OPTIMIZATION OF CHAR FOR NO_x REMOVAL

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by

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ABSTRACT

Work performed for this study demonstrates that the temperature of treatment and the identity of the treatment gas both strongly impact the surface chemistry of activated carbon. Two commercial activated carbons were treated in either N_2 or H_2 at different temperatures up to $2600^\circ C$. Several techniques - including microcalorimetry, point of zero charge measurements, thermal desorption - were used to provide insight into important aspects of the chemical surface properties. The results show that activated carbons treated at high temperatures (ca. $950^\circ C$) in hydrogen will not react with oxygen and water at ambient temperatures; moreover, surfaces created in this fashion have stable properties in ambient conditions for many months. In contrast, the same carbons treated in an inert gas (e.g., N_2) will react strongly with oxygen and water at ambient temperatures. In the presence of platinum (or any other noble metal), stable basic carbons, which will not adsorb oxygen in ambient laboratory conditions, can be created via a relatively low-temperature process. Treatment at higher temperatures ($>1500^\circ C$) produced increasingly stable surfaces in either N_2 or H_2 .

A structural model is proposed. To wit: Treatment at high temperatures in any gas will lead to the desorption of oxygen surface functionalities in the form of CO and/or CO_2 . Absent any atom rearrangement, the desorption of these species will leave highly unsaturated carbon atoms ("dangling carbons") on the surface, which can easily adsorb O_2 and H_2O . In an inert gas these "dangling carbons" will remain, but hydrogen treatments will remove these species and leave the surface with less energetic sites, which can only adsorb O_2 at elevated temperatures. Specifically, hydrogen reacts with any

highly unsaturated carbons in the surface to form methane.

At temperatures greater than 1500°C (e.g., 1800°C, 2600°C), structural annealing takes place and the consequent growth in the size of graphene layers eliminates the highly energetic dangling carbon sites. The basicity of the surface originates from two types of Lewis base sites: the localized electron pairs at the edges of the graphene layers and the delocalized π electrons on the basal planes.

A hydrogen spillover mechanism was proposed here to explain the low-temperature process for the stable basic carbon. The role played by platinum (or any noble metal) is to produce atomic hydrogen, which spills over onto the carbon surface. This atomic hydrogen hydrogasifies the most reactive, unsaturated carbon atoms at far lower temperatures than molecular hydrogen, thus leading to surface stabilization at relatively low temperatures.

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Chapter 1

INTRODUCTION

Activated carbons are well known to be excellent and versatile adsorbents and catalyst supports due to features such as highly microporous structure, inertness, good mechanical properties, high surface area, and especially variable internal surface structure and properties [1-3]. They are widely used to remove a broad spectrum of dissolved organic [4-5] and inorganic species [6-7] from both gas and liquid streams.

Among these special features of activated carbon, the high surface area and the surface chemical nature are most important for its adsorption properties. The surface of activated carbon consists primarily of basal planes as well as edges of graphitic planes which form the sides of microcrystallites. The basal planes are relatively uniform in nature and no functional groups are expected; therefore, the adsorption process on this type of surface would occur mainly as a result of physical van der Waals interaction [8]. The edges of microcrystallites contain a wide variety of functional groups and, therefore, are heterogeneous in nature. According to the affinity of the proton, these functional groups are usually characterized as acidic surface oxides (e.g., carboxyl, lactone, phenol structures) or basic surface oxides (e.g., pyrone and chromene structures) [9-12]. The population of surface functional groups largely determines the adsorption properties of the activated carbon, especially for polar or polarizable molecules [13]. Although the surface sites associated with functional groups constitute only a

small portion of the total surface area, variations in their chemical nature may produce a marked change in the adsorption capacity and selectivity of the carbon for particular molecules.

Most studies of carbon surface chemistry have focused on acidic surface oxides. Only recently has there been a shift in emphasis to the study of carbon with basic and/or hydrophobic surface properties [14-16]. The interest arises from the need to generate basic surfaces for certain applications. For example, the adsorption affinity of phenolic compounds increases with increasing basicity of the carbon surface [17-19]. The presence of basic surface groups on carbon has also been found to increase the SO₂ adsorption of activated carbon [20, 21]. Finally, it was found that basic carbons are more stable when stored in the environment in the presence of moisture. Acidic activated carbons often lose their adsorption capacity (the “aging effect”) after long storage in the presence of moisture. Since the aging effect has been ascribed to a gradual surface oxidation [22, 23], and it is known that carbons with basic property are much more resistant to surface oxidation, it has been generally accepted that carbons with basic surface properties are much more resistant to aging [24-26]. Removal of aromatic compounds (e.g., phenol) from aqueous streams also requires hydrophobic surface properties. Indeed, adsorption sites on hydrophilic (i.e., acidic) surface can be at least partially blocked by water. Therefore, it is of great application value to prepare carbons with basic and/or hydrophobic surface properties.

By the careful control of the pretreatment condition, many research groups have tried to tailor carbon surface chemistry [27-30]. It is well documented that acid sites are associated with oxygen-containing functional groups. Thus, surface acidity is generated on the surface by

carbon oxidation using a chemical or plasma treatment. Pre-oxidation of the carbon with nitric acid, H_2O_2 , O_3 , or oxygen plasma is known to increase the number of acidic groups on the surface [31-34]. The character of “basic” sites on carbon surfaces is apparently more complex. Indeed, basic surface properties are due not only to the presence of some basic surface functional groups [15, 16] (e.g., chromene and pyrone-type structure), but also to the oxygen-free Lewis base sites on the basal planes, i.e., within the graphene layers that constitute the carbon crystallites [14]. Thus, different strategies are employed to create basic carbons. One common method is to expose the carbon to a high temperature ($>975\text{K}$) in inert gas and thus remove the oxygen-containing groups. For example, activated carbons are known to acquire a basic character upon high temperature heat treatment in an inert atmosphere and subsequent exposure to air below 200°C [35]. Another way is to treat the carbon with special gases to introduce some basic surface oxides on the carbon or to saturate the carbon active sites by other atoms. Treatments with either ammonia [36, 37] or chlorine [26, 38, 39] have been shown to be effective methods to generate basic carbons. The former, carried out typically at $400\text{--}900^\circ\text{C}$, removes the acidic oxygen-containing groups and also introduces basic nitrogen-containing groups onto the carbon surface; the latter can result in the formation of covalent bonds with carbon active sites, thus inhibiting carbon reactivity [40]. Early studies by Walker and coworkers has also suggested that H_2 treatment could minimize the O_2 chemisorption on the carbon surface, and thus maintain the carbon surface in a hydrophobic state [25]. The effectiveness of this approach has been confirmed more recently [26, 41]. However, these H_2 -treated carbon were not characterized in any detail in the literature, and the types of site

responsible for such basic property were not identified. Most prior work focused on heat treatment induced changes in the quantity of carbon active sites, rather than on the changes in their nature.

In this thesis it is demonstrated that the surface chemistry of high surface area activated carbons can be dramatically impacted by the temperature or the identity of the gas employed. Specifically, calorimetric studies show that high temperature (950°C) treatments in inert atmosphere (e.g., nitrogen) can produce surfaces capable of strongly bonding significant quantities of oxygen at 298K. In contrast, treatment of the same carbon in hydrogen can create surface which will not bond oxygen at 300K. Other tests, such as point of zero charge measurements, also show dramatic changes. This profound change in surface chemistry is linked to modifications in the structure of the edge sites. These differences arise from variations in the nature of oxygen groups and carbon gasification processes as a function of the gas employed in pretreatment. In short, high temperature treatment in any gas leads to oxygen group removal as CO or CO₂. It can readily be shown that this should leave some edge carbon atoms with only one or two bonds to the remaining structure. Such “dangling carbons” clearly will be active for adsorption. Treatment in an inert gas leaves the surface in this condition. In contrast, hydrogen treatment result in an additional process: gasification of weakly bond carbon atoms to form CH₄. No “dangling carbons” capable of strong adsorption remain after a high temperature hydrogen treatment. This results in a profound difference in the surface chemistry of high temperature nitrogen-treated and hydrogen-treated surfaces. To wit: High temperature hydrogen treatments remove both oxygen groups and the “dangling carbons” that are created

during the devolatilization of the carbon oxides. In contrast, high temperature treatment in nitrogen (or other inert gases) removes oxygen groups, but does not remove the “dangling carbons”.

Chapter 2

EXPERIMENTAL TECHNIQUES AND PROCEDURES

2.1 Introduction

To characterize the chemical surface properties of activated carbon, we used multiple techniques, including elemental analysis, point of zero charge measurement, temperature programmed desorption, and microcalorimetry. In particular, microcalorimetry is the most effective technique to count and differentiate the active sites on carbon surfaces.

2.2 Sample Preparation

2.2.1 Nitrogen and hydrogen treated carbon

A commercial activated carbon, Norit C-granular, prepared from a wood precursor by phosphoric acid activation (Nc), was used as the starting material for this study. Before any treatment, the sample was ground to $<0.21\text{mm}$ (70 mesh). Since the activated carbons from natural sources all have some metal impurities, a demineralization process is desirable to remove all these possible impurities. Thus, the carbon sample was treated with 5N HCl at 60°C for 3h and then washed with distilled-deionized water until no chloride ions appeared in the distillate solution. These samples were indicated by (aw). Another activated carbon, Calgon BPL, was also chosen as the starting material.

In most of the experiments, the as-received carbon or the demineralized carbon was subjected to a high temperature treatment, either in hydrogen or in an inert gas (e.g., nitrogen).

Table 1 is a list of all samples treated, giving the treatment conditions used (gaseous atmosphere, time, and temperature). Typically 4g of Nc were heated to 950°C in ultra-high-purity N₂ or H₂ at 25°C/min. The gas flow rate was controlled at 150 mL/min. After holding at 950°C for 3 hours, the sample was cooled to room temperature and stored either in ambient air or in an environment that was free of oxygen. The treated samples were labeled as N950 for N₂-treated, or H950 for H₂-treated. Similarly, we made N500 by heating the Nc in N₂ at 500°C; we made H800, H650 and H500 by heating the Nc in H₂ at 800° C, 650 ° C and 500°C. Sample N950/H650 was obtained by hydrogen treatment followed by 950°C nitrogen treatment. To acquire information regarding structural and surface chemical effects at even higher temperatures, Nc, N950 and H950 samples were further heated in a graphite furnace in an inert atmosphere until either 1800°C or 2600°C.

2.2.2 Low-temperature generation of basic carbon surface

Two different carbons were employed in the experiments described below, an Norit C-Granular (Nc), described above, and a carbon-supported catalyst Alfa Aesar, Johnson-Matthey, Stk#38343, containing 1 wt% platinum in highly dispersed form (PtC). The particle sizes of the carbons were very different (PtC: 4 x 8 mesh, Nc<70 mesh), allowing them to be separated by sieving at the completion of all treatments and prior to any characterization tests.

