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CHEMISORPTION OF ALKANES AND ALKENES ON CARBON ACTIVE SITES

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Abstract—Chemisorption of C_1–C_4 hydrocarbons on a graphitized carbon black has been studied volumetrically at 573 K. Isotherms were of the Langmuir type with saturation reached at < 0.7 Pa hydrocarbon pressure. The molecules studied lie flat on the surface and occupy the same sites to varying degrees. The magnitude of chemisorption was affected by surface cleanliness and morphology, molecular size, active site distribution, and molecular accommodation. All the chemisorbed hydrocarbons were tightly bound and did not desorb at adsorption temperature even during evacuation. Upon heating the chemisorbed hydrocarbons thermally cracked before desorbing.

1. INTRODUCTION

The field of adsorption on carbon surfaces has merited much study in the past because of the role that adsorption has in many processes. Physical adsorption on carbon is the basis for its use in the separation of impurities from air and water and as an adsorbent in chromatographic columns for the separation of structural and stereo isomers[1]. Physical adsorption also plays a part in the use of carbon black as a filler for elastomeric reinforcement and in modifying the surface properties of carbon. Because of their well characterized low energy homogeneous surface, graphitized carbon blacks have been used as adsorbents for physical adsorption for many years[2–5]. Their surface and lack of porosity make them ideal adsorbents for studies aimed at verifying theoretical concepts.

Chemisorption on carbon is also of interest because this is the first step in a heterogeneous reaction. Chemisorption occurs when a chemical bond is formed between the adsorbate and an active site in the surface of the adsorbent. On carbon these sites are located at the edges of exposed layer (basal) planes, as well as at points of imperfections in the structure including vacancies, dislocations and steps on the outer basal plane. If the discussion is limited to hydrocarbons, the chemisorption of these species on carbon is of importance in the formation of bulk carbon from the gas phase. Monolithic pyrolitic carbon and carbon formed on the surface of cracking catalysts are examples of this type of carbon. Chemisorption of hydrocarbons on carbon also has an important role in commercial carbon black production, other combustion processes, and regeneration of spent activated carbon following hydrocarbon adsorption from water or air.

There have been numerous studies on the physical adsorption of hydrocarbons on carbon surfaces. Many different hydrocarbons, in particular alkanes and alkenes, have been physically adsorbed on carbon surfaces[6–9] over wide temperature and pressure ranges. Carbon blacks have been used in many of these studies[1, 10–12]. However, to the authors knowledge, only one article has appeared on the chemisorption of hydrocarbons on carbon. McLintock and Orr[13] chemisorbed methane and ethylene, among other gases, on evaporated carbon films and noted the change in electrical resistance of the film as a result of chemisorption. Although their work was well done, it is probably not quantitative in some respects due to sample preparation[14].

The study reported here was undertaken in order to gain a better understanding of the pyrolysis of propylene over graphitized carbon black. During the pyrolysis, not only propylene but also the pyrolysis products appeared to chemisorb on the surface[15]. It was difficult to study this chemisorption under pyrolysis conditions because other phenomena were taking place simultaneously. To overcome this difficulty, the chemisorption of propylene was studied at 573 K with a starting pressure of 1.6 Pa. In addition, a few chemisorption studies were conducted in the temperature range 373–873 K and at pressures up to 6.6 Pa. Since there is a dearth of literature on the chemisorption of hydrocarbons on a carbon surface, C_1–C_4 alkanes and alkenes were also chemisorbed under the same conditions as propylene in an attempt to further understand the chemisorption of propylene.

The purpose of this study is not to undertake the difficult task of determining how hydrocarbons chemically 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.

2. EXPERIMENTAL

2.1 *Materials*

The carbon used in this study was Graphon, a granular graphitized carbon black, obtained from the Cabot Corporation. Total impurity content was estimated by emission spectroscopy to be 80 ppm, with

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major impurities being iron and calcium. Graphon samples were pre-oxidized to 5–15% weight loss in air at 723 K. The BET (N_2) surface area of the prepared samples ranged between 80 and 90 m^2/g, while the oxygen active surface area (ASA), as determined by Laine[16], ranged between 0.8 and 1.8 m^2/g.

After pre-oxidation, the samples were treated in 0.1 MPa Cl_2 at 1173 K to remove surface metallic impurities exposed during the oxidation. After cooling, the sample was placed in the volumetric adsorption system and heated to 1223 K *in vacuo* to desorb any chemisorbed chlorine. When a residual pressure of 10^{-6} Pa was reached, the temperature was lowered to 1073 K; and 6.6 Pa H_2 was introduced to remove any chlorine that remained. The sample was kept in this H_2 atmosphere for 1 hr. After this time, the H_2 was pumped off and the temperature was again raised to 1223 K to desorb any chemisorbed hydrogen. When the residual pressure reached 10^{-6} Pa (usually overnight), the sample preparation was complete.

Gases used in this study were obtained from Air Products and Chemicals Inc. The O_2 and H_2 were of research grade with a minimum purity of 99.996%. All the hydrocarbons used had a minimum purity of 99.8%.

