Effect of Pretreatment on Surface Area, Porosity, and Adsorption Properties of a Carbon Black

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A high surface area carbon black was given a high temperature treatment at 1223 K under either H_2 or Ar to remove sulfur contaminants (1.3 wt % S) and oxygen-containing functional groups from the carbon surface. One of the carbon samples was cooled in H_2 from 1223 to 300 K to leave chemisorbed hydrogen on the surface, while another was oxidized by HNO_3 to create new oxygen-containing groups on its surface. These carbon samples, prepared by different pretreatments and later used as supports for Pd catalysts, were characterized by H_2, O_2, and CO adsorption and heat of adsorption (Q_{ad}) measurements at 300 K, N_2 physisorption, X-ray diffraction, and transmission electron microscopy. Either high-temperature treatment effectively removed sulfur from the carbon but did not alter its adsorption properties, whereas the presence of oxygen groups significantly enhanced oxygen adsorption at 300 K after a typical catalyst reduction procedure. The Q_{ad} values for the reversible adsorption of hydrogen, oxygen, and carbon monoxide at 300 K on these carbon supports were 3.8 ± 0.8, 0.6 ± 0.5, and 1.4 ± 0.5 kcal/mol, respectively, while the heat of irreversible oxygen adsorption on the HNO_3-oxidized carbon was 27 kcal/mol.

Introduction

The presence of some oxygen and hydrogen is typically associated with carbon blacks, and they may also contain sulfur, chlorine, and nitrogen, all of which are introduced during the manufacturing process, subsequent treatments, or storage. These heteroatoms may be present at edges and corners of graphitic planes or other defect sites, which are the main adsorption and reactive sites on carbon, and hence may modify their surface properties and behavior. The presence of these surface compounds determines the applications of carbon blacks in rubber, plastics, and paint industries, the lubricating properties of graphite, their use as a moderator in atomic reactors, and their adhesion to plastic matrices in carbon fibre composites.[1,2] The presence or absence of these surface groups can also modify the properties of carbon as a catalyst support, but less is known on this subject.[3–9]

In this study a turbostratic carbon black with 0.36% ash and 1.3% S was heat treated at high temperatures in H_2 or Ar to remove sulfur and surface oxygen groups, and one heat-treated carbon black was then oxidized by HNO_3 to examine the effect of reintroducing oxygen groups on surface adsorption characteristics. The adsorption characteristics of these carbons were then determined after typical catalyst pretreatment procedures and compared to the original carbon which was not heat treated as well as to a low surface area graphite. These carbons were handled anaerobically during preparation and prior to adsorption experiments because exposure to atmospheric air can cause changes in the surface groups and hence the properties of carbon supports.[2,6–10] Both the irreversible and reversible uptakes of H_2, O_2, and CO were measured, and the integral heats of adsorption of these three gases were determined at 300 K because little information about these latter parameters exists. The surface areas and pore size distributions of these carbons were determined using N_2 adsorption at 77 K, while X-ray diffraction (XRD) was used to obtain average crystallite sizes and interlayer spacings. These carbons had been previously characterized using diffuse reflectance FTIR spectroscopy to determine the types of surface oxygen-containing groups present.[11]

Experimental Section

Preparation of Carbons. Black Pearls 2000 (BP2000, Cabot Corp.), a carbon black with a specified surface area of 1475 m^2/g, an ash content of 0.36%, and 1.3 wt % sulfur, was used as the starting material. The inorganic impurities in this carbon black are given in Table 1. This carbon black was given different pretreatments to remove sulfur and change the chemical nature of the carbon surface. The more reactive sulfur in carbon blacks can be removed as H_2S by heating in H_2 at temperatures ≥973 K[12] and as CS_2 and elemental sulfur

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Table 1. Chemical Analysis of BP2000 (C-AS IS) Excluding C, H, N, O

element	weight basis[a]	atomic basis
S	1.3%	0.5%
Si	34 ppm	15 ppm
Al	34 ppm	15 ppm
Ti	<0.65 ppm	<0.2 ppm
Fe	50 ppm	11 ppm
Mg	4.3 ppm	2.1 ppm
Ca	978 ppm	293 ppm
Mn	0.84 ppm	0.2 ppm
Na	83 ppm	43 ppm
K	0.9 ppm	0.3 ppm
P	1.6 ppm	0.6 ppm