Samples were prepared in quartz boats placed within a quartz reactor (5 cm, i.d.) the same way as above (see Table 1). The PZC of the surface of this carbon (PtC) as it arrived from the supplier showed it to be basic, with a value of 9.8.

H150/PtC, H350/PtC, H425/PtC and H500/PtC listed in Table 1 are mixtures. In each case (except when indicated) the mixtures consisted of 1 part Nc and 2 parts (by mass) PtC. The mixtures were treated in H₂ at 150, 350, 425, and 500°C as noted. After treatment the two carbons were separated by sieving in all cases.

There was also one study conducted (“unmixed”) in which the two carbons were present in the furnace together, but not all were intimately mixed. Three quartz boats, each 4 cm long, were used. The furthest upstream contained only Nc, the middle boat contained a 2:1 mixture of PtC and Nc, and the third boat also contained only Nc. Each boat was separated from the others by a 5 mm gap. These carbons were treated at 500°C in flowing hydrogen (approximately 100 cm³/min, equivalent to a velocity of about 5 cm/min) using the usual procedure.

2.3 Physical Characterization

2.3.1 Surface area and porosity measurement

The surface area and porosity measurements were carried out using physical adsorption of N₂ at -196°C and CO₂ at 0°C in the Autosorb-6 volumetric system (Quantachrome Corporation). The surface areas were calculated from N₂ adsorption data using the BET equation [42]. The micropore and mesopore volumes were obtained using Dubinin-Radushkevich equation [43] and standard T-method, respectively [44].

2.3.2 True density measurement

True density was estimated with helium in a commercial picnometer (Accupic 1330, Micrometrics). The picnometer measures the volume of the particles excluding pores smaller than He atoms. Given the mass of the sample, the density is easily calculated. It is important to note that helium density excludes only closed porosity. Sometimes “true” densities are measured with water or other fluids, and these typically exclude a larger fraction of micropores.

2.3.3 X-Ray diffraction (XRD)

An XRD technique was used to study carbon structural features after treatments at very high temperature. The high-temperature samples used for these experiments were prepared in a graphite furnace in an inert atmosphere. Once the maximum treatment temperature was reached (1800 or 2600°C), it was maintained for 30 min. The XRD analysis were carried out with a Philips MPD diffractometer. Structural parameters L_c and L_a , roughly corresponding to crystallite height and width, were estimated from the (002) and (10) peaks [45-47]; the d-spacing between the graphene layers was determined from the (002) diffraction peak.

2.4 Chemical Surface Characterization

2.4.1 Elemental analysis

The composition of the treated carbon samples was also obtained because trace impurities might play a significant role in the surface chemical properties. The elemental analysis was carried out by using a LECO CHN-600 instrument. The oxygen content was estimated by difference. Before the elemental analysis, all the samples were dried and demineralized.

Since the Norit C-granular carbon is prepared from a wood precursor by phosphoric acid activation, the phosphorus contents were determined by using a Leeman Labs PS3000UV inductively coupled plasma emission spectrophotometer (ICP). Before the ICP analysis, all the sample were dried in vacuum.

2.4.2 Point of zero charge (PZC) measurement

One method to evaluate the electronic properties of carbon surfaces is by measuring the point of zero charge (PZC) [48, 49]. The PZC is the value of pH required to give a solid surface zero net surface charge. In this work, the PZC of each sample was determined using a modified version of a method proposed by Noh and Schwarz [48]. A 10 wt% carbon slurry was prepared by mixing particles of carbon (<0.21 nm) with distilled-deionized water in a plastic bottle sealed under N₂. The pH of the slurry was measured after shaking it for 24 hours. Some distilled-deionized water was subsequently added, and the previous procedure was repeated for slurries of 8, 6, 4, 2, and 1 wt%. A plot of equilibrium pH vs solid weight fraction yields a curve and the equilibrium pH at the plateau of the curve corresponds to the PZC (Figure 1).

2.4.3 Temperature programmed desorption (TPD)

In temperature programmed desorption, a sample is heated in an inert gas environment (e.g., He, N₂), in order to desorb species or decompose functional groups. The amount of gas desorbed as a function of temperature is an indication of both the adsorption strength and the concentration of species originally present [50-52]. In this study, the TPD spectra were obtained in a commercial steady-state transient kinetics apparatus (SSITKA 2000, Altamira Instruments) operated as a conventional fixed-bed reactor connected to a quadrupole mass spectrometer. Helium at 40 mL/min was used as the carrier gas. The heating profile was controlled linearly at 10°C/min to 1100°C. The TPD studies of all the samples were carried out after the microcalorimetric study, so that the oxygen adsorbed and desorbed could be roughly correlated. This procedure also allowed us to establish a correlation between the heats of oxygen adsorption and the forms of desorbed oxygen (e.g., CO, CO₂).

2.4.4 Microcalorimetry

Instrument. Microcalorimetry techniques have an excellent potential for providing unprecedented insight into the structure and surface chemistry of high surface area materials, such as acid catalysts [53], supported metal catalysts [54], as well as carbons [55-57]. They can provide precise information concerning the concentration and nature of the active sites existing on carbon surfaces.

The microcalorimeter used in this work was designed , built and developed under the direction of Dr. Jonathan Phillips. Earlier reports from this lab describe an instrument which can be built with readily available equipment[54, 57, 58]. However, the instrument described earlier

suffered from several limitations. Specifically, it could only be operated near room temperature. Thus, we developed a new design which enabled operation at temperatures as high as 200°C. This permits the study of activated adsorption and ensures that the adsorbed phase is in equilibrium with the gas phase in many cases[59, 60].

The instrument described here (Figure 2) is not only far less expensive than commercial systems, it also has some features that are not found in those systems. For example, the dose volume is at the same temperature as the sample cell/thermopile sandwich. Also, the dose volume consists of two precision Baratron pressure gauges. Thus, pressure readings are available at every instant of time. This provides detailed information regarding the kinetics of adsorption.

This instrument is designed to allow for (1) *in situ* sample preparation either in vacuum or flowing gas at temperature as high as 1100°C, (2) transfer of powder samples (as much as 8 cm³) under vacuum to the sample cell, (3) adsorption with thoroughly equilibrated gas, (4) precise determination of the amount of gas adsorbed, and (5) precise determination of the heat released at temperature ranging from 25 to 200°C.

Samples are prepared in a quartz tube, placed in a tube furnace located outside the precisely temperature-controlled convection oven (Despatch, LND 1-42-3) containing the microcalorimeter. Gas from the gas handling system can be passed through the microcalorimeter and then over the sample, or the sample can be treated under a vacuum of 1×10^{-6} torr. Following completion of the pre-treatment, the sample is transferred to the sample cell simply by tilting the convection oven to an angle of about 30-45° relative to horizontal. The cradle holding

the oven is so designed that the tilting and transfer process can be done by a single individual (Figure 2).

Gas is introduced to the sample in two steps. First, it is metered into the dose volume from the gas handling/vacuum system using a needle valve. The dose volume, which is entirely at the predetermined operating temperature, consists of two high temperature Baratron gauge heads (Model 615AD-MKS Instruments) and the tubing which connects them to (i) the vacuum/gas system and (ii) the sample cell. After a brief period of time (ca. 2 min), during which the gas equilibrates to the system, the second step is performed; gas is allowed into the sample chamber. The dose size can be adjusted so that 15 or more doses are needed to saturate the sample. The adsorption isotherms are obtained by plotting the uptake vs. equilibrium pressure at each dose.

For each dosing process, the adsorption heat released is measured by the thermopiles around the sample cell. Thus, a ballistic curve (heat output vs time) is obtained at the same time. Integrating the area under these ballistic curves gives the quasi-differential heat of adsorption. A plot of differential heat vs adsorption amount can differentiate the active sites on the carbon surface.

To get a qualitative measure of relative adsorption rates, it is standard practice in our laboratory to normalize kinetic data from the pressure gauge. First, all pressure curves were normalized to read between one (the initial dose pressure) and zero (the final/equilibrium pressure reached). Second, the normalized adsorption time was obtained as the amount of time it takes for the pressure to drop to 0.1 on the normalized scale. Finally, the normalized

adsorption parameter (NAP) for each dose was computed by dividing the normalized adsorption time for each dose by the normalized adsorption time of the first dose. A plot of NAP vs coverage yields a reasonable qualitative model of gradual changes in adsorption kinetics, reflecting both chemisorption and mass transfer processes.

Measurements. In contrast to the samples prepared for all the other characterization tests, the samples studied here were not exposed to ambient air until the analysis was completed. Using Nc , Nc(aw) and BPL as starting samples, the different samples (N950, N500, H950, H500, N950(aw), H950(aw), BPL-n950, BPL-H950 etc, as well as a physical mixture of 7 parts (by mass) of Nc and 1 part of PtC in H₂ at 500°C) were prepared *in situ* following the same procedures described earlier, followed by cooling in the same gas to room temperature. Then the samples were gravity-transferred (avoiding air exposure) to the sample cell; they were successively evacuated for 20 h at 10⁻⁶ torr. Known microdoses of O₂ were then introduced. The heat and pressure data were then collected simultaneously.

In ancillary experiments, adsorption of NO on N950 and H950 was also measured by using the same microcalorimeter and the same procedure, except that NO was the dosing gas.

By adding a branch line for a water container to the vacuum/gas handling line, this calorimeter was modified for measuring water adsorption properties of activated carbons. The oven was controlled at 70°C, as was the pretreatment furnace. All the gas handling lines (outside the oven) where water vapor can reach were wrapped with heating tape, and the temperature was controlled below 60°C. The temperature of the water outside the calorimeter

was deliberately maintained at 10°C lower than that of the calorimeter to ensure that no condensation would take place inside any part of the calorimeter itself. By carefully controlling the temperature everywhere and controlling the dosing pressure, known microdoses of water vapor were then introduced sequentially. Prior to the adsorption runs, the water was distilled, deionized and degassed. Other measurements and procedures were the same as described above.

