

## Adsorption of Oxygen and Nitrogen on Surface-Modified Carbons

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Saran carbon adsorbs more N<sub>2</sub> than O<sub>2</sub> at 25°C due to stronger interaction of the larger nitrogen molecule with adsorbent pore walls. Exchange of H ions on carboxylic acid groups located on the surface of oxidized Saran carbons and Carbolac-1 by calcium ions increases the extent of chemisorption of O<sub>2</sub> and physisorption of N<sub>2</sub>, if the carbons are outgassed to at least 180°C. The higher uptake of N<sub>2</sub> has been attributed to interaction of the nitrogen quadrupole moment with the electrostatic field gradient. It is suggested that the chemisorption of oxygen on the Ca-exchanged carbons is due to carbanion formation upon decarboxylation of the calcium salt of surface carboxylic acid groups. The addition of large amounts of chlorine to Saran carbon has a negligible effect on the ratio of N<sub>2</sub> to O<sub>2</sub> which is adsorbed.

### I. INTRODUCTION

Physical adsorption on carbon surfaces has been used extensively for purification and separation of various gases (1, 2). Since there is an increasing demand for oxygen in different technological processes, attempts have recently been made to separate oxygen from air by selective adsorption on carbons having high specific surface areas. Nandi and Walker (3) have shown that certain microporous carbons exhibit molecular sieving properties towards O<sub>2</sub> and N<sub>2</sub>, resulting in selective oxygen adsorption from air. These workers also observed that carbons having vinylidene chloride as their main organic precursor had a greater uptake of N<sub>2</sub> than O<sub>2</sub> at room temperature. Since the kinetic diameter of N<sub>2</sub> is larger than that of O<sub>2</sub> (3.64 and 3.46 Å, respectively), these results cannot be explained in terms of molecular sieving but rather by specificity in physical adsorption. Specific interactions due to electrostatic forces between various adsorbates and solid surfaces have been reported in the literature (2). Drain (4) has shown that both O<sub>2</sub> and N<sub>2</sub> have similar heats of adsorption

on nonionic solids, but in the case of ionic solids the heat of adsorption of N<sub>2</sub> is higher. He has suggested that this may be due to the larger quadrupole moment of N<sub>2</sub> compared to that of O<sub>2</sub>. Huang and Emmett (5) observed that the adsorption of molecules having high quadrupole moments is increased on cation-exchanged silica-alumina.

Carbons possess high surface reactivity and it is possible to change their surface polarity by fixing dipole groups like C-Cl or by cation exchange of surface carboxylic protons. It would be desirable to investigate if adsorption of N<sub>2</sub> on high surface area adsorbent carbons can be enhanced by interaction of the nitrogen quadrupole moment with the deliberately introduced surface dipoles or surface electrostatic field potential. The present paper is an attempt in this direction.

### II. EXPERIMENTAL

#### A. Materials

Saran carbon and Carbolac-1, a highly oxidized channel black manufactured by Cabot Corporation, were used as adsorbents. Saran carbon was prepared by the pyrolysis of Saran (a copolymer of PVDC and PVC in a ratio of

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TABLE I  
Adsorption of Oxygen and Nitrogen on Various Carbons

Sample	Surface area (m <sup>2</sup> /g)	Adsorption at 25°C and 600 Torr (cm <sup>3</sup> /g)		
		V <sub>N<sub>2</sub></sub>	V <sub>O<sub>2</sub></sub>	V <sub>N<sub>2</sub></sub> /V <sub>O<sub>2</sub></sub>
S(900°C)	882	8.6	7.7	1.12
S(CO <sub>2</sub> -19.6)	882	8.6	7.7	1.12
S(CO <sub>2</sub> -38.3)	924	8.2	8.0	1.03
S(CO <sub>2</sub> -60.4)	816	7.3	7.0	1.04
S(air-48.6)	715	6.5	6.2	1.05
S(air-63.8)	680	6.2	5.9	1.05
Carbolac-1	930	3.3	3.3	1.00
Graphon	80	0.8	0.8	1.00

about 9:1) in an argon atmosphere. The heating cycle was: a heating rate of 100°C/hr to 350°C, hold at 350°C for 2 hr, a heating rate of 200°C/hr to 900°C, and hold at 900°C for 4 hr. Saran carbon was activated to various levels of burn-off in air at 450°C and in CO<sub>2</sub> at 800°C. The experimental details of pyrolysis and activation have been described elsewhere (6).