[a] Determined at the Materials Characterization Laboratory, The Pennsylvania State University . Total ash content was 0.36%.

under vacuum or an inert gas at temperatures of 1273 K,[2] though some residual sulfur is known to exist in cokes even after exposure to temperatures as high as 1693–2673 K.[13] A high-temperature treatment (HTT) under flowing H_2 or Ar (75 sccm) for 16 h at 1223 K was used to decrease the level of sulfur impurities in the carbon, and this procedure also removes oxygen from the carbon surface.[12,14] These samples are designated as C-HTT-H_2 and C-HTT-Ar, respectively. The C-HTT-H_2 and C-HTT-Ar samples were cooled from 1273 to 300 K under the pretreatment gas; hence, the C-HTT-H_2 sample had chemisorbed hydrogen on its surface.[1,2] These carbon samples were transferred without air exposure to a N_2-purged glovebox where they were stored. The C-HNO_3 sample was prepared by boiling a portion of the C-HTT-Ar sample in 15.8 N HNO_3 for 6 h. After aqueous washes and filtration until the filtrate became clear with a neutral pH, the C-HNO_3 sample was dried overnight in an oven at 120 K and subsequently stored in a N_2-purged glovebox. The as received BP2000 carbon black will be referred to as the C-AS IS sample. The pretreatments given to the BP2000 carbon to create the different carbon samples are summarized in Table 2.

Gas Adsorption Experiments. Volumetric adsorption measurements were made using one of two stainless steel systems with either a turbomolecular pump (Balzers TSU 172) or an oil diffusion pump (Edwards Diffstak Model 63), each capable of achieving a dynamic vacuum below 10^{-6} Torr at the sample location.[15] Gas pressures were measured using either a Texas Instruments Model 145 precision pressure gage (±0.01 Torr) or a Baratron pressure gauge (±0.05 Torr). The H_2, He, and O_2 (99.999%, MG Ind.) and CO (99.99%, Matheson) were further purified by flowing them through drying tubes (Supelco), and the He and H_2 were also passed through Oxytraps (Alltech Assoc.). Gas flows were controlled by Tylan mass flow controllers.

Approximately 0.1–0.2 g of each carbon sample was initially heated to 393 K under a flow of 50 sccm He and held at 393 K for 1 h before being heated to 573 K and held in a flow of 50 sccm H_2 for 2 h. The carbon was then evacuated at 573 K for 1 h and cooled under vacuum to 300 K, the adsorption temperature. This pretreatment procedure was used since it was the pretreatment given to the Pd catalysts made with these carbon blacks as a support.[16] H_2, O_2, and CO isotherms were measured at 300 K in the pressure range 2–300 Torr, and the irreversible and reversible uptakes of each gas were determined using a dual isotherm technique with a 30 min evacuation at 300 K between the isotherms. Typically the H_2 uptake on the carbon was measured first, followed by a 1 h evacuation at 573 K, and then O_2 uptakes at 300 K were determined. The carbon sample was then pretreated again under H_2 using the previously outlined procedure after which CO uptakes were determined. H_2 and O_2 uptakes were also determined on the low surface area (22 m^2/g) Grafoil sample (Union Carbide), after treatment in H_2 at 573 K.

Pore Size Distribution. Nitrogen adsorption and desorption measurements were made using an automated gas sorption analyzer (Coulter Omnisorp 100 CX) on carbon samples previously characterized by H_2, O_2, and CO adsorption. About 0.05–0.1 g of each sample was degassed at 623 K for 2–3 h until the pressure was about 2×10^{-5} Torr, after which N_2 adsorption and desorption isotherms were obtained at 77 K using a continuous flow method in which N_2 (99.99%, MG Ind.) was continuously dosed to the sample at a very low flow rate using a mass flow controller. The volume of gas adsorbed by the sample was calculated by integrating the flow rate over time and subtracting the dead space volume, which was determined using He (99.999%, MG Ind.). Adsorption isotherms were measured up to saturation pressure and desorption isotherms were obtained down to a N_2 partial pressure of 140 Torr.