Table 1. Summary of sample treatments.

sample code	starting material	treatment
N500	Nc	N ₂ , 3h, 500°C
N950	Nc	N ₂ , 3h, 950°C
H150	Nc	H ₂ , 3h, 150°C
H350	Nc	H ₂ , 3h, 350°C
H450	Nc	H ₂ , 3h, 450°C
H500	Nc	H ₂ , 3h, 500°C
H650	Nc	H ₂ , 3h, 650°C
H800	Nc	H ₂ , 3h, 800°C
H950	Nc	H ₂ , 3h, 950°C
N950/H650	Nc	N ₂ , 3h, 950°C, then H ₂ , 3h, 650°C
H150/PtC	Nc mixed with PtC	H ₂ , 3h, 150°C
H350/PtC	Nc mixed with PtC	H ₂ , 3h, 350°C
H425/PtC	Nc mixed with PtC	H ₂ , 3h, 425°C
H500/PtC	Nc mixed with PtC	H ₂ , 3h, 500°C
H500/PtC ^a	Nc mixed with PtC	H ₂ , 3h, 500°C
H500/PtC ^b	Nc mixed with PtC	H ₂ , 3h, 500°C
H500/PtC ^c	Nc mixed with PtC	H ₂ , 3h, 500°C
N950(aw)	Nc(aw)	N ₂ , 3h, 950°C
H950(aw)	Nc(aw)	H ₂ , 3h, 950°C
Nc/1800	Nc	N ₂ , 30min, 1800°C
N950/1800	N950	N ₂ , 30min, 1800°C
H950/1800	H950	N ₂ , 30min, 1800°C
Nc/2600	Nc	N ₂ , 30min, 2600°C
N950/2600	N950	N ₂ , 30min, 2600°C
H950/2600	H950	N ₂ , 30min, 2600°C
BPL-N950	BPL	N ₂ , 3h, 950°C
BPL-H950	BPL	H ₂ , 3h, 950°C

PtC: commercial activated carbon-supported catalyst containing 1 wt% Pt;

Nc, BPL: commercial activated carbons; aw = acid wash.

^a With PtC reused twice. ^b With PtC reused three times. ^c PtC:Nc = 1:2 by mass.

Note: for all the samples prepared from Nc, prefix Nc- is omitted.

Figure 1. Graphical representation of PZC (point of zero charge).

Figure 2. Cut-away (a) side-view (b) top-view of microcalorimeter system.

Chapter 3

RESULTS

3.1 Physical Properties

Table 2 shows that the treatments used in this study produce relatively minor changes in the physical (textural) properties of as-received Nc carbons and BPL carbons. The surface areas and pore volumes of Nc generally decrease slightly, while He density increases after treatments in N₂ or H₂. Removal of abundant oxygen-containing functional groups from carbon Nc (Table 4), which contains well developed mesoporosity, apparently causes a structure rearrangement that results in only a small loss of its microporosity. However, the results are opposite for BPL: The surface areas and pore volume increase slightly; in the absence of significant mesoporosity, removal of the much less abundant oxygen apparently exposes some additional micropore surface.

Acid washing, on the other hand, did result in small but consistent decreases in the BET surface area, concomitant increases in the mesopore volume, as well as very significant decreases in the volume of narrow micropores (Table 2). This last finding is somewhat puzzling, but its origin (or confirmation) was not investigated further. The XRD results (Table 3) showed no significant structural changes as long as the treatment temperature did not exceed 950°C. At higher heat treatment temperatures, as expected, this nongraphitizable material clearly became more ordered. This is illustrated in Figure 3 and is reflected in the following facts [61]: (a) At 2600°C there are at least two types of (002) reflections; a very sharp peak superimposed on

the broader peak is indicative of localized graphite-like character in the predominantly amorphous (turbostratic) material. (b) The values of L_c , L_a and d_{002} obtained from the broad part of the double peaks change with treatment temperature. Specifically, the L_c and L_a values reflect a gradual increase in size of the graphene layers once treatment temperatures higher than 950°C are employed, while the concomitant decrease in d_{002} indicates a gradual aligning of the graphene layers. Finally, no major difference in structural changes is evident between N_2 - and H_2 -treated samples; a small but consistent increase in L_a/L_c ratio is observed, especially after H_2 treatment.

3.2 Chemical Properties

Table 4 contains the data on elemental analysis and mass loss for the as-received and treated carbon samples. The starting activated carbon Nc has a relatively high oxygen content due to the presence of a large number of oxygen-containing surface groups. Below 1000°C, H_2 -treatment is more effective than N_2 -treatment in reducing the affinity of activated carbon for O_2 adsorption for either as-received or acid-washed activated carbon Nc (Table 4). The ratio O/C decreases as the severity of treatment increase for both N_2 and H_2 . As for the weight loss, the sample after H_2 -treatment lost much more weight than after N_2 -treatment at the same temperature. It is also obvious that the higher the treatment temperature, the more weight the sample lost.

The N_2 -treated sample clearly contained significant oxygen, whereas the H_2 -treated sample had virtually none. This indicates that the H_2 -treated samples resist reoxidation, at least

at ambient conditions. The chemical analysis indicates another apparent anomaly: H950 has an even lower H/C ratio than the N950 sample. In fact, as the severity of H_2 treatment increases, the H/C ratio in the carbon decreases. This means that high temperature treatment ($>500^\circ\text{C}$) will remove hydrogen from the surface, and hydrogen does not re-adsorb on high temperature H_2 -treated carbon.

Chemical analysis of Nc, N950, H950 in Table 5, in which oxygen content was determined directly, is consistent with Table 4. This indicates that the method to obtain oxygen content by difference is suitable here, and there is no significant impurity except the elements shown in the table. In addition, it is clear that the oxygen content on BPL carbon is much lower than that on Nc. This could explain the different surface properties of these two carbons following similar treatments.

3.3 Electrochemical Properties

Figure 4 and Table 6 summarize the electrochemical properties of the samples. The low values of PZC for the as-received Nc are indicative of the presence of acidic surface groups. After N_2 - and H_2 -treatments, the PZC values become higher. Indeed, for H_2 -treated samples, the surface turned from acidic to basic. For example, after exposing sample N950(aw) to ambient air, its PZC is much lower (6.1) than that of H950(aw) (8.6). From Table 6, it is also clear that as the severity of the H_2 -treatment increases, the PZC value of the carbon increases.

Measurement of PZC as a function of time (Figure 5) shows that H₂-treatment results in the creation of a stable basic surface. It is evident that the PZC value of H950 decreases marginally over a period of 30 days and then is virtually unchanged over the next 150 days.

It was also found that the chemical character of the treated Nc samples was profoundly impacted by the mixing process with PtC. The PZC values of Nc separated from the mixture by sieving are remarkable (Table 6 and Figure 6). After treatment at 500°C the PZC was 9.0, which is as high as that for sample H950 and far higher than that of H500 (5.6). Even after reducing the relative fraction of PtC, from 2 PtC: 1 Nc to 1 PtC: 2 Nc, a virtually identical PZC value (8.8) was obtained. Stability tests also indicate that the surfaces of Nc treated in the mixtures are stable. As shown in Figure 5, there was very little change in the PZC of the Nc removed from the Nc/PtC mix and exposed to ambient laboratory conditions for months. In fact, it is virtually as stable as the H950 sample.

The PZC values of each of the batches of Nc carbon from the unmixed experiment were also measured. The Nc carbon in the upstream boat had a PZC value of 7.0, while the PZC value of the Nc in the downstream boat was 7.5 (Figure 6) and the PZC of the Nc in the middle boat (after separation from PtC) was 9.0. For comparison, the PZC of Nc treated at the same position as the middle boat (with no platinum present at all) was 5.6. It is clear (and indeed remarkable!) that the presence of platinum increases the PZC value even if the metal is not intimately mixed with the carbon.

The PZC of BPL (7.1) indicates that its surface does not have many acidic groups, which is consistent with its low oxygen content. Both BPL-N950 and BPL-H950 are basic due

to further reduction of surface oxygen at high temperature. However, the PZC of BPL-H950 is higher.

3.4 Adsorption of O₂

Nc carbon. Figures 7 and 8 summarize the microcalorimetry data. As expected, the clean carbon surface (N950) with an abundance of free carbon active sites chemisorbs O₂ the most; indeed, when allowance is made for uncertainties in the area occupied by an adsorbed oxygen atom and in the true total surface area of the carbon, it is concluded that the uptake at the highest pressure corresponds to a large fraction of the carbon surface area. Also, when H₂ replaces N₂ in the 950°C treatment, the subsequent O₂ uptake is drastically suppressed. This uptake decreases monotonically with increasing severity of H₂ treatment, and is in agreement with the elemental analysis data (Table 4). The differential heats of adsorption (Figure 7) follow the same trend: the clean carbon surface (N950) possesses the greatest number of high-energy sites (>100 kcal/mol). As the severity of treatment in H₂ increases, the number of sites stabilized by hydrogen increases and/or the high-energy sites are increasingly removed by carbon hydrogasification (see the mass loss data of Table 1).

Figure 9 summarizes the O₂ chemisorption results on H₂-treated samples at elevated temperature. As expected from studies on other carbon materials [62-67], adsorption is seen to be a kinetically controlled process. Very little oxygen chemisorbs at room temperature, whereas the uptake at 150°C is quite significant. Suppression of adsorption by acid washing appears to be more pronounced at the higher adsorption temperature as well. Another notable fact is that all the adsorption takes place with heats of ca. 80 kcal/mol or less (Figure 9a).

Finally, it is important to note the monotonic rise in coverage with O_2 pressure (Figure 9b). In contrast to the behavior of partially stabilized carbon samples, there is no evidence of a pressure reversal in any of the isotherms for samples treated in H_2 at $950^\circ C$.

In contrast to the H_2 -treated samples, N_2 -treated activated carbons adsorb significant amounts of O_2 even at room temperature and they exhibit very similar low-coverage adsorption behavior at 25 and $150^\circ C$ (Figure 10b). In agreement with the results of Figure 10b, O_2 at low surface coverage is seen to probe sites of similar energy at 25 and $150^\circ C$ (Figure 10a). Notable is also the fact that the heat of adsorption on the N950 samples is far greater than that on the H950 samples (Figure 10a). On the other hand, the effect of acid washing is quite similar for the H_2 - and N_2 -treated samples: greater suppression is evident at the higher adsorption temperature (Figure 10b). Also there are some sites on N_2 -treated carbons that only adsorb O_2 at elevated temperatures (activated adsorption). Finally, as illustrated in Figure 10b, a consistent pressure reversal (negative slope) is evident at very low pressures in the isotherm of all N_2 -treated samples.

Plots of NAP vs. surface coverage (Figure 11) show qualitative adsorption kinetics, reflecting both chemisorption and mass transfer processes. The rate of O_2 chemisorption on high energy sites (which are most abundant in sample N950 and least abundant in sample H950) is high and constant. Subsequent to the coverage of these sites, adsorption on the less energetic sites becomes progressively slower and the NAP increases exponentially. In the final stages of adsorption, as the physisorption regime is approached, the adsorption rates increase, as expected. Physisorption is known to be a very rapid process [68]. Thus, the time for pressure

to equilibrate, only in physisorption doses, reflects the time it takes for mass transfer to produce equilibrium throughout the bed, including within pores. Chemisorption is far slower than physisorption. Qualitatively, for chemisorption doses, kinetics is clearly dominated by adsorption rates and not by mass transfer. Finally, it is interesting to observe a reasonable correspondence between the energetics of adsorption (Figures 9a and 10a) and the adsorption kinetics (Figure 11). For example, the high energy sites in sample N950 are covered by ca. 300 $\mu\text{mol O}_2/\text{g carbon}$ (Figure 10a); the chemisorption rate on these sites is seen to be relatively constant and to start to increase only beyond $\sim 300 \mu\text{mol O}_2/\text{g carbon}$ (Figure 11a).