2.2 *Apparatus and procedure*

Adsorption was carried out at 573 K in a volumetric apparatus with a total volume of 17.9 l. The Pyrex high vacuum system was interfaced to a mass spectrometer and to a fused quartz reactor which held the sample. The reactor was of double wall design, with the annular volume evacuated to prevent diffusion into the reactor tube from the atmosphere at high temperature. A Lindberg resistance furnace, in conjunction with a West controller and chromel-alumel thermocouple, controlled the temperature of the sample. A CEC model 21-614 residual gas analyzer was used to check the purity of each gas and to monitor the gas phase during adsorption and desorption. Vacuum to 10^{-4} Pa was obtained using a liquid nitrogen-trapped silicon oil diffusion pump in conjunction with a rotary floor pump. Higher vacuum (to 10^{-6} Pa) was obtained using a Varian Vacion pump. Adsorption and desorption was followed using an MKS Baratron differential capacitance manometer with a sensitivity of 10^{-3} Pa. Pressures less than 10^{-3} Pa were estimated from the discharge current of the Vacion pump.

Before a Graphon sample was used for chemisorption, the O_2 Active Surface Area (ASA) was determined by the method of oxygen chemisorption first used by Laine *et al.*[16]. Using this technique, a pretreated Graphon sample that had been cleaned in vacuo (10^{-6} Pa) at 1223 K was exposed at 573 K for 24 hr to O_2 at a starting pressure of 66 Pa. At the end of this time, the sample was evacuated to a pressure of 10^{-6} Pa with the temperature held at 573 K. The pumping was then terminated and the sample was raised to 1223 K and held at that temperature for 15 min. The amount of CO and CO_2 that desorbed was measured with the mass spectrometer. The sample was then evacuated at 1223 K until the residual pressure was 10^{-6} Pa. Knowing the number of moles of each gas desorbed and taking the area of an edge carbon site that chemisorbed an oxygen atom as 0.083 nm^2, the surface area occupied by chemisorbed oxygen could be determined[16].

For chemisorption experiments, the system was first evacuated. The gas to be chemisorbed was then introduced at a starting pressure of 1.6–6.6 Pa to all the system but the mass spectrometer and the reactor. The system pressure was measured with the Baratron. With the reactor temperature held constant (373–873 K), the gas was then allowed to expand into the reactor containing a Graphon sample previously cleaned *in vacuo* (10^{-6} Pa) at 1223 K. When the rate of chemisorption decreased to a negligible value (in 60 min for all gases but methane), the pressure was recorded and the reactor was evacuated to 10^{-6} Pa at adsorption temperature. Gas was then reintroduced at the same starting pressure and for the same period of time as the first adsorption. Using this approach, the amount adsorbed during the second adsorption 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. The vast majority of chemisorption work was done at 573 K and 1.6 Pa starting pressure. However, data for isotherms at 373, 573 and 873 K were collected over the pressure range 1.6–6.6 Pa.

After completion of the two adsorption cycles, samples were either removed, heated quickly (10 K/min) to 1223 K under vacuum to clean them for subsequent adsorption or heated slowly to study the desorption products. The desorption products were studied using two slightly different methods. In both techniques, the samples were evacuated at adsorption temperatures until the residual pressure was 10^{-6} Pa. The system was isolated from the vacuum pumps. Then the temperature of the samples was raised in 100 K increments with the temperature isothermal at each step for 1 hr. The gas phase was then sampled with the mass spectrometer. Two different methods of sampling were used. Using the first technique, the gas phase was pumped out after each 1 hr isothermal soak time before the temperature was again raised. A second technique allowed all the desorbed products to remain in the gas phase throughout the desorption and subsequently crack to carbon, which deposited on the substrate surface, and H_2.

3. RESULTS AND DISCUSSION

3.1 *Adsorption*

Except for the most active gases, the surface had to be very clean for chemisorption to occur. To clean the surface of previously adsorbed species, the sample was heated to 1223 K and pumped on until the residual pressure reached 10^{-6} Pa. When the surface was clean, it showed a strong attraction for molecules

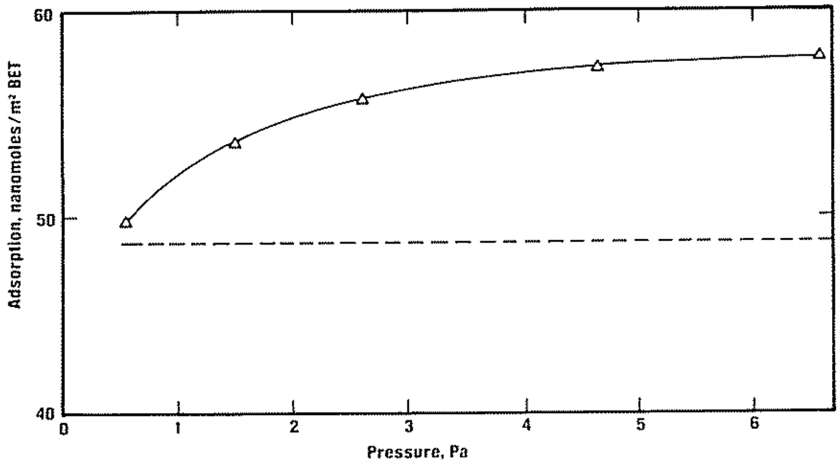

Fig. 1. Propylene adsorption at 573 K on a 14% burn-off graphon sample. —, total adsorption; - - -, chemisorption.

with a π bond. Surface coverage by a chemisorbed alkene was two to three times that of the corresponding alkane. The time which elapsed at 573 K for the rate of chemisorption to decrease to a negligible value ranged from less than 15 min for butadiene and propylene to 2 hr for methane.