X-ray Diffraction. XRD measurements were made ex situ using an automated Rigaku Geigerflex diffractometer with a Cu Kα radiation source and a graphite monochromator. Approximately 0.02–0.05 g of each carbon black and Grafoil sample, previously used for gas adsorption and stored in a desiccator, was scanned from 2θ values of 5–80° at a rate of 4°/min. Scanning was also carried out around each peak at lower rates of 0.5–2°/min in order to obtain more well-defined peaks. Crystallite size parameters L_c and L_a were calculated from the line width of the C (002) and C (10) peaks, respectively, using the Scherrer equation with Warren's correction—$d = K\lambda/\{\beta^2 - B^2\}^{1/2} \cos\theta$—with a value of either $K = 0.9$ for L_c or $K = 1.84$ for L_a,[17,18] $\lambda = 1.542$ Å, and values of 0.17° and 0.22° at 2θ values near 20° and 43°, respectively, for the instrumental line broadening, B. Finally, the interlayer spacing, d_{002} was calculated using the formula $d_{002} = \lambda/2 \sin\theta_{002}$. The limitations of these calculations are discussed elsewhere.[19]

Transmission Electron Microscopy. TEM measurements were made ex situ on samples of these carbon blacks after impregnation of $Pd(AcAc)_2$ dissolved in THF, evacuation, and reduction at 573 K. A Philips 420T transmission electron microscope (spatial resolution ~0.4 nm) was used at an operating high tension voltage of 120 kV. The samples were ultrasonically dispersed in acetone and a drop of this solution was placed on a 400-mesh, carbon-coated copper grid obtained from Structure Probe Inc. (West Chester, PA), then evaporated under a heat lamp. The micrographs were typically taken at magnifications of 135 000×–250 000×, and diffraction patterns were also taken using the selected area electron diffraction method in which the incident beam on the specimen is made as nearly parallel as possible so that the central spot and any crystal diffraction spots are sharp.

Heat of Adsorption Measurements. Energy changes during reversible and irreversible adsorption of H_2, O_2, or CO at 300 K were determined using a modified Perkin-Elmer DSC-2C differential scanning calorimeter. The gas handling system allows switching between a portion of the carrier gas (Ar or He) and the adsorbate (H_2, O_2, or CO). Ar and He (99.999%, Liquid Carbonic) and O_2 and H_2 (99.999%, MG Ind.) were purified by passing each through a drying tube (Supelco, Inc.), and the Ar, He, and H_2 were purified further by flowing each through an Oxytrap (Alltech Assoc.). Further details regarding the calibration and operation of the DSC are given elsewhere.[20,21]

The heats of adsorption of the various gases were measured on samples of carbon black and Grafoil after their use in adsorption experiments, and these values were also obtained for a fresh sample of C-HNO_3. Approximately 3.5 mg of each sample was loaded into the DSC sample cell, and the same weight of nonporous glass beads was placed in the reference cell. The sample and reference were given the pretreatment

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Table 2. Pretreatments Used for Carbon Black Samples

C sample	pretreatment	wt %				air exposure
		S	C	H	N	
C-AS IS	none; BP2000[a] as received	1.3	97.73	0.36	0.77	yes
C-HTT-H_2	heat BP2000[a] in 75 sccm H_2 for 16 h at 1223 K	0.1	*b*	*b*	*b*	no
C-HTT-Ar	heat BP2000[a] in 75 sccm Ar for 16 h at 1223 K	0.1	98.42	0.15	1.34	no
C-HNO_3	boil C-HTT-Ar in 15.8 N HNO_3 for 6 h in air	0.1	89.88	0.75	0.79	yes
Grafoil	heat Grafoil[c] in He and then in H2 for 4 h at 1273 K	<0.05				yes

[a] Black Pearls 2000 carbon black (1475 m^2/g) from Cabot Corp. [b] Not analyzed. [c] Grafoil (22 m^2).