### B. Treatment of Samples

1. *Modification of chlorine content.* Chlorine contents of selected Saran carbons were decreased by treatment in hydrogen at 800°C for 8 hr and increased by treatment with chlorine at 450°C for 10 hr (7). Following chlorination, the samples were washed with distilled water and dried at 120°C in vacuum. Chlorine contents of the treated samples were determined by the Parr method.

2. *Oxidation with nitric acid.* Surface carboxylic groups on the Saran carbons were introduced by oxidation with nitric acid. For this purpose, 3 g of carbon were heated to dryness with 20 cm<sup>3</sup> of concentrated nitric acid. After oxidation, the samples were washed with distilled water and dried at 120°C.

3. *Exchange with calcium ions.* Calcium ions were introduced on the oxidized samples of Saran carbon and Carbolac-1 by treatment with 2 M calcium acetate solution at 60°C. The calcium-exchanged carbons were washed with distilled water and dried in an air oven at 120°C. The calcium content of the treated

samples was determined gravimetrically as calcium oxide by burning the sample at 950°C.

### C. Adsorption Isotherms

Adsorption of O<sub>2</sub> and N<sub>2</sub> was measured at 25°C in a conventional volumetric apparatus. Before making an adsorption run, the sample was normally outgassed overnight at 120°C. Thirty minutes was allowed for each adsorption point, with equilibrium reached within this time period. All adsorption volumes given in the paper are reported at STP conditions.

## III. RESULTS AND DISCUSSION

Adsorption isotherms of N<sub>2</sub> and O<sub>2</sub> on unactivated Saran carbon and Carbolac-1 are shown in Fig. 1. The isotherms are linear and reversible over the entire pressure range studied. Volumes of N<sub>2</sub> and O<sub>2</sub> adsorbed on various samples at 600 Torr are given in Table I. Experimental uncertainty in amounts adsorbed was ±0.1 cm<sup>3</sup>/g. Saran samples (S)

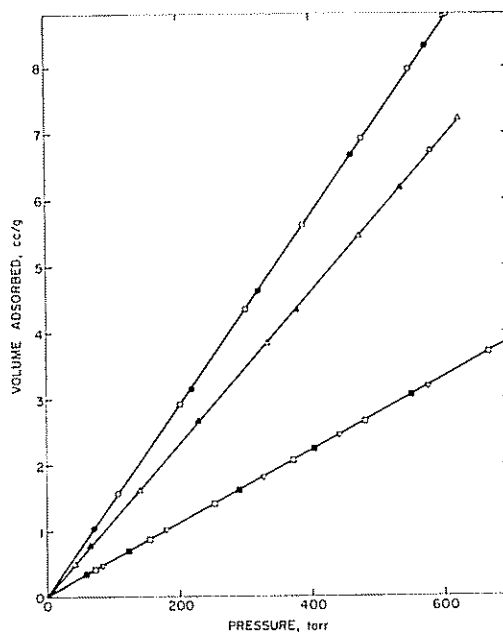


FIG. 1. Sorption isotherms of nitrogen and oxygen at 25°C on Saran carbon and Carbolac-1. Saran carbon: O, N<sub>2</sub>; Δ, O<sub>2</sub>. Carbolac-1: ∇, N<sub>2</sub>; □, O<sub>2</sub>. Solid points denote desorption data.

TABLE II  
Adsorption of Nitrogen and Oxygen on Saran Carbons as Influenced by Chlorine Content

Sample	Surface area (m <sup>2</sup> /g)	Chlorine content (%)	Adsorption at 25°C and 600 Torr (cm <sup>3</sup> /g)		
			V <sub>N<sub>2</sub></sub>	V <sub>O<sub>2</sub></sub>	V <sub>N<sub>2</sub></sub> /V <sub>O<sub>2</sub></sub>
S(900°C)	882	0.03	8.6	7.7	1.12
S(900°C)H <sub>2</sub>	857	nil	8.4	7.3	1.15
S(air-63.8)	680	0.01	6.2	5.9	1.05
S(air-63.8)Cl <sub>2</sub>	520	21.6	3.8	3.5	1.09

are designated as to the activating gas, CO<sub>2</sub> or air, and the level of carbon burn-off. Surface areas, as determined by CO<sub>2</sub> adsorption at 25°C, using the Dubinin-Polanyi equation (6) are also given in Table I. Results obtained for a graphitized carbon black, Graphon, which has a homogeneous surface and is devoid of porosity, are also included in Table I. Considering the results, it is seen that in the case of Carbolac-1 and Graphon, uptake of O<sub>2</sub> and N<sub>2</sub> is equal. However, in the case of unactivated Saran carbon, uptake of N<sub>2</sub> is significantly higher than that of O<sub>2</sub>. Activation of Saran up to 19.6% burn-off does not change its adsorption capacity for N<sub>2</sub> or O<sub>2</sub>. Upon further activation, the uptake of both N<sub>2</sub> and O<sub>2</sub> decreases and the ratio V<sub>N<sub>2</sub></sub>/V<sub>O<sub>2</sub></sub> also decreases to a value only slightly above one.