A calorimetric study of a mixture (1 PtC:7 Nc) was performed after treatment in hydrogen at 500°C. As shown in Figure 12, this sample adsorbed far less oxygen (per gram of Nc) than the H500 sample. Moreover, approximately 50% of the oxygen that was adsorbed probably adsorbed on the platinum surface. (The PZC and other measures of Nc properties from mixed samples were performed after separation by sieving. In contrast, this was not feasible for calorimetric experiments.) Once the adsorption on the platinum component was subtracted, it was found that the amount of oxygen adsorbed, on a gram carbon basis, was virtually identical with the amount adsorbed on the H950 sample. Thus, the calorimetric study verified that the Nc prepared in a mix is stable and adsorbs far less oxygen than H500.

In sum, the important differences detected calorimetrically between N950 and H950 samples are (a) the far greater amount of oxygen adsorption on N950, (b) the higher heats of adsorption on N950, (c) the pressure reversal (due to CO evolution) on N950, and (d) the fact

that virtually all oxygen adsorption is activated on H950. On the other side, the nature of activated adsorption (heats, rates, quantity) on N₂-and H₂-treated samples is very similar.

BPL carbon. Oxygen adsorption on BPL carbon follows the same trend as that on Nc carbon. As shown in Figures 13 and 14, there are distinct differences in the amounts and heats of adsorption as a function of the gas employed during high temperature treatment. It is evident both from the heats (Figures 13a and 14a) and the uptakes (Figures 13b and 14b) at 25°C that the N₂-treated sample adsorbs considerably more oxygen with higher heats than the H₂-treated sample. This same difference is found when adsorption is carried out at 150°C. These results show that the N₂-treated sample contains a greater concentration of active sites than does the H₂-treated sample.

It must be noted that, the heats and amounts of oxygen adsorption on the BPL sample are considerably less than those observed for Nc sample. On the Nc sample heats greater than 100 kcal/mol were recorded even up to 300 μmols/ g carbon. On BPL the highest heat was only about 80 kcal/mol O₂. On the other hand, the H₂-treated BPL and Nc carbons are qualitatively similar. For example, in both cases very little oxygen adsorbs at 25°C and the heat of adsorption is extremely low. Also, on both high temperature hydrogen treated samples the amount adsorbed is far greater at 150°C than at 25°C. The reasons for these differences are not entirely clear, but they were not analyzed further in this study.

3.5 Adsorption of NO

As shown above, sample H950 does not adsorb oxygen at 25°C. Yet, it may adsorb NO at 25°C because NO is more reactive in many cases than oxygen [69]. Preliminary tests show that H₂-treated activated carbon will selectively adsorb NO. As shown in Figure 15, the amount of NO adsorbed on the H₂-treated sample is significant at 25°C, whereas the amount of oxygen adsorbed on the same material is almost negligible. There are some surprises in these results which suggest the need for further study. For example, the measured heats of adsorption follow a non-equilibrium pattern. As discussed elsewhere, this can be explained if a linear free energy relationship is not assumed [60]. More NO than oxygen adsorbed on N₂-treated samples as well (Figure 16). Still, the relative selectivity was not as great as that found for the H₂-treated sample.

Figures 17 and 18 give the plots of NAP vs. surface coverage of the NO adsorption on H950 and N950. It is interesting to observe that there is a correspondence between the energetics of the adsorption and the adsorption kinetics. However here we still can not give a satisfying interpretation.

3.6 Adsorption of H₂O

Experiments were conducted to explore the influence of both hydrogen and nitrogen treatments at 950°C on the ability of Nc carbon to adsorb water. Additional experiments were conducted to determine the effect of subsequent mild surface oxidation on the adsorption of water. The mild oxidation experiments were intended to verify the hypothesis that only on acid

sites does true condensation occur. On surfaces without any type of such primary adsorption sites PAS only physical adsorption was detected.

Isotherms (Figure 19a) demonstrate that pretreatment conditions dramatically impact the amount of water adsorbed. Several features require particular attention. First, the amount of water ultimately adsorbed is a function of treatment. There is a dramatic difference between the H_2 -treated sample which adsorbs virtually no water at any pressure and the other two samples which adsorb a considerable amount at high relative humidities. Second, the shapes of isotherms are also a function of treatment. On the H_2 -treated sample water adsorption increases almost linearly with pressure, whereas on the other two samples the uptake increases significantly when a threshold pressure is reached (0.3 p/p_0 on Nc and 0.6 p/p_0 on N950). Third, at low pressures the amount of water adsorbed on the N_2 -treated sample is significantly greater than that on the untreated sample. For values of p/p_0 greater than approximately 0.45 the amount of water on the untreated sample is greater than that on the N_2 -treated sample.

There are also dramatic changes in the heats of adsorption as a function of both the amount adsorbed and the relative pressure for different sample treatment, as shown in Figures 19b and 19c. Most water on the untreated sample adsorbs with a heat slightly greater than 44 kJ/gmol (the heat of water condensation). On the N_2 -treated sample the heat is quite high at first and then very gradually decreases until it too is similar to that of water condensation. The amount of water adsorbed with a “condensation heat” is clearly less on the N_2 -treated sample than on the untreated sample. At even higher coverages on both of these samples measured heats clearly are less than the heat of condensation.

On the H_2 -treated sample the heat-coverage relations show a completely different pattern. Most significant is the observation that no adsorption takes place with the heat of condensation (Figures 19b and 19c). Initially a very small amount of adsorption occurs at heats higher than that of condensation. This is followed by heats substantially below that of condensation.

Further experiments were conducted to determine the effect of deliberately increasing the number of surface acid sites. As shown in Figure 20, when the N950 sample is exposed to flowing oxygen at 150°C for 3h, it adsorbed far more water than when it was not previously exposed to oxygen. Moreover; the value of p/p_0 at which there is a dramatic increase in the amount of adsorbed water is far lower on the O_2 -treated sample (Figure 20a). Figure 21 shows that the amount of water adsorbed on a “mildly oxidized” H950 surface (treated for 3h at 150°C in oxygen) is higher than that on H950 surface.

The heat of adsorption characteristics are also different in a significant fashion. As shown in Figure 20b, far less water is “strongly” adsorbed with (heats higher than the heat of condensation) on the O_2 -exposed N_2 -treated sample; moreover, the highest heats are far lower. It is also noteworthy that most of the adsorption occurs with a heat value less than that expected for condensation.

3.7 Desorption

The TPD results are complementary to the results obtained by calorimetry. Figure 22 shows the desorption spectra for as-received Nc activated carbon. As is typical for high-

surface-area chars [70-72] a broad, low-temperature CO₂ peak and higher-temperature CO peaks are the dominant fingerprint features, reflecting the fact that each additional bond to a chemisorbed atom weakens the bonding of the carbon atom to the graphite-like lattice. The spectra obtained after controlled O₂ adsorption experiments in the calorimeter (and subsequent exposure to room-temperature air) are summarized in Figures 23-26 and Table 7. In agreement with the calorimetric results, they indicate that much more oxygen is adsorbed on the N₂-treated samples than on H₂-treated samples. They also reflect the fact that H950 adsorbed much more oxygen at 150°C than 25°C and that the suppression of O₂ adsorption by acid washing is more pronounced at 150°C for both H950 and N950 (Table 7). There is, however, at best a semi-quantitative agreement between the total oxygen uptakes determined by the two techniques. (The agreement with the data shown in table 4 is even less quantitative because of the inherent limitations of oxygen determination by elemental analysis.) The correlation coefficient is of the order of 0.96. This is not too surprising, given the possibility of O₂ adsorption or desorption during sample transfer and of incomplete complex recovery by desorption at 950°C. For example, it is seen in Table 7 that for samples from the adsorption experiments at 150°C the TPD-derived values are consistently higher, in agreement with the expectation that additional uptake (of weakly bound O₂, see figures 25 and 26) would occur upon room-temperature air exposure.

The CO₂ desorption peak shown in Figure 23 and Figure 24 appears in the same temperature range as the CO peaks. The appearance of this CO₂ is attributed in part to the *secondary* reaction between CO and surface oxygen ($\text{CO}=\text{C}(\text{O})\rightarrow \text{CO}_2$) in the pores of these

high-surface-area carbons [73]. This feature of the desorption spectra is in contrast to the CO₂ peaks shown in Figure 22, Figure 25, and (to lesser extent) Figure 26, where the low-temperature portions of the broad CO₂ peak are evident. The significance of these results is discussed in the next section. Finally, there is a good correlation between the results shown in Figure 10b and the trend observed in Figure 25: Low-temperature CO₂ desorption is most prominent for the same sample (N950/150) for which the low-heat O₂ adsorption at high surface coverage is most evident.

Table2. Summary of textural properties of as-received and surface treated carbons.

Sample code	BET surface area (m ² /g)	DR micropore volume (cm ³ /g)	Mesopore volume (cm ³ /g)	Helium density (g/cm ³)
Nc	1378	0.31	0.55	1.623
N950	1257	0.37	0.50	2.128
H500	1224	0.30	0.55	
H650	1224	0.30	0.55	
H800	1028	0.30	0.40	
H950	1241	0.34	0.49	2.124
Nc (aw)	1319	~0.02	0.67	
N950(aw)	1171	~0.02	0.62	
H950 (aw)	1053	~0.02	0.59	
BPL	1080	0.4745	0.0498	2.182
BPL-N950	1142	0.4940	0.0591	2.196
BPL-H950	1159	0.4984	0.0742	2.192

Table 3. Structural parameters for selected carbons (in Å)

	D_{002}	L_c	L_a	L_a/L_c
Nc	3.78	9.02		
N950	3.78	10.8	30.4	2.8
H950	3.78	10.1	35.4	3.5
Nc/1800	3.68	11.1	41.7	3.7
N950/1800	3.68	10.3	40.5	3.9
H950/1800	3.68	11.3	48.6	4.3
Nc/2600	3.44	18.1	52.0	2.9
N950/2600	3.44	18.1	62.4	3.4
H950/2600	3.44	20.4	72.8	3.6

Table 4. Chemical analyses of as-received and chemically modified carbons^a.

