PA 16802

Introduction

The physical adsorption of hydrocarbons on graphitized carbon blacks has been studied under various conditions (1-3). However, there is virtually no literature on the chemisorption of hydrocarbons on these materials or on any carbon other than evaporated carbon films (4). This might be due, in part, to the rather small active surface area (<0.6% of the total area) that chemisorbed hydrocarbons will occupy on a graphitized carbon black. This surface area that is active for hydrocarbon chemisorption is analogous to the oxygen active surface area (ASA), as measured by Laine et al. (5), on the same material.

The purpose of this study is not to undertake the difficult task of determining how hydrocarbons bond to the surface but rather to determine the "reactivity" of various hydrocarbons to the surface and what factors have the greatest effect on their adsorption. The gases used were C₁ to C₄ alkanes and alkenes.

Experimental

The graphitized carbon black used in this study was Graphon, supplied by the Cabot Corp. Samples were burned off to 5-15% weight loss in air at 450°C. The samples were subsequently treated in 1 atm of Cl₂ at 900°C to remove metallic surface impurities. After pumping to 10⁻⁸ Torr with the temperature again at 900°C, the samples were treated with H₂ at a starting pressure of .05 Torr to remove chemisorbed chlorine. Finally, the samples were pumped to 10⁻⁸ Torr and the temperature was raised to 950°C to remove chemisorbed H₂.

The BET area of the prepared samples ranged between 80-90 m²/g, while the oxygen active surface area, as determined by Laine (5), ranged between 0.8-1.8 m²/g.

Adsorption was carried out at 300°C in a volumetric apparatus with a total volume of 17.9ℓ. Adsorption was followed using a Baratron electronic differential manometer with a sensitivity of 1x10⁻⁵ Torr.

The rate of chemisorption of all the gases except methane decreased to a negligible value in 1 hr. In order to determine the amount chemisorbed, gas was introduced at 12 mTorr and the quantity of gas adsorbed in 1 hr recorded. The sample was then pumped to 10⁻⁸ Torr with the temperature held constant, and gas was reintroduced at 12 mTorr for 1 hr. Using this approach, the amount adsorbed during the second cycle was taken as equal to the gas physically adsorbed, while the difference in the amount adsorbed in the two cycles was taken as the amount chemisorbed.

*Supported, in part, by a Gulf Oil Company Fellowship.

After completion of the two adsorption cycles, the samples were pumped to 10⁻⁸ Torr at adsorption temperature. The temperature was then raised stepwise to 900°C in a closed system and products of desorption measured. The samples were cleaned by heating at 950°C until the pressure dropped to 10⁻⁸ Torr, prior to commencing a new adsorption run.

A CEC Model 21-614 residual gas analyzer was used to check the purity of each gas (>99.9%) and to monitor the gas phase during adsorption and desorption. A Vac-ion pump was used in conjunction with an oil diffusion pump and a rotary floor pump to obtain a pressure of 10⁻⁸ Torr.

Results and Discussion

Chemisorbed species cannot be removed at adsorption temperature but desorb only at elevated temperatures. Isotherms for these adsorptions are of the Langmuir type, with saturation being reached at a pressure <5 mT. The amount of each gas chemisorbed increased with burn-off of the Graphon.

All gases studied are listed in order of decreasing surface coverage in the first column of Table 1. The surface area covered by each adsorbate (m²/g) is placed in square brackets, the numbers running diagonally down the table from left to right, that is from butadiene to methane. The numbers represent average areas covered during the series of runs. These areas were calculated from the product of the number of molecules adsorbed and the surface area that each molecule occupies. Estimated molecular surface areas (A²) are given in parenthesis in column 1 of Table 1. The calculation of these molecular areas for the hydrocarbons consisted of constructing each molecule, considering both ionic and van der Waals radii, and measuring the surface area covered by their projection. Since extensive work has been done on the dissociative chemisorption of oxygen and hydrogen on Graphon (5,6), these molecules were included for comparison and the molecular areas calculated by the previous workers were used for these gases.

For all but the most active gases, the surface had to be very clean for chemisorption to take place. Times for the rate of chemisorption to decrease to a negligible value ranged from <15 min for n-butane and butadiene to several hours for methane. During adsorption of each gas, the gas phase was monitored. In each case, only the adsorbate could be detected. No hydrogen was seen in the gas phase so if C-H bonds were broken during chemisorption, the hydrogen also chemisorbed.

In order to determine what factors affect chemisorption, a series of blockage runs was made for each pair of gases. These runs involve adsorbing a gas and pumping off the physically adsorbed portion. (This is the gas shown as pre-adsorbed in Table 1.) Then a second, different gas

was adsorbed (shown as blocked gas in Table 1) without desorbing the chemisorbed portion of the first gas. Another adsorption was then performed to determine what portion of the blocked gas was physically adsorbed so that the amount of blocked gas chemisorbed could be determined. As is seen in Table 1, the preadsorbed gas blocked chemisorption of the second gas to a varying degree. The percentages given are those of sites blocked; for example ethylene, which occupies 0.46 m²/g, blocks 90% of the 0.57 m²/g area that propylene would normally occupy on a clean surface. Where two different percentages are given for a single pair of gases, the top one was determined early in the series; and the bottom values were determined near the end of the series.