used prior to chemisorption measurements, except that it was carried out in a gas mixture of 20% H_2/80% Ar at 40 sccm and a purge with 45 sccm of an Ar/He mixture (77% Ar) for 1 h at 573 K was used rather than evacuation. After this pretreatment, the samples were cooled to 300 K, a step change was made to a constant H_2, O_2, or CO partial pressure (between 75 and 125 Torr), and the exotherm due to gas adsorption was recorded as a function of time and integrated to give the total energy change. After the initial gas exposure, the sample was purged with pure He or Ar at 300 K for 1 h to remove the reversibly adsorbed gas, and the gas was reintroduced to measure the energy change for reversible adsorption. The difference between the total energy change and the reversible energy change was used to obtain the energy change for any irreversible uptake. Typically the heat of H_2 adsorption was measured first on a given sample, then a 1-h Ar purge at 573 K was used and the heat of O_2 adsorption was measured next. Finally, the heat of CO adsorption was measured after once again pretreating the sample.

Thermogravimetric Analysis. A portion of the C-HNO_3 sample (0.04 g) previously used in chemisorption was loaded into a quartz bucket attached to a Cahn microbalance, and heated under 100 cm^3/min of He (99.999%, MG Ind.) at 5 K/min from 573 to 1273 K, and the weight loss was monitored. The experimental setup is described in detail elsewhere.[22]

Results

BET Surface Area and Pore Size Distributions. Type I N_2 isotherms, with the steep initial branch at lower pressures indicating the presence of micropores, were obtained for the carbons; however, a hysteresis loop characteristic of capillary condensation indicated the presence of mesopores.[23,24] A typical isotherm is shown for the C-HTT-Ar sample in Figure 1a. For all samples, the hysteresis loop between the adsorption and desorption branches was similar to type B or H3, which has been associated with slit-shaped pores occurring in aggregates of platelike particles.[25] Surface areas and pore volumes were calculated using different models which are appropriate for the combined presence of micropores and mesopores, as discussed below. The IUPAC definitions of micro-, meso-, and macropores are as follows: micropores have width $w < 20$ Å, mesopores have $20\ \text{Å} \le w < 500$ Å, and macropores have $w \ge 500$ Å.[25]

The BET plots were linear in the P/P_0 region from 0.05 to 0.3 and BET surface areas were calculated using 16.2 Å^2 for the cross-sectional area of an adsorbed N_2 molecule. *t* plots were obtained by plotting the volume adsorbed vs the statistical film thickness of adsorbate, and they indicated the presence of both micropores and macropores.[26] The statistical thickness was derived from the surface area of a model, nonporous, carbon–nitrogen system, and a typical *t* plot is shown for the C-HTT-Ar sample in Figure 1b. The slope of the second linear region was used to obtain the surface area contained in mesopores and macropores, and the intercept at $t = 0$ was used to obtain the micropore volume. The micropore area was calculated by subtracting the meso- and macropore contribution from the BET surface area. The MP method, which is an extension of the t-plot method, was also used to obtain micropore size distributions and micropore volumes from the thickness plot.[27] A differential mesopore size distribution plot was obtained based on the Barrett et al. treatment of the Kelvin equation using the desorption isotherm.[28] A cylindrical pore model with open-ended pores and the absence of a pore network is assumed in this approach, hence this distribution must be regarded with caution.

The Dubinin-Radushkevich (D–R) equation, which is an adaptation of the Polanyi–Dubinin equation addressing adsorption in small pores, was also used to obtain estimates of micropore volume.[29] The D–R plots deviate from linearity, they are convex to the abscissa, and they display an upward turn due to multilayer adsorption and capillary condensation in mesopores as saturation pressure is approached,[23] as shown in Figure 1c; thus the extrapolation to obtain micropore volume must be corrected for mesopore adsorption, which contributes to the uptake at lower pressures.[30] The Horvath and Kawazoe method, which is based on Lennard-Jones potential functions, was used to obtain a micropore size distribution.[31] The specific surface areas and pore volumes calculated from the different methods are listed in Table 3.