Carbon	wt% C (daf)	wt% H (daf)	wt% N (daf)	wt% O ^b (daf)	H/C (M)	O/C (M)	ash (wt%)	S (wt%)	P (wt%)	wt% loss
Nc	82.3	2.3	0.3	15.1	0.335	0.138	0.70	0.02	0.12	
N500	90.0	2.3	0.4	7.3	0.301	0.061				6.7
N950	94.2	0.6	0.6	4.6	0.076	0.037	0.67	0.01	0.09	8.3
H500	91.8	2.3	0.6	5.3	0.301	0.043				11.2
H650	94.8	1.6	0.5	3.1	0.203	0.025				12.6
H800	97.0	0.9	0.9	1.2	0.111	0.009				17.5
H950	99.0	0.4	0.3	0.3	0.048	0.002			0.07	20.2
H500/PtC	95.5	2.2	0.6	1.7	0.276	0.013				15.5
Cbk	96.3	0.6	0.1	3.0	0.075	0.023				
CbkH950	98.5	0.3	0.5	0.7	0.037	0.005				3.0
Nc(aw)	83.6	2.3	0.4	13.7	0.330	0.122	0.35	>0.01		
N950(aw)	94.8	0.5	0.6	4.1	0.063	0.032	0.34	>0.01		
H950(aw)	98.4	0.4	0.3	0.9	0.049	0.007	0.35	>0.01		
Nc/1800	99.6	>0.01	0.2	0.2	~0	0.002	>0.01	>0.01		
H950/1800	99.7	>0.01	0.2	0.1	~0	0.001	>0.01	>0.01		
Nc/2600	100.0	>0.01	>0.01	>0.01	~0	~0	>0.01	>0.01		
N950/2600	100.0	>0.01	>0.01	>0.01	~0	~0	>0.01	>0.01		

^a wt% = weight percent; daf = dry, ash-free; ^b Obtained by difference.

Table 5. Chemical analyses of as-received and chemically modified carbons (in which oxygen was determined directly).

Sample	wt% C	wt% H	wt% N	wt% S	wt% O	wt% Ash
Nc	82.11	2.72	0.18	0.03	14.97	0.54
N950	93.00	0.67	0.21	0.02	5.12	-
H950	97.46	0.48	0.17	0.01	1.49	-
BPL	88.15	0.33	0.60	0.85	2.66	5.71
BPL-N950	90.97	0.33	0.60	0.87	2.39	-
BPL-H950	90.18	0.30	0.54	0.06	0.34	-

Table 6. Electrochemical properties of as-received and surface-treated carbons.

Sample code	PZC	Sample code	PZC
Nc	2.5	H500/PtC	9.0
PtC	9.8	H500/PtC ^a	8.5
Ptc-Ox	3.6	H500/PtC ^b	8.5
		H500/PtC ^c	8.8
N500	3.8		
N950	5.2	Nc(aw)	3.0
		N950(aw)	6.1
H150	2.5	H950(aw)	8.6
H350	2.7		
H425	3.3	Nc/1800	8.9
H500	5.6	N950/1800	8.8
H650	6.3	H950/1800	8.5
H800	7.5	Nc/2600	7.6
H950	9.0	N950/2600	7.5
		H950/2600	7.2
H150/PtC	2.6		
H350/PtC	3.6	BPL	7.1
H425/PtC	7.0	BPL-N950	8.9

		BPL-H950	9.5
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^a With PtC reused twice. ^b With PtC reused three times. ^c PtC:Nc = 1:2 by mass.

Table 7. Amounts of CO, CO₂ and O₂ calculated from TPD experiments and of O₂ adsorbed in the calorimetry experiments.

Carbon	TPD (μmol/g)			Calorimetry	
	CO	CO ₂	O ₂ equiv.	O ₂ (μmol/g)	
				(a)	(b)
Nc	2444	859	2081		
N950/150	1211	307	913	800	600
N950(aw)/150	777	202	591	450	300
N950/25	757	127	506	550	425
N950(aw)25	533	194	461	390	260
H950/150	324	180	342	250	175
H950(aw)/150	438	120	339	225	165
H950/25	48	31	55	120	25
H950(aw)/25	36	21	39	110	24

(a) Total amount of oxygen adsorbed in the calorimeter.

(b) Oxygen more strongly adsorbed. Calculated by extrapolation of the isotherm's plateau (see

Figures 9b and 10b).

Note: N950/150 is N950 obtained after O₂ adsorption calorimetry experiment at 150°C. All the other samples are designated by the same way.

Figure 3. Representative x-ray diffractograms for activated carbon H950 and carbons obtained after heat treatments at 1800 (H950/1800) and 2600°C (H950/2600).

Figure 4. Mass titration curves for as-received and surface-treated carbons.

Figure 5. Changes in the point of zero charge of H950 and H500/PtC upon exposure to ambient air.

Figure 6. Variations in the point of zero charge (PZC) with treatment temperature (in H_2) for as-received Norit C carbon (▲) and for surface-modified carbon samples in the presence of a Pt catalyst: ■, Norit C mixed with commercial activated carbon containing 1% Pt catalyst (in a ratio of 1;2); ○, Norit C treated in a different boat downstream; ◆, commercial activated carbon containing 1% Pt, previously exposed to concentrated nitric acid at 60°C for 64 h.

Figure 7. Differential heats of oxygen adsorption as a function of surface coverage for surface-treated Nc activated carbons at 25°C.

Figure 8. Oxygen adsorption isotherms at 25°C for surface-treated Nc activated carbons.

Figure 9a. Differential heats of O₂ adsorption at 25 and 150°C as a function of surface coverage for as-received and acid washed H₂-treated activated carbons.

Figure 9b. O₂ adsorption isotherms at 25 and 150°C for as-received and acid washed H₂-treated activated carbons.

Figure 10a. Differential heats of O₂ adsorption at 25 and 150°C as a function of surface coverage for as-received and acid washed N₂-treated activated carbons.

Figure 10b. O_2 adsorption isotherms at 25 and 150°C for as-received and acid washed N_2 -treated activated carbons.

Figure 11a. Plots of the normalized adsorption parameter vs. surface coverage for O_2 adsorption at 25°C for surface treated activated carbon Nc.

Figure 11b. Plots of the normalized adsorption parameter vs. surface coverage for O₂ adsorption at 150°C for surface treated activated carbon Nc.

Figure 12a. Heats of O₂ adsorption as a function of surface coverage at 25°C on as-received and surface-treated carbons.

Figure 12b. O₂ adsorption isotherms at 25°C on as-received and surface-treated carbons.

Figure 13a . Heats of O₂ adsorption on N₂-treated BPL carbon at 25°C and 150°C.

Figure 13b. O_2 adsorption isotherms on N_2 -treated BPL carbon at 25°C and 150°C.

Figure 14a. Heats of O₂ adsorption on H₂-treated BPL carbon at 25°C and 150°C.

Figure 14b. O_2 adsorption isotherms on H_2 -treated BPL carbon at 25°C and 150°C.

Figure 15a. Heats of adsorption of NO and O₂ as a function of surface coverage at 25°C for H₂-treated activated carbon H950.

Figure 15b. O_2 and NO adsorption isotherms at 25°C for H_2 -treated activated carbon H950.

Figure 16a. Heats of adsorption of NO and O₂ as a function of surface coverage at 25°C for N₂-treated activated carbon N950.

Figure 16b. O₂ and NO adsorption isotherms at 25°C for N₂-treated activated carbon N950.

Figure 17. Plot of heat and the normalized adsorption parameter vs. surface coverage for NO adsorption on H950 at 25°C.

Figure 18. Plot of heat and the normalized adsorption parameter vs. surface coverage for NO adsorption on N950 at 25°C.

Figure 19a. Water vapor adsorption isotherms at 70°C for activated carbon Nc and carbons treated in N₂ (N950) and in H₂ (H950).

Figure 19b. Heats of water vapor adsorption as a function of surface coverage at 70°C on activated carbon Nc and carbons treated in N₂ (N950) and in H₂ (H950).

Figure 19c. Heats of water vapor adsorption as a function of relative pressure at 70°C on activated carbon Nc and carbons treated in N₂ (N950) and in H₂ (H950).

Figure 20a. Water vapor adsorption isotherms at 70°C on N950 and O₂ exposed N950.

Figure 20b. Heats of water vapor adsorption as a function of surface coverage at 70°C on N950 and O₂ exposed N950.

Figure 20c. Heats of water vapor adsorption as a function of relative pressure at 70°C on N950 and O₂ exposed N950.

Figure 21a. Water vapor adsorption isotherms at 70°C on H950 and O₂ exposed H950.

Figure 21b. Heats of water vapor adsorption as a function of surface coverage at 70°C on H950 and O₂ exposed H950.

Figure 21c. Heats of water vapor adsorption as a function of relative pressure at 70°C on H950 and O₂ exposed H950.

Figure 22. Temperature Programmed Desorption spectra for the as-received activated carbon
Nc: ○, CO; ●, CO₂.

Figure 23. Temperature Programmed Desorption spectra for the N950 obtained after O₂ adsorption calorimetry experiment at 25°C. ○, CO; ●, CO₂.

Figure 24. Temperature Programmed Desorption spectra for the N950(aw) obtained after O₂ adsorption calorimetry experiment at 25°C. ○, CO; ●, CO₂.

Figure 25. Temperature Programmed Desorption spectra for the N950 obtained after O₂ adsorption calorimetry experiment at 150°C. ○, CO; ●, CO₂.

Figure 26. Temperature Programmed Desorption spectra for the N950(aw) obtained after O₂ adsorption calorimetry experiment at 150°C. ○, CO; ●, CO₂.

Chapter 4

DISCUSSION

4.1 Effects of Chemical Treatments

In this discussion, it is shown that very simple ideas regarding the structure and formation mechanism of surface active sites can explain the myriad observations presented in the preceding chapter. In essence, the model is simple: inert gas treatment removes CO and CO₂ in such a fashion that “dangling carbons” and other highly unsaturated sites are formed. These sites are highly active for strong oxygen, NO and water adsorption. In contrast, hydrogen treatment removes not only oxygen groups, but unsaturated carbons as well. The remaining unsaturated edge atoms are of low activity and hydrophobic. Thus, water and oxygen adsorption are suppressed under ambient conditions.

Consider the chemical surface effects produced in carbon N950. It is well known that essentially all oxygen-containing functional groups are removed during this treatment[74, 75], but the resultant surface is very active and both elemental analysis (Table 4) and microcalorimetry (Figures 7 and 8) show significant oxygen adsorption upon re-exposure to O₂ (air) at room temperature. Indeed, Table 6 and Figure 4 confirm the acidic nature of the stabilized form of this carbon, in agreement with the findings of Lau et al.[75] on aging effects in carbon blacks.