It is not possible to calculate closely the fraction of total area of the carbons occupied by the N<sub>2</sub> or O<sub>2</sub> adsorbate because adsorption is taking place much above the critical temperature of the molecules. However, coverage is certainly low; it is estimated to be in the range 0.015 to 0.04 of the total surface; if a value of 16 Å<sup>2</sup> is taken for the molecular area.

The higher uptake of N<sub>2</sub> on Saran carbons may be due to the presence of residual amounts of chlorine (0.03%, Table II) retained even after carbonization. This chlorine, when attached to edge carbon atoms, can give rise to C-Cl dipoles. Although quadrupole-dipole interactions are generally weak, higher adsorption of N<sub>2</sub> on Saran carbons may be explained by specific interactions between C-Cl surface dipoles and the permanent quadrupole moment of a nitrogen molecule. In order to examine

this aspect further, the chlorine content of unactivated Saran carbon was decreased by hydrogen treatment. The surface area, chlorine content, and amounts of O<sub>2</sub> and N<sub>2</sub> adsorbed on the treated samples are given in Table II. It is seen that the removal of traces of chlorine from the Saran carbon does not significantly change the extent of adsorption of O<sub>2</sub> and N<sub>2</sub>. In order to see if adsorption of N<sub>2</sub> can be enhanced by fixation of large amounts of chlorine, a Saran carbon activated to 63.8% weight loss in air was treated with chlorine gas at 450°C. This treatment resulted in the fixation of 21.6% by weight of chlorine. Taking 8.2 Å<sup>2</sup> as the area for a chemisorption site on carbon (8), it is estimated that about 44% of the carbon surface is covered with chlorine atoms. After chlorination, there is a considerable decrease in total surface area as well as the amounts of O<sub>2</sub> and N<sub>2</sub> adsorbed but no significant change in the V<sub>N<sub>2</sub></sub>/V<sub>O<sub>2</sub></sub> ratio (Table II).

It appears that chemisorbed chlorine effectively blocks some of the micropores, thus resulting in loss of area. Dacey and Thomas (9) and Barton *et al.* (10) have shown that Saran carbon has a uniform array of slit-shaped

TABLE III  
Characteristics of Calcium-Exchanged Samples

Sample	Surface area (m <sup>2</sup> /g)	Calcium content	
		(mmoles/g)	(μmoles/m <sup>2</sup> )
S(air-63.8)HNO <sub>3</sub>	550	—	—
S(air-63.8)HNO <sub>3</sub> -Ca	490	1.85	3.8
Carbolac-1	930	—	—
Carbolac-1-Ca	900	0.52	0.58

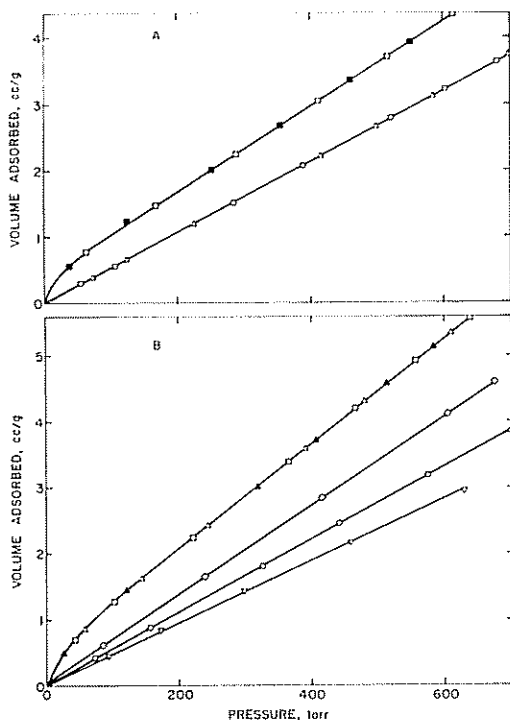


FIG. 2. Sorption isotherms of nitrogen at 25°C on Saran carbons (A) and Carbolac-1 (B).  $S(\text{air-63.8})\text{HNO}_3$ : before Ca-exchange  $\circ$ , 120°C; after Ca-exchange  $\triangle$ , 120°C;  $\square$ , 250°C. Carbolac-1: before Ca-exchange  $\circ$ , 120°C; after Ca-exchange:  $\nabla$ , 120°C;  $\diamond$ , 180°C;  $\square$ , 250°C;  $\triangle$ , 350°C. Solid points denote desorption data.