It was observed that the isotherm for hydrocarbon chemisorption on Graphon was of the Langmuir type, with saturation coverage reached at less than 0.7 Pa at 573 K. Figure 1 shows an isotherm for the chemisorption of propylene at 573 K. This isotherm is typical of that found for all the hydrocarbons studied. The upper solid curve represents the total (chemical and physical) adsorption of propylene, while the lower dashed line represents the amount of propylene chemisorbed. The amount of propylene chemisorbed was defined as the amount that was adsorbed and could not be removed by evacuation for 1 hr at 10^{-6} Pa at adsorption temperature. The physically adsorbed propylene was defined as the difference between the total amount adsorbed and that chemisorbed.

During the adsorption of each hydrocarbon, the gas phase was monitored. In each case only the adsorbate was detected. No H_2 was seen in the gas phase; so if C–H bonds were broken during chemisorption, the hydrogen was also chemisorbed.

Table 1 lists in order of decreasing surface coverage all the gases studied. The estimated molecular area covered by the chemisorbed hydrocarbon molecule was calculated in this study. The calculation consisted of constructing each molecule to scale, considering both covalent and Van der Waals radii and measuring the surface covered by their projection. Since extensive work has been done on the dissociative chemisorption of O_2 and H_2 on Graphon (17–24), these molecules were included for comparison. The molecular areas calculated by previous workers were

Table 1. Specific surface areas occupied by chemisorbed species on a 14% burn-off graphon sample at 573 K

Gas	Molecular Area for Chemisorbed Species, nm^2	Total Surface Coverage, m^2/g	Molecular Area for Physically Adsorbed Species, nm^2
butadiene	0.296	0.59	--
propylene	0.234	0.57	0.292
oxygen	0.166	0.52	--
ethylene	0.205	0.46	0.234
n-butane	0.276	0.33	0.383
isobutane	0.252	0.30	0.372
propane	0.226	0.27	0.301
ethane	0.197	0.16	0.249
cyclopropane	0.202	0.16	--
hydrogen	0.166	0.09	--
methane	0.162	0.01	0.164

Table 2. Surface areas occupied by the chemisorption of different gases at 573 K on graphon samples of varying burn-off

Sample	% Burn-Off 723 K	% Burn-Off 1223 K	% Burn-Off Total	Oxygen ASA(m^2/g)	% Increase	Propylene ASA(m^2/g)	% Increase	Ethylene ASA(m^2/g)	% Increase	n-Butane ASA(m^2/g)	% Increase
1	0	0	0	0.264	--	0.056	--	0.033	--	0.012	--
2	0	0.61	0.61	0.94	356	0.44	786	0.32	969	0.18	1500
3	4.9	0.85	5.75	2.25	852	1.06	1893	0.72	2181	0.46	3833
4	24.1	0.40	24.5	5.00	1893	1.89	3375	1.19	3606	0.87	7250

used for these gases. The specific areas covered by each molecule physically adsorbed were determined by Hoory *et al.*[8]. These values are included only for comparison, since at 1.6 Pa starting pressure the amount physically adsorbed is less than 10% of the amount chemisorbed. The surface area (m^2/g) covered by each chemisorbed gas at 573 K was calculated from the product of the number of molecules adsorbed at saturation and the surface area that each molecule occupied. For the hydrocarbons, the amount chemisorbed tends to increase with an increase in molecular weight and degree of unsaturation of the molecule.

It was observed (Tables 2 and 3) that the surface area covered by each chemisorbed gas increased with both temperature and sample burn-off. Table 2 shows that the surface coverage at 573 K increased with burn-off, as expected, since the active surface area (ASA) had increased. It should be noted that there is an inconsistency among Tables 1–3. For example, the amounts of propylene chemisorbed on samples of similar burn-off are not the same from table to table.

Laine *et al.*[16] showed that there is a close relationship between the Graphon sample burn-off and the active surface area generated during burn-off at 923 K. This is true only for a very pure Graphon sample with a low concentration of surface impurities. If the Graphon sample has an appreciable amount of impurities, such as the sample used in this study (~80 ppm), there will not be a good correlation between sample burn-off and active surface area unless the ASA is measured after carbon deposition on the impurities[14]. If surface impurities exposed upon oxidation are not removed, they will chemisorb species and increase the apparent ASA. If the surface impurities are removed by Cl_2 at 1223 K, the sample will undergo additional oxidation due to trace amounts of O_2 in the Cl_2. This oxidation at 1223 K generates much more ASA per unit weight loss than oxidation at 723 K. For instance, a weight loss of 0.6% at 1223 K as a result of exposure to Cl_2 containing trace amounts of O_2 will generate nearly as much ASA as a 5% weight loss at 723 K in O_2. Thus, two samples of similar initial burn-off can have vastly different active surface areas after chlorination.

Values in the tables are internally consistent; but since the tables were generated at different times using different tanks of Cl_2, there is no consistency among the tables. However, Tables 1 and 4 are consistent with each other, since they show data for the same sample. Values in Tables 1–4 were measured after the first hydrocarbon adsorption–desorption cycle.

Table 3. Chemisorption of selected gases on graphon samples of different ASA at 573 and 873 K

Gas	Burn-Off, %	Area Covered, m^2/g 573 K	Area Covered, m^2/g 873 K	Area Covered, % of Total 573 K	Area Covered, % of Total 873 K
Propylene	5.2	0.41	0.33*	0.49	0.40
	11.0	0.68	0.60*	0.74	0.64
Ethylene	5.2	0.24	0.37	0.28	0.44
	11.0	0.44	0.78	0.56	0.84
Propane	5.2	0.12	--	0.14	--
	11.0	0.38	0.42	0.41	0.46
Methane	5.2	-0.02	0.14	-0.02	0.17
	11.0	-0.02	0.43	-0.02	0.47

*In error due to cracking.