Consider now the chemical surface effects produced in carbon treated with H₂. As the severity of treatment increases, the weight loss increases as well. This could be due to the

removal of carbon atoms by hydrogasification or to the removal of carbon, oxygen, and hydrogen atoms by decomposition of functional groups (e.g., desorption of COOH, C=O, or C-O-C groups). The comparison of H/C ratios (Table 4) is intriguing: treatments in both N₂ and H₂ cause important reductions in H content, but as the severity of H₂ treatment increases, the H/C ratio in the carbon decreases. On the other hand, as this severity increases, the basicity of the carbon increases (Table 6); its affinity for oxygen decreases correspondingly (Figures 7 and 8). Clearly, there is no correlation between the degree of hydrogen incorporation into the carbon and carbon's basicity (or carbon's affinity for oxygen). This finding is consistent with the notion [14] that the main contribution to carbon surface basicity is not from functional groups at the edges of carbon crystallites (where most of the functional groups reside) but from oxygen-free Lewis base sites within the graphene layers (which do not require stabilization by hydrogen).

The chemical surface effects produced from BPL are similar to that from Nc: At room temperature, high temperature N₂-treated sample readsorbs O₂ easily, while high temperature H₂-treated sample is more resistant to O₂ attack. Both of N₂-or H₂-treated BPL do adsorb oxygen (activated chemisorption) at elevated temperature.

4.2 Surface Stabilization Model

The results presented in Figures 5-8 and Tables 4-6 allow us to postulate the mechanisms of surface stabilization that are summarized in Figure 27 and discussed in detail next.

Structure A shows the key features of interest at the edges of a carbon crystallite. Additional acidic oxygen surface groups (carboxyl, phenolic, etc.) [27, 30] are not shown because their fate is thought to be identical to that shown here for the lactone and pyrone groups. Thermal treatment removes oxygen in the form of CO₂ (predominantly at lower temperatures) and CO (predominantly at higher temperatures), leaving unsaturated carbon atoms (“dangling carbons”) at the edges, structure B. The subsequent fate of this highly unstable structure of carbon active sites was proposed as structures C, D, E, and F, which can explain our experimental findings. Structure B, which results from thermal treatment in the inert N₂ gas, include two types of active sites: (i) “dangling carbons” which is single bonded to the basal plane (type I). (ii) edge sites forming an in-plane σ pair, with sp^2 hybridization (type II, in Coulson's terminology [76]). Obviously, sites of type I makes this surface very reactive and, upon subsequent exposure to room-temperature air, O₂ will readily chemisorb on it.

Structure C and D in Figure 27 illustrate the two mechanisms by which surface stabilization is achieved in the presence of H₂. In the more straightforward one, leading to structure D, hydrogen treatment removes the least saturated carbon atoms (“dangling carbons”) from the edges (probably as methane) and also forms stable C-H bonds with the carbon active sites. The fact that hydrogen will interact with carbon at elevated temperatures to produce methane is well documented [77]. The suggestion that hydrogasification takes place in the present case, especially at higher temperatures, is consistent with the large weight losses observed following hydrogen treatments (Table 4); the only new idea in the present model is the

hypothesis that weakly bonded carbons are more readily (selectively) hydrogasified and that the reactive type I sites are thus eliminated under these conditions.

The mechanism leading to structure C is more complex. The need for its contribution to the stabilization of structure B - primarily in H₂ and to some extent in N₂ - is a consequence of two experimental facts: (a) the H/C ratio of the sample treated in H₂ is not larger than that of the sample treated in N₂ at the same temperature (Table 4); (b) no significant increase in microporosity was detected upon H₂ treatment despite the large weight loss, especially at higher temperature (Table 2). Condensation of the graphene layers, e.g., in the presence of the transient CH₂ radicals, is the process that we propose to be responsible for these findings. On one hand, the much greater abundance of such radicals in the presence of H₂ is another explanation for the consequent low concentration of the very active type I sites in structure C. On the other hand, there is evidence in the literature [78] for gasification-induced carbon densification (illustrated in structure C). It is also worth noting that structure C in particular could easily lead to the formation of pyrone-type surface groups [15, 79] upon carbon re-exposure to O₂ at room temperature.

The structure E, and F are proposed to be equilibrium with C and D, particularly in the case that the hydrogen treatment temperature is relative low.

The unusually high differential heats of oxygen adsorption (125 kcal/mol) observed in this study (Figure 7) can also be explained by this model. These heats are probably too high to be explained by the formation of oxygen complexes at “low energy” edge sites, such as type II (Figure 27). In contrast, chemisorption of O₂ at sites of type I could release considerably more

heat than the average heats observed on carbons, especially under nondifferential conditions. As shown in the Figure 27, “dangling carbon” (type I) atoms have already broken two basal-plane bonds and are in a higher energy state than the normal edge atoms with only one broken basal-plane bond. Therefore, they can more strongly bond with oxygen (higher heats) than the edge atoms with two nearest-neighbor basal planes, thus accounting for the higher heats of adsorption observed.

One question remains regarding the heats of oxygen adsorption. There are several possible reasons why such high values (>100 kcal/mol) apparently have not been reported before. While this question is the subject of our continued research, one obvious explanation is that their detection requires the use of both a clean surface and a truly differential microcalorimeter. The contention that both conditions were met in our study is further supported by the results shown in Figure 8 and Figure 28. The anomalous behavior shown in Figure 8 (decreasing “equilibrium” pressure with increasing surface coverage at very low equilibrium pressure) is an artifact which is a consequence of the existence of highly reactive sites on the surface of incompletely stabilized carbons (e.g., N950, N500, H800, and N950/H650, but not H875 and H950). That is, the first microdoses of O_2 introduced in the calorimeter at room temperature, produce some CO by gasification of the highly reactive sites of type I which are thus responsible for the very high heats of adsorption observed. This is illustrated in Figure 28, obtained in a separate experiment. Sample N950 was prepared in a quartz reactor connected to a quadrupole mass spectrometer; after cooling to room temperature, it was contacted with $50\text{ cm}^3/\text{min}$ He containing 5% O_2 . The production of CO, i.e., 2 mol of gas produced for every

mole of gas consumed ($2C^* + O_2 = 2CO$), is indeed consistent with the anomalous low-coverage isotherm behavior shown in Figure 8.

According to this model, the nature of some of the active sites is drastically different after treatments in H_2 vs N_2 . After treatment in H_2 , divalent in-plane sigma pairs at the edges of graphene layers (type II sites, in Coulson's terminology) are thought to be the dominant active sites [76]. After treatment in N_2 , on the other hand, the highly reactive, highly energetic “dangling carbon” sites appear to be dominant. Adsorption of O_2 on these structures is illustrated schematically in Figure 29. The high-energy sites in N_2 -treated samples (Figure 29a) can be titrated either at 25 or 150 °C, but the lower-energy sites (e.g., those that are predominant in H_2 -treated samples) are only accessible at higher adsorption temperatures (Figure 29b). This is true for both as-received and acid-washed Nc and also BPL carbons. Clearly, the characteristics of activated adsorption, in terms of quantity and heat, are very similar on both H_2 - and N_2 -treated samples (Figures 9, 10, 13, 14). This indicates that both surfaces have the same type of lower-energy sites. The difference between them is simply the lack of high-energy sites on the H_2 -treated surface.

One exception in the behavior of as-received vs acid-washed Nc is revealing, however, it may have important practical implications: the acid-washed N950 sample is the least sensitive to an increase in the adsorption temperature (Figure 10). This finding is thought to be evidence for the selective poisoning of the high-energy sites by acid washing. Upon treatment with HCl, strong C-Cl bonds are formed on a portion of the carbon surface and they are left intact by N_2 treatment at 950°C [28]. In contrast, H_2 treatment of acid-washed carbon at 950°C restores

the oxygen chemisorption capacity of this portion of the carbon surface, albeit by creating sites of lower activity.

Further insight and correlating evidence about the nature of carbon active sites of H₂- vs N₂-treated carbons is provided by analyzing the TPD results. In a detailed study of O₂-activated microporous chars derive from a phenol-formaldehyde resin, Zhuang et al.[80-82] observes two characteristic patterns of CO, CO₂ evolution. In one case the leading edge of the dominant CO₂ peak, centered at ~630°C, occurs at temperature below the onset of significant CO evolution. In the other case, the dominant CO₂ peak is centered at a somewhat higher temperature but the key point is that it is completely under the CO evolution peak, similar to the TPD patterns observed by Calo and Hall [73]. Interestingly, they do not discuss these differences, even though Calo and Hall attribute CO₂ evolution in the latter case simply to secondary reactions between CO and surface oxygen. Instead, Zhuang et al.[80] interpreted their CO₂ peaks as evidence for the presence of acid anhydride and lactone groups on the carbon surface. A less prominent low-temperature CO₂ peak, centered at ~260°C, was attributed to the conversion of lactone and acid anhydride groups to carboxyl groups in the presence of moisture.

On the basis of these considerations, our results are thought to indicate, at least in part, the presence of CO- (e.g., carbonyls) and CO₂-yielding C-O surface groups (e.g., lactones). This is supported by the fact that both TPD and microcalorimetry data show the existence of low-energy sites on both the as-received Nc carbon (Figure 22) and the N950 carbons after

O₂ adsorption at 150°C (Figures 25 and 26). In agreement with much of the detailed literature on this topic, the CO₂-yielding sites are seen to be less active than the CO-yielding sites.

Finally, it is important to note that the proposed model is also consistent with the measured properties of all H₂-treated samples. As the temperature of H₂ treatment increases, the quantity of adsorbed oxygen decreases (Figures 7 and 8); the initial heat of adsorption also decreases (Figure 7). This is in agreement with well-known linear free energy correlations: as the temperature of hydrogen treatment is lowered, more and more of the active sites of progressively higher energy (e.g., types I) “survive”. Indeed, the weight loss-which is taken to correlate with the extent of hydrogasification-increases as the treatment temperature increases. The model is also consistent with the chemical analyses (Table 4) which do not show an increase in H/C ratio following hydrogen treatment at increasing temperatures. A temptingly simple alternative model, according to which hydrogen atoms “passivate” all the surface sites by forming C-H bonds, can thus be discarded. At intermediate temperatures (which will depend on carbon reactivity), a trade-off appears to exist. On one hand, the relatively high H/C ratios (e.g., 0.203 for sample H650) suggest that many reactive sites have indeed been passivated (by C-H bond formation). On the other hand, the weight loss, PZC, and microcalorimetry data show that many reactive sites remain on the surface (e.g., from the decomposition of relatively unstable carboxyl groups) which are not hydrogasified and thus susceptible to O₂ readsorption.