micropores of 5.5 to 6 Å in width. Thus in the case of unactivated Saran carbon, adsorption of  $\text{O}_2$  and  $\text{N}_2$  occurs in a pore system of molecular dimensions so that interaction of the adsorbed species with more than one pore wall need be taken into account. Since the kinetic diameter of  $\text{N}_2$  is slightly larger than that of  $\text{O}_2$ , stronger interaction of  $\text{N}_2$  with the pore walls is expected. This would lead to a higher uptake of  $\text{N}_2$  compared to that of  $\text{O}_2$ . This explanation is supported by the fact that upon activation of Saran carbon, the ratio  $V_{\text{N}_2}/V_{\text{O}_2}$  decreases (Table I). Since activation would enlarge the pore sizes, it would be expected to result in a greater decrease in interaction of  $\text{N}_2$  than  $\text{O}_2$  with two pore walls. This explanation also receives support from the fact that in the case of nonporous Graphon and Carbolac-1,

which possesses micropores in the range 7–11 Å (11), uptake of both  $\text{N}_2$  and  $\text{O}_2$  are equal (Table I).

Adsorption of  $\text{O}_2$  and  $\text{N}_2$  was next studied on calcium exchanged samples. Their calcium contents and surface areas are given in Table III. Following oxidation with nitric acid, the surface area of the Saran sample decreases by about 20%. Furthermore upon exchange with calcium ions, surface areas of Carbolac-1 and the oxidized Saran carbon decrease by about 3 and 10%, respectively. Calcium-exchanged Carbolac-1 has a lower content of calcium per unit area than does the calcium-exchanged Saran sample. This is presumably because treatment with nitric acid in the case of the Saran carbon is a more drastic oxidative treatment, resulting in the formation of a higher concentration of surface carboxylic acid groups, than the air oxidative treatment undergone by Carbolac-1 during its production.

Adsorption isotherms of  $\text{N}_2$  on the oxidized Saran carbon as well as calcium-exchanged samples are given in Fig. 2. Prior to adsorption runs, the Ca-exchanged samples were outgassed overnight at temperatures varying from 120 to 350°C. Considering first the results for the samples outgassed at 120°C, it is seen that in the case of the Saran sample, exchange with calcium ions does not cause any change in the extent of  $\text{N}_2$  adsorption. However, the uptake on Carbolac-1 decreases slightly upon ion exchange. It is noteworthy that for both the Ca-exchanged samples, uptake of  $\text{N}_2$  increases when samples are outgassed above 120°C. In the case of Carbolac-1 outgassing above 250°C has no additional effect on  $\text{N}_2$  uptake. Adsorption of  $\text{N}_2$  on the Ca-exchanged samples is reversible. It is significant that the shape of the isotherms on the Ca-exchanged samples is modified following evacuation above 120°C. This indicates a change in the energetics of the adsorption process.

Sorption isotherms of  $\text{O}_2$  plotted in Fig. 3 illustrate the effect of exchangeable calcium ions on the extent of adsorption. It is seen that when the carbon samples are heated above 120°C prior to adsorption runs, the presence of

TABLE IV  
Effect of Exchangeable Calcium Ions on Adsorption of Oxygen and Nitrogen