Table 4. Blocking experiments at 573 K on 14% burn-off graphon

	GAS PREADSORBED										
	butadiene	propylene	O_2	ethylene	n-butane	iso-butane	propane	ethane	cyclopropane	H_2	methane
butadiene	(0.59)	$\underline{81}$ $\overline{83}$	$\underline{71}$ $\overline{64}$	$\underline{79}$ $\overline{72}$	$\underline{74}$ $\overline{81}$	$\underline{64}$ $\overline{76}$	$\underline{67}$ $\overline{68}$	$\underline{67}$ $\overline{65}$	$\underline{57}$	$\underline{22}$	$\overline{14}$
propylene	100	(0.57)	96	90	98	97	96	92	84	22	18
O_2	$\underline{89}$ $\overline{89}$	$\underline{83}$ $\overline{83}$	(0.52)	$\underline{77}$ $\overline{85}$	$\overline{87}$	$\overline{87}$	$\overline{86}$	$\overline{77}$	$\overline{65}$	$\overline{30}$	$\underline{11}$ $\overline{11}$
ethylene	100	$\overline{99}$	$\overline{97}$	(0.46)	$\overline{99}$	$\overline{98}$	$\overline{98}$	$\overline{93}$	$\overline{88}$	$\underline{22}$ $\overline{26}$	$\overline{18}$
n-butane	100	100	99	91	(0.33)	100	100	100	67	26	18
iso-butane	100	100	100	97	100	(0.30)	100	100	75	$\overline{26}$	4
propane	100	100	100	98	100	100	(0.27)	100	87	$\overline{26}$	5
ethane	100	100	100	100	100	100	100	(0.16)	91	$\overline{26}$	5
cyclopropane	100	100	100	100	100	100	100	100	(0.16)	$\overline{26}$	9
H_2	100	100	100	100	100	100	100	100	100	(0.09)	30
methane	100	100	100	100	100	100	100	100	100	100	(0.09)

It was observed (Table 3) that the amount of propylene chemisorbed appeared to decrease as the temperature was increased from 573 to 873 K. However, the less active gases increased their coverage with increasing temperature. This change in surface coverage with temperature was due to competition between adsorption and desorption or cracking. Both adsorption and desorption are activated processes; thus their rates increase with temperature. At 573 K, desorption and cracking rates were negligible for all the gases studied. Thus, propylene chemisorbed to a greater extent on the ASA and covered a larger area than methane that chemisorbed on only the most active sites. The same relationship between the propylene and methane coverage also existed at 873 K, but this is not apparent from Table 3. For methane, the increase in the rate of desorption and cracking between 573 and 873 K was negligible, compared to the increase in the rate of chemisorption. Thus, there was a measurable increase in methane surface coverage at 873 K. For propylene, the increase in the rate of cracking between 573 and 873 K was not negligible compared to the increase in the rate of chemisorption. Since a manometer was used to measure the amount chemisorbed (by following the decrease in total pressure), it was not possible to separate the pressure decrease due to chemisorption from the pressure increase due to cracking. Thus, if a small amount of propylene cracked, especially to H_2, the pressure drop as measured and attributed to chemisorption would be greatly reduced. A small amount of cracking would have the effect of making the propylene ASA appear smaller than it actually was.

By comparing the amount of propylene and ethylene chemisorbed at 873 K (Table 3), one can see that cracking did indeed affect the measured ASA. At all temperatures, a more active molecule, such as propylene, should chemisorb to a greater extent than a less active molecule such as ethylene. Since this is not the case, the value for surface coverage by propylene at 873 K must be considered to be low.

3.2 *Desorption*

The chemisorbed hydrocarbon molecule would not desorb at adsorption temperature, even with pumping. To study desorption the temperature was raised in steps and the gas phase was monitored. In general, the hydrocarbon molecule that originally chemisorbed constituted less than 1% of the desorbed products, because it cracked on the surface before desorption.

Figure 2 shows the desorption products from propylene chemisorbed at two different temperatures. For propylene and other hydrocarbons chemisorbed isothermally in the temperature range 373–873 K, the main desorption product was H_2. When propylene was chemisorbed at 873 K, the only desorption product besides H_2 was methane. As the chemisorption temperature was lowered, other additional hydrocarbons appeared in the desorption products of chemisorbed propylene. For instance, when propylene was chemisorbed at 573 K some propylene

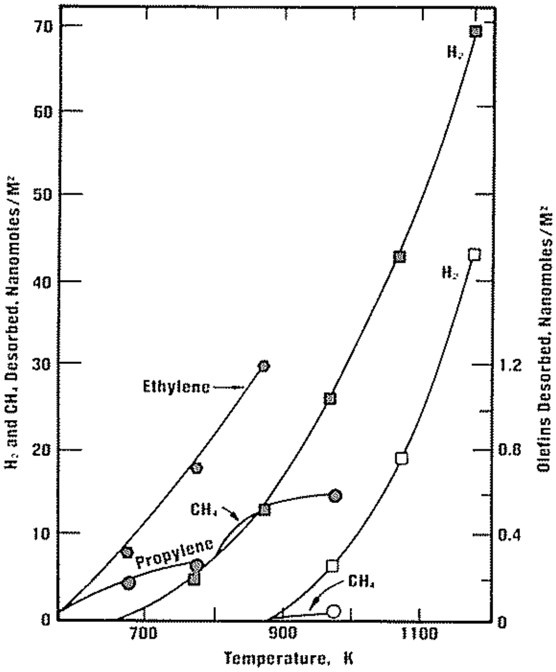

Fig. 2. Gas phase products resulting from step.wise desorption following propylene chemisorption at 573 K (closed symbols) and 873 K (open symbols).

and ethylene were also observed in the desorption products. In the desorption products of a 373 K propylene chemisorption, there was even some butene observed in addition to the other products.