4.3 NO Selective Adsorption

The fact that some active sites remain oxygen-free at room temperature could have important practical applications. For example, other compounds with a lower activation energy than O_2 could be selectively adsorbed, in the presence of O_2 , by these sites. Indeed, our results show the amount of NO strongly adsorbed (heat of adsorption $>20\text{kcal}$) at 25°C by a H_2 -treated sample is almost 20 times greater than the amount of O_2 strongly adsorbed. the total amount of NO adsorbed is more than 10 times more than the adsorbed O_2 (Figure 15a). Actually, in the work of Zarifyanz et al.[83], room temperature irreversible adsorption of NO was also shown to occur on a freshly cleaved graphite surface to a much larger extent than adsorption of O_2 . Furthermore, it was also shown that the sample with preadsorbed NO did not adsorb any O_2 . These findings are consistent with the notion that NO not only occupies the active sites attacked by O_2 at room temperature but also adsorbs on (at least some of) the sites that are not occupied by O_2 at room temperature.

4.4 Carbon Basicity

The presence of oxygen on the carbon surface is known to have a profound influence on the behavior of this material as an acid or a base [30]. This in turn is crucial for the effectiveness of carbons as catalyst supports [3] or liquid-phase adsorptions [18]. Recently, it has been confirmed [14] that the alkaline character of solid carbons is dependent not only on the absence of oxygen-containing surface groups but also, perhaps more importantly, on the Lewis base character of the graphene layers in the carbon crystallites. It was of interest, therefore, to analyze the relative roles of those two factors by varying the heat treatment

temperature (HTT) in both N_2 and H_2 over a wide range. Table 6 confirms the fact that carbons treated in H_2 , at temperatures below 1000°C , are much more basic than those treated in an inert atmosphere.

Tables 3 and 4 show that, as the HTT increases, the concentration of (primarily acidic) oxygen functional groups decreases dramatically while the average size of the graphene layers increases to some extent. While no significant structural differences were observed at the same HTT between N_2 - and H_2 - treated samples (Table 3), the extent of growth of graphene layers (L_a/L_c) is consistently higher for the H_2 -treated samples. This finding correlates in general with the somewhat lower O/C ratios and PZC values of the latter samples (Tables 4 and 6).

A surprising and very significant result is the lower PZC value for samples subjected to 2600°C than for those subjected to 1800°C . A similar maximum in the carbon suspension pH as a function of HTT was reported recently by Ishihara et al.[84], who offered no explanation for it. We propose that the following phenomena are responsible for this maximum in carbon basicity at intermediate HTT: (a) At relatively low temperatures, the removal of acidic oxygen functional groups leads to the increasing dominance of the residual basic sites, both the more stable oxygen-containing groups (e.g., pyrone-like structures) and the oxygen -free edge sites (e.g., Type II, see Figure 27) as well as basal-plane carbon sites. (b) At relatively high temperatures (e.g., in excess of 1800°C), where the effect of oxygen-containing basic groups becomes negligible, the observed basicity is a result of “competition” between Lewis-base-type edge sites and Lewis-base basal plane sites. The concentration of the former is known to

decrease with increasing HTT (Table 3). Obviously, then, this appears to have the dominant effect on carbon basicity.

4.5 Carbon Hydrophobicity

This investigation demonstrates that calorimetry can provide clarification of the present understanding of the nature of water adsorption on carbon. Most important, it shows that a calorimeter can be employed to discover the dominant mechanism of water adsorption, as a function of carbon surface chemistry, saturation pressure, temperature, etc. Specifically, the present data suggest there are three modes of water adsorption on carbon, and each can account for a significant amount of adsorption. Moreover, the extent of these types of adsorption observed on any particular carbon surface is clearly a function of the surface chemistry. First, there is chemical adsorption (heats greater than 50 kJ/mol H₂O), which can occur between unsaturated carbon surface sites and water. Second, water “condenses” at primary adsorption sites (PAS) with heats around 45 kJ/mol H₂O. Both of acid oxygen containing groups and the chemisorbed water molecules can be the PAS. As generally agreed, in this step, the hydrogen bonding between the water and PAS, or between water and water play an important role [85]. The steep rise of the isotherm is a function of the number and character of PAS sites, as well as the pore structure. Third, there is physical adsorption with heats around 25 kJ/mol H₂O, in which only weak dispersion interaction occur between water and hydrophobic carbon basal planes. The present set of data from Nc carbons provides evidence

to support the existence of all three types of adsorption. The particular “mix” and extent of each type is shown to be a function of surface pretreatment.

N950. It is particularly instructive to begin with a discussion of water adsorption on the nitrogen treated Norit carbon N950, as adsorption on this sample appears to occur via all three modes. Initial adsorption heats on this sample ($p/p_0 < 0.4$, or coverage < 1 mmol H₂O/g carbon) are high, and clearly consistent with chemical adsorption. It was anticipated that chemical adsorption would occur on this sample, as previous work established that the treatment given leaves a high concentration of highly unsaturated carbon atoms (“dangling carbons”) on the surface. Indeed, the amount of chemically adsorbed water observed in this case is similar to the amount of oxygen which strongly adsorbs on equivalent samples.

Next, there is a plateau in the measured heat of adsorption at about 45 kJ/mol H₂O. This value is virtually identical to that anticipated for heat from condensation around PAS. Thus, following the lead of earlier workers [86], we assign adsorption which occurs at this heat to condensation. In fact, there is a relatively limited amount of condensation that takes place ($0.4 < p/p_0 < 0.7$, or for coverage between 1 and 2 mmol/g carbon). As the initial high temperature treatment removes all oxygen functional groups, it is reasonable to suggest that it is actually adsorbed water molecules which in this case are acting as PAS for condensation. This is not a new concept. Chemically adsorbed water has been proposed to act as PAS by others as well [87]. Still, it is apparent that only a small fraction of the chemically adsorbed water molecules are acting as PAS. Indeed, the ratio of chemically adsorbed to condensed water on this sample

is only about one. In fact, it is generally understood that some acid sites are “better” PAS than others [88, 89].

At high relative pressures ($p/p_0 > 0.7$, or coverage > 2 mmol/ gm carbon) the heat of adsorption clearly is less than that associated with condensation. Low heats of this character are generally associated with simple physical adsorption. In fact, previous groups computing the heats of water interaction with various surface groups indicate that the heats could be less than that of condensation [87, 90]. (The relatively high heat of water condensation reflects the formation of hydrogen bonds.) Thus, we postulate that the low heat processes are a form of physical adsorption.

The clear distinction in the heats of adsorption between “condensation” and “physical adsorption” suggests a distinction in the character of the two processes. It is understood that condensation involves the formation of a three dimensional liquid water phase, nucleated by a primary adsorption site, in the pores with the heat of condensation reflecting primarily hydrogen bonding between water molecules. In contrast, physical adsorption is assumed to be a monolayer structure, thus adsorption energy is determined by weak carbon-water interactions, not water-water hydrogen bonds. The notion that condensation/multilayer adsorption can only take place around special sites (PAS) is generally accepted. In fact, in recent models it has been shown that certain arrangements of PAS can significantly reduce the critical size of a stable water droplet. In particular it was shown that the critical size for near neighbor oxygen functional groups is far less than that around single acid sites [91]. Moreover, in the absence of PAS, critical radii are large, and stable droplets are not expected to form below saturation

pressure. The fact that a significant amount of monolayer water adsorption can take place at low heats does not appear to be generally understood.

One question which naturally arises is the capacity of the Norit C for a monolayer of physically adsorbed water. A calculation based on the measured BET area of the material and the assumption that each molecule requires 25 Å of surface area [92] indicates that the total monolayer capacity of Norit C is more than 10 mmol H₂O/g carbon. This is clearly more than the amount observed.

In the absence of direct heat measurements, that is with only isotherm data, all of the adsorption taking place above $p/p_0=0.4$ might mistakenly be associated with condensation. This may have been done in previous investigations. It is also true that in the existing literature the difference between condensation and physical adsorption is generally not clearly expressed.

Untreated Nc. There are two significant distinctions to be made between N950 and untreated Norit C. First, very little chemisorption occurs on the latter, and second significantly more condensation takes place. There are also similarities. Most important is the fact that physical adsorption dominates in both cases for $p/p_0 > 0.7$.

The calorimetry data also suggests a basis for the “crossover” of the the isotherms of the Norit treated in nitrogen and the untreated material. At low p/p_0 more water is found on the N950 sample because chemical adsorption takes place on it, whereas on the untreated sample, there is almost no active site capable of water chemisorption. On this surface, water can only adsorb on PAS (unremoved oxygen) through hydrogen bonds. From about $p/p_0 > 0.4$ to p/p_0

<0.6 condensation occurs on both materials. As there are more PAS sites on the untreated sample, more condensation occurs on this surface than on the N950 sample. Thus, the total amount of water on the untreated sample surpasses that on N950 sample over this range of partial pressures. At higher p/p_0 values physical adsorption dominates on both samples.

It is assumed here, as elsewhere [93, 1], that the amount of water which will condense is a function of the density of PAS. Complete pore filling is not observed until a minimum PAS density exists. Here we advance a new explanation for this frequent observation. Specifically, it is suggested that complete pore filling will take place in any pore, or pore network, containing a true PAS. Yet, it is clear that for carbons not all pores are connected. Thus, assuming a random distribution of PAS in pores, not all pores and pore networks will contain PAS until a certain apparent “density” of PAS exist. Earlier models implied that PAS needed to have a certain proximity for complete pore filling to occur. This implies that droplets around any PAS have a maximum size. We do not believe this is physically reasonable.

H950. The H₂-treated sample N950 was found extremely hydrophobic. Initially there is a very small amount of chemical adsorption, and this is followed by very, very small amount of physical adsorption. This result was anticipated as several prior studies [94] have shown that high temperature H₂-treated graphites and activated carbons are hydrophobic. and also consistent with our earlier studies of the surface chemistry following hydrogen treatment. Indeed, in earlier studies it was found that the H₂-treated surface was quite basic and had no active sites capable of adsorbing oxygen at low temperatures. Moreover, it was argued that on H₂-treated

surfaces there are two types of basicity: localized less active sites and the basal planes themselves. Thus, not only is no chemisorption of the variety measured on the N950 anticipated, but also it is reasonable to expect that the basal plane basicity will even reduce the extent of condensation in the pores.

Oxygen exposed N950 and H950. The first indication of differences in behavior as a function of O₂ exposure induced modifications in surface chemistry can be seen in the heat of adsorption at low coverages. Water adsorption on the freshly prepared (no O₂ exposure) N₂-treated carbon N950 led to a great deal of strong chemical adsorption of water, whereas, far less water strongly adsorbed on the O₂-exposed N950. This is anticipated as the freshly treated surface has no oxygen groups, while it has a significant amount of unsaturated (“dangling carbons”) edge sites. The initial water reactions are thus anticipated to be chemical adsorptions at these active sites. In contrast, O₂ exposure should result in most of the unsaturated edges becoming saturated with oxygen. Thus, as measured, once in the calorimeter less water will interact in a chemical fashion, and only at weaker unsaturated sites which didn't become oxygen saturated during O₂ exposure at room temperature.