The type and distribution of the sites has the greatest effect on the chemisorption of hydrocarbons on Graphon. On each hydrocarbon adsorption-desorption cycle, the surface is slightly changed. However, the greatest change comes with the first hydrocarbon cycle on each new sample of Graphon, resulting in approximately a 40% decrease in the amount of any gas that can subsequently be chemisorbed. All the data presented here were taken after the first hydrocarbon cycle. The structure and orientation of the adsorbate have less of an effect on adsorption than do surface changes. Adsorption is greater for double bonds and larger molecules. However, with increasing molecular length (>3 carbon atoms), the factor of size may come into play to decrease adsorption. Blockage by the preadsorbed gas depends on these factors, in addition to the percentage of common sites they occupy.

The fact that the surface changes slightly with each hydrocarbon cycle is attributed to carbon

deposition. That is, during desorption at elevated temperatures, most of the adsorbate carbon stays on the surface, as a result of cracking of the adsorbate and most of the hydrogen is desorbed as hydrogen gas.

The carbon left on the surface is probably on the sites active for hydrocarbon chemisorption. These new sites are still active. The cumulative effect is to gradually decrease the active area available to some of the molecules depending on their size and activity. After the initial hydrocarbon cycle, surface coverage and blockage is small for each subsequent cycle. For example, the chemisorption of n-butane decreased only 15% following more than 100 cycles. Thus the same sample can be used for numerous blockage runs with good reproducibility.

References

1. Hoory, S. E. and Prausnitz, J. M., Trans. Faraday Soc., 63, 455 (1966).
2. Friederich, R. O. and Mullins, J. C., Ind. Eng. Chem. Fund., 11, 439 (1972).
3. Stacy, T. D., Hough, E. W., and McCain, W. D., J. of Chem. and Eng. Data, 13, 74 (1968).
4. McLintock, I. S. and Orr, J. C., Third Conf. Ind. Carbon and Graphite, 201 (1970).
5. Laine, N. R., Vastola, F. J., and Walker, P. L., Jr., J. Phys. Chem., 67, 2030 (1963).
6. Bansal, R. C., Vastola, F. J. and Walker, P. L., Jr., Carbon, 9, 185 (1971).

TABLE 1
BLOCKING EXPERIMENTS AT 300°C ON 14% BURN-OFF GRAPHON

Blocked Gas, %	Gas Preadsorbed										
	C=C-C=C	C=C-C	O ₂	C=C	C-C-C-C	^C C-C-C	C-C-C	C-C	^C C-C	H ₂	CH ₄
C=C-C=C (29.6)	[0.59]	$\frac{81}{83}$	$\frac{71}{64}$	$\frac{79}{72}$	$\frac{74}{81}$	$\frac{64}{76}$	$\frac{67}{68}$	$\frac{67}{65}$	$\frac{57}{57}$	$\frac{22}{22}$	$\frac{14}{14}$
C=C-C (23.4)	~100	[0.57]	96	90	98	97	96	92	84	22	18
O ₂ (16.6)	$\frac{89}{89}$	$\frac{83}{83}$	[0.52]	$\frac{77}{85}$	$\frac{87}{87}$	$\frac{87}{87}$	$\frac{86}{86}$	$\frac{77}{77}$	$\frac{65}{65}$	$\frac{30}{30}$	$\frac{11}{11}$
C=C (20.5)	~100	$\frac{99}{99}$	$\frac{97}{97}$	[0.46]	$\frac{99}{99}$	$\frac{98}{98}$	$\frac{98}{98}$	$\frac{93}{93}$	$\frac{88}{88}$	$\frac{22}{26}$	$\frac{18}{18}$
C-C-C-C (27.7)	~100	~100	99	91	[0.33]	~100	~100	~100	67	$\frac{26}{26}$	18
^C C-C-C (25.1)	~100	~100	~100	97	~100	[0.30]	~100	~100	75	$\frac{26}{26}$	4
C-C-C (22.6)	~100	~100	~100	98	~100	~100	[0.27]	~100	87	$\frac{26}{26}$	5
C-C (19.7)	~100	~100	~100	~100	~100	~100	~100	[0.16]	91	$\frac{26}{26}$	5
^C C-C (20.2)	~100	~100	~100	~100	~100	~100	~100	~100	[0.16]	$\frac{26}{26}$	9
H ₂ (16.6)	~100	~100	~100	~100	~100	~100	~100	~100	~100	[0.09]	30
CH ₄ (16.2)	~100	~100	~100	~100	~100	~100	~100	~100	~100	~100	[0.01]