The BET surface areas of C-AS IS and C-HTT-Ar were quite similar; however, the C-HNO_3 catalyst had a lower surface area, as expected from earlier work,[4,32] although a HNO_3 treatment has also been reported to increase surface area.[33] The surface area of C-HTT-H_2 is expected to be fairly similar to the C-HTT-Ar since similar heat treatment temperatures were used. The decrease in surface area for C-HNO_3 is accompanied by a decrease in both micropore and wider pore volumes,

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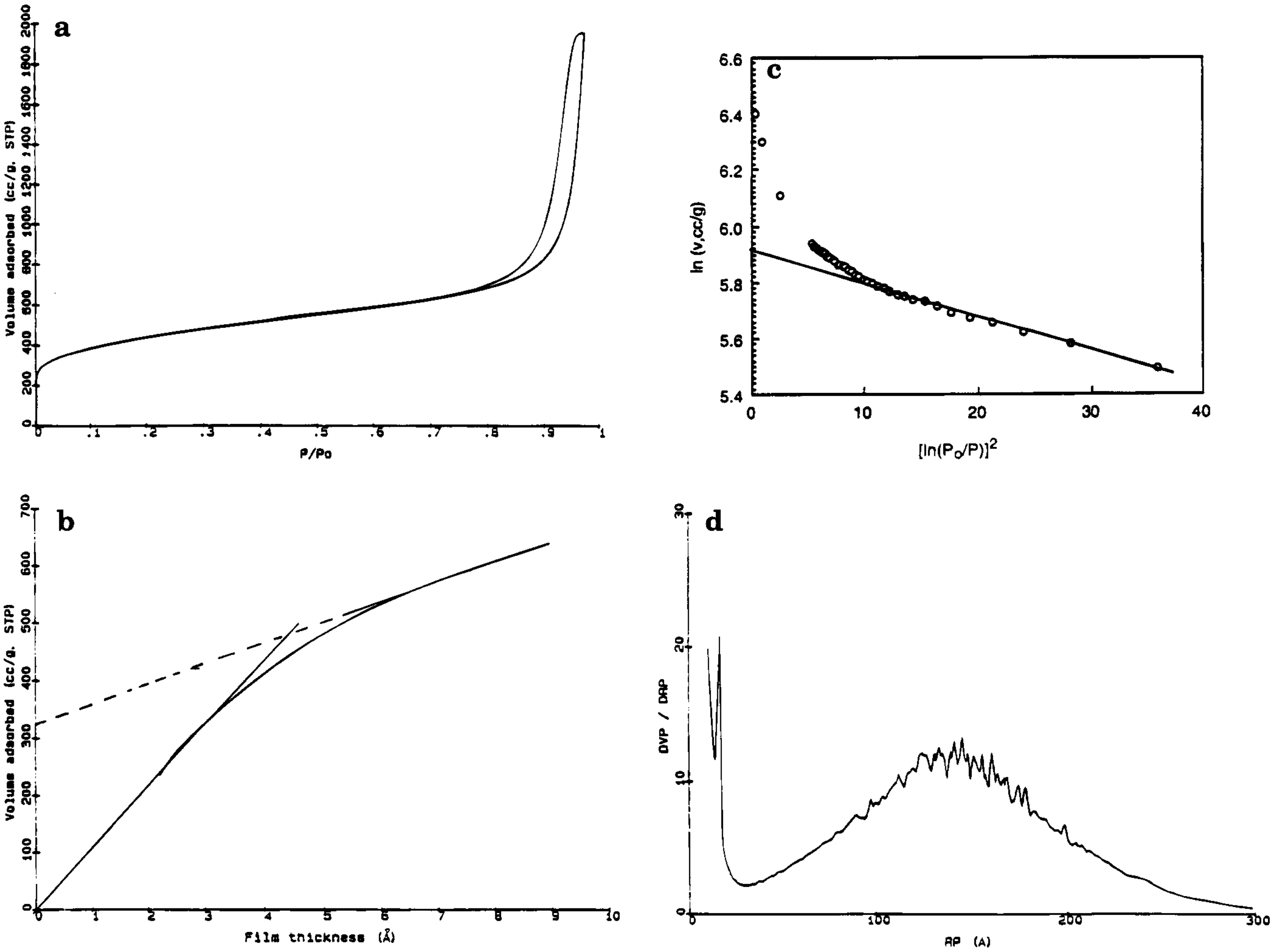

Figure 1. (a) N_2 adsorption and desorption isotherms at 77 K for C-HTT-Ar. (b) *t* plot for N_2 adsorption at 77 K on C-HTT-Ar. (c) D–R plot for N_2 adsorption at 77 K on C-HTT-Ar. (d) Pore size distribution for C-HTT-Ar using N_2 adsorption at 77 K.