There is also a lower threshold for rapid condensation on the O₂ exposed sample. The threshold is related to the density of primary adsorption sites. This is expected to be initially higher on the O₂-exposed sample, because the surface of this sample contains oxygen groups. In contrast, water introduced to the fresh sample is divided between two duties; chemically adsorbing thus forming primary adsorption sites, and condensing on them. The net effect, is that

at any pressure there are probably fewer PAS on the fresh sample. Another major difference, one with potential practical consequences, is that ultimately far more water adsorbs on the O₂-exposed sample. Possibly the acid groups formed from adsorbed oxygen make stronger primary adsorption sites.

The impact of surface chemistry is also evident in the contrast between adsorption on H₂- and N₂- prepared Norit C. Freshly prepared H₂-treated material adsorbs virtually no water. After “mild oxidation” at 150°C, a sample adsorbs significant more water; although, there is still no “threshold” for rapid condensation. Again, these observations are consistent with the model and expected surface chemistry of this carbon. H₂-treated Norit C is known to have virtually no oxygen groups. Also, the unsaturated edge sites are known to be “inert” at low temperatures, but are capable of adsorbing oxygen at elevated temperature as shown by prior calorimetric studies. On high temperature N₂-treated Norit C, highly unsaturated (“dangling carbons”) edge sites, which adsorb oxygen rapidly at low temperature, are formed. These studies show that the edge sites on Norit C following H₂ treatments are far less unsaturated, and hence oxygen adsorption on these surfaces requires activation. Thus, high temperature oxygen treatment is required to create acid-oxygen groups on H₂-treated Norit C. Such sites are needed to act as PAS for water adsorption at 300 K. However these sites on H950 are much less than that on N950.

4.6 Low-Temperature Generation of Basic Carbon Surfaces by Hydrogen Spillover

Perhaps the most significant result of the present work is the empirical finding that stable basic carbons can be produced at far lower temperatures in the presence of platinum than in its absence. The PZC studies demonstrated that the basicity of the Nc carbon treated in a mixture with platinum-containing carbon (PtC) is always higher than that of the Nc carbon treated at same temperature in the absence of noble metal. In fact, the PZC values of the Nc carbon treated in the mixtures were found to be equivalent to that of the Nc carbon treated at temperatures at least 400°C higher in the absence of platinum. Also, microcalorimetric and long-term PZC studies showed that Nc carbon gains stability against readsorption of oxygen at far lower temperatures when some platinum is present in the mixture.

Other findings are consistent with the suggestion that platinum (or another noble metal) is a key ingredient required to lower the temperature at which stable basic carbons are formed. First, PtC carbon, a high-surface-area carbon material containing platinum particles dispersed on its surface, becomes basic and stable after hydrogen treatments at remarkably low temperatures. Second, even the Nc carbon that is not in intimate contact with platinum-containing carbon becomes basic at lower temperatures than Nc Carbon Treated neat.

Earlier work suggests an explanation for the action of the platinum [95-97]. It is postulated that platinum particles dissociate hydrogen molecules, creating hydrogen atoms that “spill over” to the carbon surface, both via surface and gas phase diffusion [98], hydrogasifying the most reactive surface carbon atoms (Figure 30). That is, the hydrogen atoms remove carbon atoms (probably as methane) that are left in a highly unsaturated state [76] due to the thermal removal of neighboring carbon atoms, as CO₂ or CO. The following two-step process is thus

hypothesized to take place during the hydrogen treatment of Nc carbon mixed with PtC at 500°C. First, the Nc carbon loses most of its oxygen as CO₂ (and some CO) owing to thermal decomposition of the surface oxygen groups (a process possibly accelerated in the presence of hydrogen atoms). Subsequently, hydrogen atoms generated by the platinum “hydrogasify” the highly unsaturated carbon atoms that are left behind by this thermal process.

The above model suggests that the difference between Nc treated neat in hydrogen at 500°C and Nc treated in the presence of platinum at the same temperature is solely the number of residual highly reactive carbon atoms on the surface. The same Nc treated in H₂ in the presence of platinum will have very few such sites, while Nc treated without platinum present will have a significant number of highly unsaturated carbon atoms. These sites in the sample treated neat quickly adsorb oxygen upon air exposure at room temperature, returning the surface to an acidic condition. In contrast, on Nc treated with platinum present all unsaturated carbon atoms that remain are capable of adsorbing oxygen only at elevated temperatures. Indeed, it has long been known that on some carbon active sites oxygen will not adsorb at temperatures of less than 300°C [74].

There are other possible hypotheses that might explain the role of H atoms in stabilizing the surface. Indeed, it has been shown previously that high temperature H₂ treatment (e.g., H950) accomplishes three tasks: (i) it removes surface oxygen; (ii) it stabilizes some of the reactive carbon sites by forming stable C-H bonds; (iii) it hydrogasifies the most reactive carbon atoms. Data in Table 4 and Figure 12 and 5 indicate that the third process is the most significant when hydrotreating in the presence of platinum, as postulated. First, sample H500/PtC exhibits

initial heats of O₂ adsorption that are comparable to those of sample H950 and lower than those of sample H500 (Figure 12a), suggesting that oxygen adsorbs on sites similar to those found on the former. There is no evidence of adsorption on highly reactive sites. Second, the extent of room temperature O₂ adsorption of sample H500/PtC is much lower than that of samples H500 and N500 (Figures 12b and 8). Third, the weight loss during treatment of sample H500/PtC is higher than that of samples N500 and H500 and consistent with gasification. All these observations are consistent with the postulate that at 500°C H atoms generated by spillover are effective at removing highly reactive carbon atoms. It is concluded that experimental evidence supports the postulate that low-temperature stabilization in the presence of platinum occurs primarily by the hydrogasification of the most reactive carbon atoms (“dangling carbons”).

It remains unclear, however, whether a secondary action of hydrogen atoms is to increase the rate of decomposition of oxygen-containing surface groups. The results are not conclusive. As noted above, sample H500/PtC has a basicity and stability very similar to that of H950, yet its oxygen content is significant. This result does not support an acceleration of oxygen removal by hydrogen atoms. In contrast, the oxygen content of H500/PtC is significantly lower (by a factor of 3) than that of H500. This latter observation could be interpreted as evidence that hydrogen atoms enhance surface oxygen removal. Nevertheless, it is possible that the difference in oxygen content between H500 and H500/PtC can be traced to the fact that only the former sample had a significant number of highly reactive carbon atoms following treatment and that subsequent air exposure resulted in higher oxygen uptake prior to elemental

analysis. This interpretation is certainly supported by the calorimetric results, which show that H500 adsorbs significant amounts of oxygen whereas H500/PtC does not.

Figure 27. Proposed model for the stabilization of carbon surfaces upon heat treatment (Δ) in N_2 (inert gas) and H_2 . For simplicity and illustrative purposes, only two types of oxygen surface groups (pyrone and lactone) and two types of carbon active sites are shown. These two types are in the order of increasing stability: (i) type I, “dangling carbon” sites (with only one nearest neighbor basal plane carbon); (ii) type II, divalent in-plane σ pairs, $\text{Ar}-\bullet*$ (where $*$ represents a localized π electron). Structures B is formed in N_2 , while structures C, D, E and F are formed in H_2 .

Figure 28. Mass spectrometric analysis of gases evolved upon *in situ* exposure of sample N950 to O₂ at room temperature (5% O₂ in He at 1 atm).

Figure 29. Proposed model for the adsorption of O_2 at carbon active sites of different nature and stability: (a) low-temperature adsorption on highly energetic sites of type I (“dangling carbon”); (b) high-temperature adsorption on less energetic sites of type II (divalent in-plane σ pairs).

Figure 30. The graphical representation of hydrogen spill over model.

Chapter 5

CONCLUSIONS

The influence of two treatment parameters, temperature and gas identity, on the surface chemistry of activated carbons was clarified with the help of a wide variety of analytical techniques. It is shown that both the nature and the number of active surface sites can be manipulated by adjusting these two parameters.

Below 1000°C, gas identity was found to be crucial. Treatment in N₂ at 950°C removes the oxygen functional groups, leaving the surface with at least two types of sites: (a) highly energetic “dangling carbon” sites, capable of adsorbing oxygen, and then H₂O at room temperature and (b) graphene layer edge sites which only adsorb oxygen at elevated temperatures. Treatment in H₂ at 950°C not only removes oxygen, but also remove “dangling carbons”, leaving a stable basic surface nearly free of very active sites and thus incapable of adsorbing O₂ and H₂O at ambient temperature.

The removal of oxygen in the form of CO and CO₂ during high-temperature N₂ treatment leaves unsaturated carbon atoms at crystallite edges; these sites are very active for subsequent oxygen adsorption. In contrast, high-temperature H₂ treatment accomplishes three tasks: (a) it also removes surface oxygen; (b) it stabilizes some of the (re)active sites by forming stable C-H bonds; (c) it gasifies the most reactive unsaturated carbon atoms. The relative contributions of these three effects depend on the temperature of H₂ treatment.

Treatment at higher temperatures ($>1500^{\circ}\text{C}$) produced stable surfaces in either N_2 or H_2 . Structural annealing takes place at these temperatures and the consequent growth in the size of graphene layers eliminates the highly energetic sites. Both PZC and XRD measurements indicate that this growth is only slightly more favorable in H_2 than in N_2 . Curiously, however, the basicity of the surface goes through a maximum with increasing heat-treatment temperature. This finding suggests that, of the two types of Lewis base sites, the localized electron pairs at the edges of the graphene layers are more important than the delocalized π electrons on the basal planes.

In the presence of platinum (and most likely other noble metals), capable of creating and spilling over hydrogen atoms, stable and highly basic surfaces can be produced at temperatures of 500°C or less.

In sum, an oxygen free, highly basic, hydrophobic and stable surface of activated carbon can be created at 950°C in H_2 , or at relatively low temperature treatment of carbon mixed with a noble metal. These carbons hold potential commercial value, not only because they can be shipped and stored without any concern for loss of properties ('aging effect'), but also because they have unique and tailorable adsorption properties, such as selective adsorption of NO in the presence of O_2 , or enhanced capacity for phenol adsorption from solution. Furthermore, they may contain an unusual energetic distribution of active sites, which may have new chemical and catalytic applications.

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PUBLICATIONS

A. Refereed Publications in Journals

Menéndez, J.A., Phillips, J., Xia, B. and Radovic, L.R., "On the Modification and Characterization of Chemical Surface Properties of Activated Carbon: In the Search of Carbons with Stable Basic Properties." *Langmuir* **12**, 4404 (1996).

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B. Presentations at Conferences, Symposia, etc.

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