The desorption products other than methane and H_2 usually disappeared from the gas phase (due to cracking) when the temperature was raised 200 K above the adsorption temperature. Methane itself cracked and disappeared from the gas phase above 973 K. As is evident in Fig. 2, the main gaseous product in all desorptions was H_2; so the majority of the carbon was left on the surface as a deposit. If the reactor was not pumped out after each isothermal step, all the gas phase hydrocarbon products cracked; and all the carbon in the chemisorbed hydrocarbon remained on the surface. Depending on the hydrocarbon chemisorbed, between 30 and 50% of the chemisorbed hydrogen desorbed at 1223 K without pumping. The remainder desorbed with pumping.

In all desorptions some CO and CO_2 were observed in the products. This occurred even if the pressure was kept at 10^{-7} Pa after cleaning. The clean surface was so active toward oxygen that it chemisorbed on the most active sites before the intended chemisorption could begin. On an original Graphon sample not subjected to preoxidation, the oxygen coverage amounted to about 10% of the propylene coverage, whereas on a 15% burn-off sample, the oxygen coverage amounted to less than 1% of the propylene coverage.

3.3 *Effect of cycling*

It was stated above that on desorption some or all of the carbon from the chemisorbed hydrocarbon stayed on the surface as a deposit. This deposit decreased the active surface area. This decrease was most pronounced following the first hydrocarbon adsorption–desorption cycle on a Graphon sample. On this first cycle for propylene, the ASA was observed to decrease up to 40%, depending on the extent of burn-off of the sample. After this initial hydrocarbon adsorption–desorption cycle, the decrease in ASA on each subsequent cycle was negligible. In fact, after an additional 100 cycles the ASA decreased only about 15% for the sample having an original burn-off of 14%. Thus, after the first cycle, chemisorption was observed to be very reproducible. All the chemisorption data presented in this paper were obtained after the first cycle.

After the first cycle, the deposit resulting from an adsorption–desorption cycle slightly decreased the ASA but did not deactivate it. As shown elsewhere[15, 25], the carbon deposited remains on the sites active for chemisorption and pyrolysis and becomes a new active site.

After the initial adsorption–desorption cycle, the observed ASA decrease varied for each molecular species chemisorbed. It will be shown that the factors of molecular size, orientation to the surface, surface site geometry, and site energy all appear to affect surface coverage and decrease in ASA. Reduction of sites active for the chemisorption of oxygen and small normal-hydrocarbons of less than four carbons was negligible (Fig. 3). Reduction of ASA active for butadiene chemisorption was significant.That is, the ASA decreased 20% after 100 cycles (Fig. 4). Reduction in the chemisorption of the larger molecules and not the smaller ones as a result of carbon deposition suggests a size effect. This size effect could be due to molecular sieving or to surface

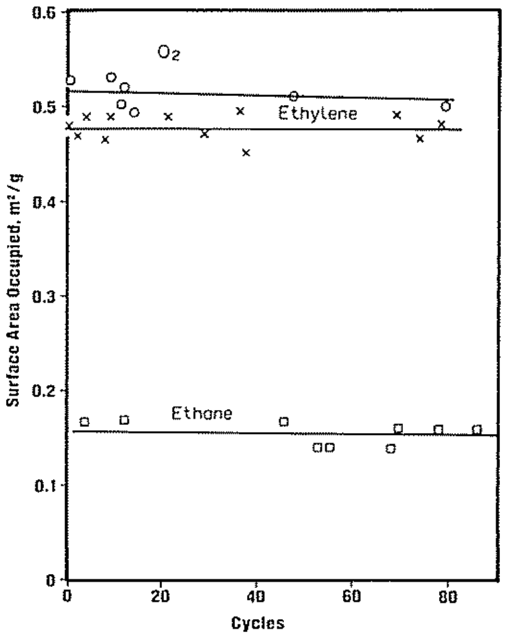

Fig. 3. Effect of cycling on surface coverage for burned-off graphon sample. ○, O_2; ×, ethylene; □, ethane.

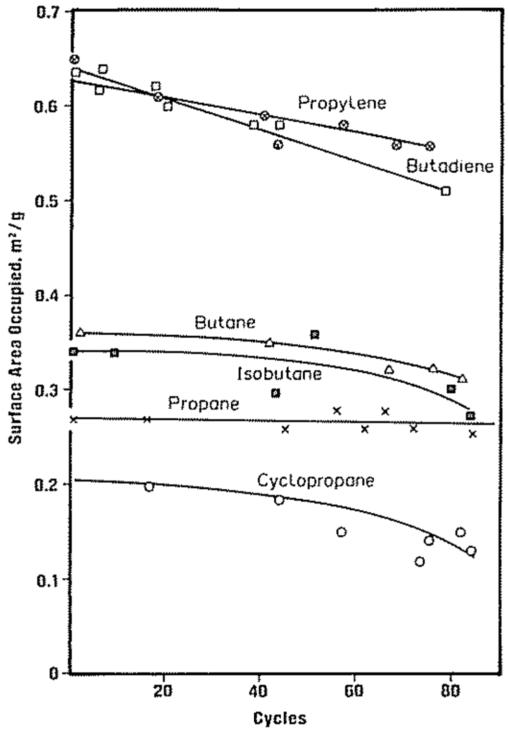

Fig. 4. Effect of cycling on surface coverage for burned-off graphon sample. ⊗ propylene; □, butadiene; △, *n*-butane; ▨, iso-butane; ×, propane; ○, cyclopropane.