Table 3. BET Surface Areas and Pore Volumes Obtained from Nitrogen Adsorption and Desorption Experiments at 77 K

carbon	BET area, m^2/g	*c*, BET eq	*t* plot area, m^2/g^a	micropore area, m^2/g^b	V_{total}, cm^3/g^c	$V_{meso+macro}$, cm^3/g^d	V_{micro}, cm^3/g^e	V_{micro}, cm^3/g^f	V_{micro}, cm^3/g^g
C-AS IS	1523	796	515	1008	3.10	2.56	0.46	0.51	0.57
C-HTT-Ar	1541	511	533	1030	3.05	2.58	0.45	0.52	0.58
C-HNO_3	1378	315	315	887	1.85	1.36	0.33	0.45	0.51

[a] Mesopore and macropore area from *t* plot over film thickness of 6–10 Å. [b] Subtraction of *t* plot area from BET area. [c] From the MP method. [d] From desorption isotherm using the Kelvin equation. [e] From the MP method. [f] From *t* plot method over film thickness of 6–10 Å. [g] From the Dubinin–Radushkevich equation.

as seen in an earlier study.[4] The high values of the BET constant, c, between 300 and 800 are consistent with the existence of microporosity in the carbon black and are similar to values previously obtained with another carbon black.[34] The highest *c* value, obtained with C-AS IS, may indicate a greater interaction between N_2 and the initial functional groups on the surface of this untreated carbon because the microporosity for that sample is similar to those for the other catalysts. The calculated mesopore size distributions for the carbon samples have a maximum at a pore width between 180 and 320 Å, and the distribution for C-HTT-Ar is shown in Figure 1d. The C-HNO_3 sample had the smallest mesopores. These pore size distributions always exhibited an apparent peak near a width of 36 Å (r = 18 Å), which is an artifact arising from the tensile strength of N_2 and the breakdown of the Kelvin equation below a pore width of 40 Å.[23] The peak in the micropore size distribution for all the carbons was at $w \simeq 5.4$ Å using the Horvath–Kawazoe method and $w \simeq 12$ Å with the MP method. These values are consistent with the belief that the microporous structure in carbons is a tangled network of defective graphitic planes and that the micropores represent spaces between layer planes with dimensions from 3.4 to 8 Å, as determined by TEM.[35]

X-ray Diffraction and Transmission Electron Microscopy. The X-ray diffraction patterns for the various carbon samples are shown in Figure 2. For graphite, the (002) peak is expected at 26.38°, the (100) peak at 42.22°, and the (101) peak at 44.39° (JCPDS card 41-1487). The peaks for Grafoil were closest to these values, as shown in Figure 2c,d. For the amorphous carbon black samples, a broad peak correspond-