Sample	Degassing Temp (°C)	Adsorption at 25°C and 600 Torr (cm <sup>3</sup> /g)			
		Cycle I		Cycle II	
		V <sub>N<sub>2</sub></sub>	V <sub>O<sub>2</sub></sub>	V <sub>N<sub>2</sub></sub>	V <sub>O<sub>2</sub></sub>
S(air-63.8)HNO <sub>3</sub>	120	3.2	3.2	3.2	3.2
S(air-63.8)HNO <sub>3</sub>	250	3.2	3.2	3.2	3.2
S(air-63.8)HNO <sub>3</sub> -Ca	120	3.2	3.2	3.2	3.2
S(air-63.8)HNO <sub>3</sub> -Ca	250	4.3	15.5	3.8	3.1
Carbolac-1	120	3.3	3.3	3.3	3.3
Carbolac-1	250	3.3	3.3	3.3	3.3
Carbolac-1-Ca	120	2.9	2.9	2.9	2.9
Carbolac-1-Ca	180	4.1	3.6	3.3	3.3
Carbolac-1-Ca	250	5.3	6.4	3.9	3.3
Carbolac-1-Ca	350	5.3	6.6	3.8	3.3

calcium ions significantly increases the extent of O<sub>2</sub> adsorption. For instance, for the samples outgassed at 250°C, the presence of calcium ions increases the uptake of O<sub>2</sub> on the Saran and Carbolac-1 samples, by factors of about five and two, respectively, at an adsorption pressure of 600 Torr. Furthermore, in the case of the Ca-exchanged samples, a significant amount of O<sub>2</sub> is fixed irreversibly and cannot be desorbed even after prolonged outgassing at ambient temperature. The irreversible fixation of O<sub>2</sub> appears to be due to the presence of calcium ions because the unexchanged samples did not fix any O<sub>2</sub> under identical experimental conditions.

Nitrogen and oxygen isotherms were also measured on the Ca-exchanged samples following irreversible fixation of O<sub>2</sub>. The amounts of N<sub>2</sub> and O<sub>2</sub> adsorbed are given in Table IV. Adsorption in Cycle I refers to the uptake of N<sub>2</sub> followed by outgassing at room temperature and subsequent adsorption of O<sub>2</sub>. Adsorption in Cycle II refers to N<sub>2</sub> and O<sub>2</sub> uptakes, respectively, on the same sample containing O<sub>2</sub> retained irreversibly in Cycle I. It is seen (Table IV) that on the Ca-exchanged samples outgassed above 120°C, uptake of both O<sub>2</sub> and N<sub>2</sub> in adsorption Cycle II are significantly less than in Cycle I. The results for Cycle II also show that whereas the uptake of N<sub>2</sub> on the Ca-exchanged samples outgassed at 250°C and 350°C is greater than that on the un-

exchanged samples, the amount of oxygen adsorbed is the same in the two cases.

It has been noted earlier that the adsorption of N<sub>2</sub> on Ca-exchanged samples is enhanced only if the samples are outgassed above 120°C. A possible explanation of this finding is the screening effect of water adsorbed on the ionic sites. It is known (12) that the replacement of surface hydrogen ions of carboxylic acid groups by metal cations appreciably enhances the moisture sorption capacity of carbons. It appears that adsorbed water held by electrostatic forces to the cations is not completely desorbed at 120°C so that adsorbed water prevents interaction between N<sub>2</sub> and calcium ions. However, when adsorbed water molecules are progressively removed on outgassing above 120°C, electrostatic interaction between the N<sub>2</sub> quadrupole moment and the surface field gradient can result in enhanced uptake of N<sub>2</sub>.

The quadrupole energy ( $\phi$ ) for a linear molecule possessing a quadrupole moment  $Q$  [ $Q_{N_2} = -1.52 \times 10^{-40}$  esu A<sup>2</sup> (13)] in an electrostatic field gradient  $E'$  is given by

$$\phi = -\frac{1}{2}QE'$$

The value of the electrostatic field gradient at a distance  $r$  from an isolated charge  $+ne$  is given by  $E' = -2ne/r^3$ . In order to estimate the energy of adsorption, it is necessary to know the electrostatic field and field gradient in the vicinity of the adsorption sites. Assuming

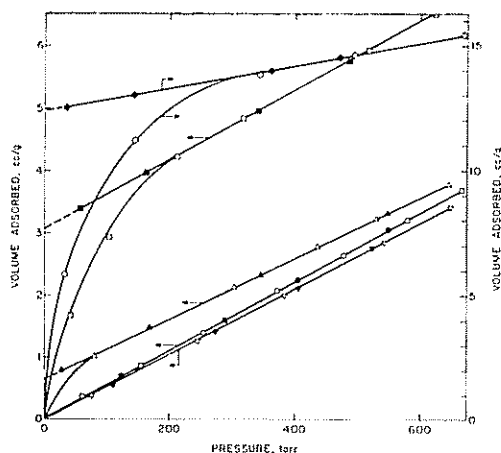


FIG. 3. Sorption isotherms of oxygen at 25°C on Saran carbons and Carbolac-1. *S*(air-63.8)HNO<sub>3</sub>: before Ca-exchange  $\nabla$ , 250°C; after Ca-exchange  $\diamond$ , 250°C. Carbolac-1: before Ca-exchange  $\circ$ , 250°C; after Ca-exchange  $\triangle$ , 180°C;  $\square$ , 250°C. Solid points denote desorption data.