morphology changes. A reduction in ASA active for chemisorption caused by molecular sieving would result from carbon deposition on pore walls, particularly at apertures. This deposition would cause a decrease in pore diameter. When the pore diameter is smaller than the kinetic diameter of the molecule to be chemisorbed, the ASA on the pore walls will be inaccessible for chemisorption. Changes in surface morphology resulting in a decrease in optimum site geometry for chemisorption might also be the cause of the reduction in area active for chemisorption. For instance, butadiene might require three or four sites in a row, whereas ethylene might require only one or two sites. If deposition occurred so that only two sites in a row were available, this would reduce the ASA active for butadiene chemisorption but not for ethylene chemisorption.

Molecular sieving can be easily ruled out. For instance, it was observed that there was a significant reduction in the area active for propylene and butane with cycling. However, no reduction in the area active for propane chemisorption was observed. Since the minimum kinetic diameter is almost identical for all three molecules, their behavior with hydrocarbon adsorption–desorption cycling should be similar if the reduction in active area was due to molecular sieving. This was not observed.

The effect of the interaction of molecular size, surface morphology, and active site distribution on surface coverage can be seen in Table 2. Looking at the columns labeled percentage increase for each gas, one can see how surface coverage increases with burn-off relative to the unoxidized sample. Since oxygen dissociatively chemisorbs, with each atom requiring only a single site, the oxygen ASA is most likely a measure of the total number of active sites on the surface and is not very dependent on surface morphology or active site distribution. The increase in oxygen ASA with burn-off should then track the increase in the total number of active sites on the surface if there are no surface impurities. For larger molecules, more than one active site or more area around each site is needed. As a result, not all the active sites on the surface are available for chemisorption by these molecules. This is evident, e.g. in Table 2.

It is known that Graphon, the adsorbent used in these studies, is composed of crystallites ($L_a = 7/\text{nm}$, $L_c = 4/\text{nm}$) and that individual particles are polyhedral in shape. The faces of these polyhedra are basal planes[26–28]. The active sites on unoxidized samples are predominately located at the intersection of these basal planes. Other imperfections reside in the surfaces of the polyhedral faces[29]. When Graphon is oxidized, mass loss occurs predominantly at the intersections of the basal planes. This results in wedge-shaped volumes in the polyhedra where carbon has been gasified. As oxidation proceeds these wedge-shaped volumes enlarge. The surface exposed at these wedges is composed of edges of basal planes and is chemically active. The *n*-butane data in Table 2 is probably a result of the enlargement of these wedges. A 0.61% weight loss increases the *n*-butane chemisorption 15-fold while the total ASA probably increased only a little more then 3-fold. For smaller molecules, burn-off does not have as dramatic an effect on their chemisorption. These results are easily explained assuming the ASA is located on the surface of these wedge-shaped volumes.

Inferences can also be made as to how the molecules are oriented on the surface. For example, since cyclopropane surface coverage (Fig. 4) is initially greater than that of ethane and decreases to less than that of ethane (Fig. 3), cyclopropane must lie flat on the surface with the plane of its carbon atoms parallel to the surface. Both Cling[11] and Hoory *et al.*[8] found that physically adsorbed hydrocarbons lie flat rather than on end. If only two of the carbon atoms of cyclopropane were close to the surface with the other carbon atom plane perpendicular to the surface, the surface coverage should not drop below that of ethane. The coverage of cyclopropane should always be greater than that of ethane in this case, since the ability of hydrocarbons to form bonds with the surface should increase with carbon number. This increase in bonding ability is due to the greater ability of the molecule to delocalize electrons and, in non-cyclic molecules, to also rotate to better accommodate itself to the surface site geometry.

Comparing the decrease in the surface coverage of propylene (13%) following 100 cycles to that of propane (<1%), one can see the effect of the double bond. Propylene coverage was greater than twice that of propane (Fig. 4). Presumably, the additional ASA covered by propylene was by comparison less active than that which chemisorbed propane. Since both molecules are of about the same size and the decrease in propane coverage with cycling was negligible, the decrease in propylene surface coverage with deposition was due to blockage or deactivation of the rather inactive sites that chemisorbed propylene and not propane.

The decrease in the coverage by butadiene following hydrocarbon adsorption and desorption (Fig. 4) is an example of the effect of a combination of factors. A portion of the decrease (~ 55%) was due to blockage or deactivation of the rather inactive sites on which only the double bond will chemisorb. The remainder of the decrease in surface coverage was due to the length of the carbon chain and is equivalent to the decrease experienced by *n*-butane.

This blockage or deactivation of the less active sites seen in propylene and butadiene coverage was probably also responsible for the large decrease in ASA after the initial hydrocarbon adsorption–desorption cycle. It was observed that after the first cycle and amount of gas chemisorbed in 1 hr decreased while the amount chemisorbed during the first minute remained unchanged. Assuming that most active sites were responsible for the rapid chemisorption, it was the less active sites that were deactivated.

3.4 *Blockage experiments*

In order to better understand the chemisorption of hydrocarbons and, in particular, to determine whether the various molecules occupied the same sites, a series of blockage experiments was conducted for each pair of gases. Results on a 14% burn-off Graphon sample are shown in Table 4. These experiments involved adsorbing gas on a clean Graphon surface and pumping off the physically adsorbed portion. (This gas is shown as the preadsorbed gas in Table 4.) Then a second, different gas (blocked gas in Table 4) was adsorbed 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.

Referring to Table 4, the numbers in brackets running diagonally down from left to right are the *average* surface areas (m^2/g) covered by each adsorbate during the series of runs. These surface areas are the same as those given in Table 1. As can be seen in Table 4, the preadsorbed gas blocked chemisorption of the second gas to varying degrees. The percentages given are those of sites blocked; e.g. ethylene, which occupies 0.46 m^2/g, blocks 90% of the 0.57 m^2/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 value was determined near the end of the series.

While performing the blocking experiments it was observed that the total surface coverage by the pair was dependent upon the order of adsorption. If a less active molecule was adsorbed first, it blocked sites on which the more active gas usually chemisorbed, and the total surface area covered by the pair of gases was always less than the surface covered by the more active gas itself. If the more active gas was adsorbed first, the total surface coverage always at least equaled that of the more active gas. The total exceeded that of the more active gas if the second molecule was smaller. These observations held for all pairs of gases except ethylene/butadiene and propylene/butadiene. In these cases the butadiene was very active and appeared to chemisorb on top of the first gas. The total area covered by the pair exceeded the area covered by butadiene itself by 17%.

As was stated above, surface cleanliness was important in determining the extent of surface coverage. Cleanliness was least important for O_2, because it is very active and dissociatively chemisorbs needing only two adjacent sites. As one goes down the column in Table 4, cleanliness becomes increasingly important. In fact, methane and hydrogen will not chemisorb unless the surface is very clean.

Information can also be gained from this table as to the effect of size and π bonds on surface coverage. It can be seen that all the normal and branched chained alkanes chemisorb on the same sites since they mutually and totally block one another. Oxygen and the alkenes adsorb on these same sites as well as less active ones.

It was observed that *n*-butane surface coverage decreased 14% with one hundred adsorption–desorption cycles, while the ethane surface coverage did not decrease. From Table 4 it can be seen that the pre-adsorption of ethane, which occupies 0.16 m^2/g, totally blocks adsorption of *n*-butane which occupies 0.33 m^2/g. From these data it can be inferred that *n*-butane lies relatively flat on the surface and needs more than two sites to chemisorb.

From results on the decrease in surface coverage with cycling and data in Table 4, it is apparent that the site energy and site geometry, the size and orientation of the molecule, and the accommodation of the molecule (both electronic and rotational) all affect the amount of surface covered by a chemisorbed molecule. The surface sites themselves have the greatest effect on surface coverage, as seen by the large decrease in surface coverage after the first hydrocarbon adsorption–desorption cycle. Molecular differences are of less importance in determining the extent of surface coverage. It was observed that double bonds and increased molecular length both increased chemisorption. However, the size of the molecule was observed to have an appreciable negative effect on surface coverage when the molecular length reached four carbon atoms. That is, it was observed, for example, that butane coverage was greater than that of propane, but the butane coverage decreased significantly with cycling while the propane coverage did not. It appears that extensive chemisorption studies with different molecules would be an effective method for characterizing active sites on carbon surfaces.

Table 4 also contains information useful in interpreting hydrocarbon pyrolysis results, which was the original impetus for this study. For instance, one might expect the H_2 formed during pyrolysis to reduce the rate of hydrocarbon pyrolysis by blocking active sites. The table shows that H_2 is not very active for chemisorption compared to propylene. Even on a clean surface, hydrogen would only block 22% of the sites active for propylene chemisorption. Thus in a pyrolysis system where most of the propylene ASA is already covered with propylene one would not expect hydrogen to have much of an effect. This was indeed seen to be the case[14, 25].

When comparing Table 1 with Table 4, the reader might assume that there is an inconsistency. For instance, oxygen covers a smaller surface area than propylene (Table 1) but more effectively blocks propylene than propylene blocks oxygen (Table 4). One might assume from these data that the molecular areas given in Table 1 are incorrect. That is thought not to be the case. Rather it is thought that the blockage results from this pair of gases are due to relative molecular size and site geometry effects. This is deduced from the fact that if oxygen were more active for chemisorption and covered a larger surface area it would totally block propylene chemisorption. That is, an oxygen molecule is smaller and, therefore, would have access to all sites accessible to propylene.

The calculated molecular areas chemisorbed by oxygen have a firmer foundation than those for the hydrocarbons. Implicit in the calculation for the area chemisorbed by an oxygen atom or a hydrogen atom is that they each chemisorb on one carbon site with an area of $0.083\ \mathrm{nm}^2$. No such firm information exists for the hydrocarbons as to how many active sites are covered by each molecule. Most probably, propylene, for example, does not always chemisorb on three active sites. It might chemisorb in some cases on only one dangling site. Likewise, propylene might block access to some sites that it does not chemisorb on. Thus, to assume that the calculated molecular area for propylene $0.23\ \mathrm{nm}^2$ is an accurate measure of active surface area covered might not always be true. However, the arrangement in Table 1, according to decreasing surface coverage, appears to be correct.