that the specific adsorption sites are the calcium ions, the exact position of the other atoms and ions in the neighborhood of the calcium ions, as well as the electrostatic charge distribution, must be known. As discussed below, changes in the surface groups containing calcium ions occur upon heating in such a manner that it is not possible to estimate the electrostatic field gradient in the vicinity of the calcium ions. However, the increase in amount of N<sub>2</sub> adsorbed per calcium ion gives interesting information on the energetics of surface interactions. It is seen (Table V) that the increase in N<sub>2</sub> uptake is considerably different for the two carbons. These results suggest that the interaction between the N<sub>2</sub> molecule and the field gradient is weaker for the Saran sample.

TABLE V

Increase in Nitrogen Adsorption on Calcium-Exchanged Samples Outgassed at 250°C

Sample	N <sub>2</sub> adsorbed (cm <sup>3</sup> /g) Before exchange	N <sub>2</sub> adsorbed (cm <sup>3</sup> /g) After exchange	$\Delta N_2$ (cm <sup>3</sup> /g)	$\frac{\Delta N_2}{Ca}$ (moles/mole)
<i>S</i> (air-63.8)HNO <sub>3</sub>	3.2	4.3	1.1	0.026
Carbolac-1	3.2	5.3	2.1	0.17

TABLE VI

Oxygen Fixed on Calcium-Exchanged Carbons

Sample	Oxygen fixed (cm <sup>3</sup> /g)	O <sub>2</sub> (moles) Ca (mole)
<i>S</i> (air-63.8)HNO <sub>3</sub> -Ca	12.4	0.60
Carbolac-1-Ca	3.1	0.53

The fact that O<sub>2</sub> is irreversibly fixed on the Ca-exchanged samples outgassed above 120°C (Fig. 3) suggests that during the heat treatment, in addition to removal of adsorbed water molecules, functional groups on the carbon surface also undergo certain distinct chemical changes. It has been reported (14) that strongly acidic surface carboxylic acid groups decompose above 150°C. It is known (15) that decarboxylation proceeds more readily in the case of a metal salt of a carboxylic acid than for the acid itself. The mechanism of decomposition of carboxylate groups depends on the nature of the cation as well as the organic acid. It is generally agreed (15) that decarboxylation of a salt of a carboxylic acid in the presence of water proceeds through the formation of a carbanion; the ease of the reaction increases with increase in the stability of the produced carbanion. In the present study the Ca-exchanged carbons are thought to be associated with significant amounts of water held by electrostatic forces to the cationic species. It is possible that following decarboxylation of surface groups, the carbon crystallite to which a carboxylic acid group was attached acquires a negative charge, that is, it behaves as a carbanion. During the decarboxylation process, there may be some surface rearrangement of ionic species with the result that their exact location is difficult to ascertain. Therefore, it would be difficult, as discussed earlier, to determine the interaction energy of N<sub>2</sub> and the adsorption sites.

Bohme and Young (16) have reported that carbanions react with molecular O<sub>2</sub> at room temperature via a variety of steps including electron transfer, hydride transfer and rearrangement. In particular they reported that

the following reaction takes place:



The  $O_2^-$  ion may further react with free radicals giving new products and also with the calcium ion giving calcium oxide. Such a mechanism could explain the decrease in  $N_2$  adsorption following irreversible fixation of oxygen, as explained below. Amounts of oxygen fixed irreversibly on the two samples are given in Table VI. It is noteworthy that the ratio of oxygen fixed to the calcium content is similar for both samples, indicating that about one oxygen atom is fixed for two calcium cations.

The decrease in  $N_2$  uptake after oxygen fixation may be due to a decrease in the number of cationic sites and/or to a weakening of the electrostatic field gradient. Both these factors could contribute to a decrease in specific interaction of  $N_2$  with the surface.

The slight difference in  $O_2$  and  $N_2$  uptake in adsorption Cycle II (Table IV) could be due to the pore wall effect referred to earlier in this paper and/or to the presence of the calcium salt of surface carboxylic acid groups which are not decarboxylated up to the maximum degassing temperature used.

#### ACKNOWLEDGMENT

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