Other evidence that the calculated molecular areas are approximately correct comes from the blockage experiments. For example, if one assumes that oxygen and propylene chemisorb on the same sites and that the oxygen atom occupies $0.083\ \mathrm{nm}^2$, then the molecular area occupied by propylene can be calculated from the propylene/oxygen series using eqn (1)

$$A_p = \frac{2A_o(M_o - M_{o-p})}{M_p} \qquad (1)$$

where A_p is the molecular area occupied by propylene, A_o is the molecular area occupied by oxygen atom, M_o are the molecules of oxygen chemisorbed on clean surface, M_p are the molecules of propylene chemisorbed on clean surface and $M_{o\text{-}p}$ are the molecules of oxygen chemisorbed after propylene chemisorption.

The molecular area for propylene is calculated from eqn (1) to be $0.238\ \mathrm{nm}^2$. This value is in surprisingly close agreement to that calculated by another method and presented in Table 1. This agreement and that from other adsorption pairs lends credence to the accuracy of the values in Table 1.

4. CONCLUSIONS

The chemisorption of hydrocarbons on graphitized carbon black is of the Langmuir type, with saturation reached at < 0.7 Pa hydrocarbon pressure at 573 K. The active sites must be clean for chemisorption to occur. No H_2 was seen in the gas phase; so if adsorption is dissociative, hydrogen also chemisorbs. The hydrocarbons studied lie flat on the surface and occupy the same sites to varying degrees. Some of the prismatic carbon surface (ASA) is not available for each molecule studied. This is due to effects of molecular size, surface morphology, active site distribution, and molecular accommodation. Chemisorbed hydrocarbons do not desorb at adsorption temperature even during evacuation. Upon heating, the chemisorbed species thermally crack before desorbing with the principle gas phase product being H_2. The vast majority of the carbon derived from the hydrocarbon remains on the surface.

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REFERENCES

1. N. N. Augul and A. V. Kiselev, *Chemistry and Physics of Carbon* (Edited by P. L. Walker, Jr.), Vol. 6, pp. 1–115. Marcel Dekker, New York (1970).
2. C. H. Amberg, W. B. Spencer and R. A. Beebe, *Can. J. Chem.* **33**, 305 (1954).
3. R. A. Beebe, and D. M. Young, *J. Phys. Chem.* **58**, 93 (1954).
4. R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, *J. Am. Chem. Soc.* **69**, 95 (1947).
5. W. R. Smith and M. H. Polley, *J. Phys. Chem.* **60**, 689 (1956).
6. M. M. Selim and T. A. El-Nabarawy, *Carbon* **18**, 287 (1980).
7. R. O. Friederich and J. C. Mullins, *Ind. Eng. Fundam.* **11**, 439 (1972).
8. S. E. Hoory and J. M. Prausnitz, *Trans. Far. Soc.* **63**, 455 (1967).
9. T. J. Nakahara, *Chem. Engng Data* **20**, 195 (1975).
10. T. D. Stacy, E. W. Hough and W. D. McCain, *J. Chem. Engng Data* **13**, 74 (1968).
11. J. H. Clint, *J. Chem. Soc., Faraday Trans. I* **68**, 2239 (1972).
12. A. V. Kiselev, *Proc. 2nd Int. Cong. Surface Activity* **2**, 168 (1957).
13. I. S. McLintock and J. C. Orr, *3rd Conf. Ind. Carbons and Graphites*, 201 (1970).
14. W. P. Hoffman, Ph.D. Thesis. The Pennsylvania State University (1979).
15. W. P. Hoffman, F. J. Vastola and P. L. Walker, Jr., In press. *Carbon*.

16. N. R. Laine, F. J. Vastola and P. L. Walker, Jr., *J. Phys. Chem.* **67**, 2030 (1963).
17. R. C. Bansal, F. J. Vastola and P. L. Walker, Jr., *Carbon* **9**, 185 (1971).
18. F. J. Vastola, P. J. Hart and P. L. Walker, Jr., *Carbon* **2**, 65 (1964).
19. R. Phillips, F. J. Vastola and P. L. Walker, Jr., *Carbon* **8**, 197 (1970).
20. R. C. Bansal, F. J. Vastola and P. L. Walker, Jr., *Carbon* **8**, 443 (1970).
21. R. O. Lussow, F. J. Vastola and P. L. Walker, *Carbon* **5**, 591 (1967).
22. P. L. Walker, Jr., R. C. Bansal and F. J. Vastola, *The Structure and Chemistry of Solid Surfaces*, p. 81. Wiley, New York (1969).
23. R. C. Bansal, F. J. Vastola and P. L. Walker, Jr., *J. Colloid Interface Sci.* **32**, 187 (1970).
24. N. R. Laine, F. J. Vastola and P. L. Walker, Jr., *Proc. 5th Conf. on Carbon* **211** (1963).
25. W. P. Hoffman, F. J. Vastola and P. L. Walker, Jr., In press. *Carbon*.
26. L. L. Ban, *Surface and Defect Properties of Solids*, Vol. 1, pp. 54–94. The Chemical Society, London (1972).
27. H. Akamatu and H. Kuroda, *Proc. 4th Carbon Conf.* pp. 355–369. Pergamon Press, New York (1961).
28. E. A. Kmetko, *Proc. 1st and 2nd Carbon Conf.*, pp. 21–29. University of Buffalo, Waverly Press, Baltimore (1956).
29. J. B. Donnet, *Carbon* **20**, 266 (1982).