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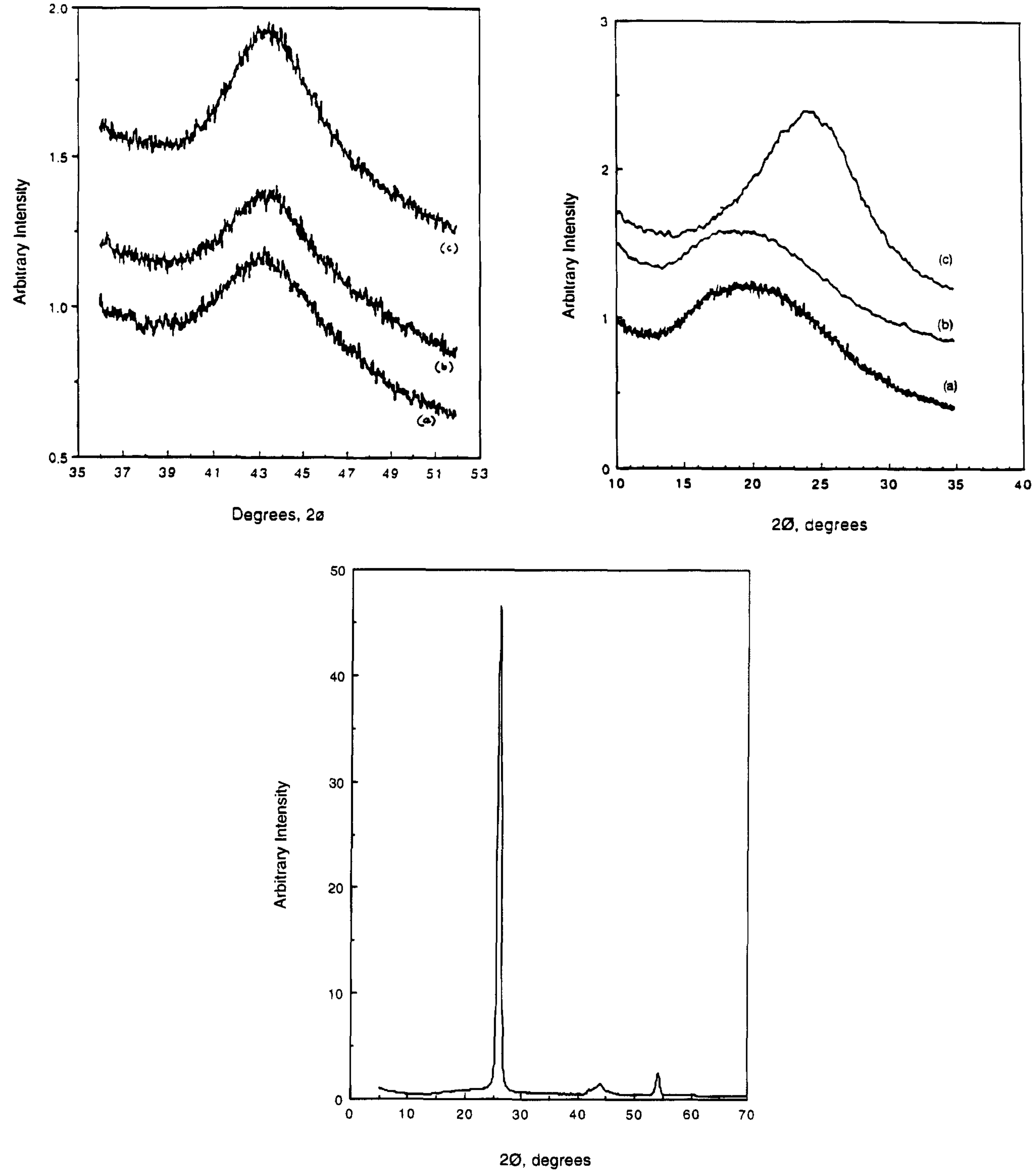

Figure 2. (a, top) Comparison of XRD patterns for carbon black samples: (a) C-AS IS, (b) C-HTT-Ar, (c) C-HNO_3. (b, middle) Comparison of XRD patterns for carbon black samples: (a) C-AS IS, (b) C-HTT-Ar, (c) C-HNO_3. (c, bottom) XRD pattern for Grafoil.

ing to the (002) reflection is shifted downwards and is seen around 22.4 ± 2.2°. The shift of the (002) reflection to lower values leads to the larger d_{002} values shown in Table 4. Further, as expected for turbostratic two-dimensional ordering, the (100) and (101) peaks merge into a broad (10) peak around 43.46 ± 0.15°. The dimension along the c-axis, L_c, and the crystallite width, L_a, were calculated using line broadening of the (002) and (10) peaks, respectively; here L_c represents a measure of the average stacking height of aligned graphitic planes, and L_a is indicative of their average diameter.[36] It must be remembered that these values may be weighted in favor of larger crystals if a distribu-

Table 4. Carbon XRD Peak Positions, Lattice Spacing and Crystallite Size after 2 h in H_2 at 573 K

carbon	C (0002) peak (2θ)	C (10) peak (2θ)	C(110) peak (2θ)	d_{002}, Å	L_c, Å	L_a, Å
C-AS IS	20.79	43.31		4.27	8.1	41
C-HTT-H_2	20.95	43.37		4.24	7.9	38
C-HTT-Ar	20.15	43.61		4.41	8.7	37
C-HNO_3	24.61	43.44		3.62	10.6	41
Grafoil	26.2, 54.4	42, 44.2	77.0	3.40	104.4	

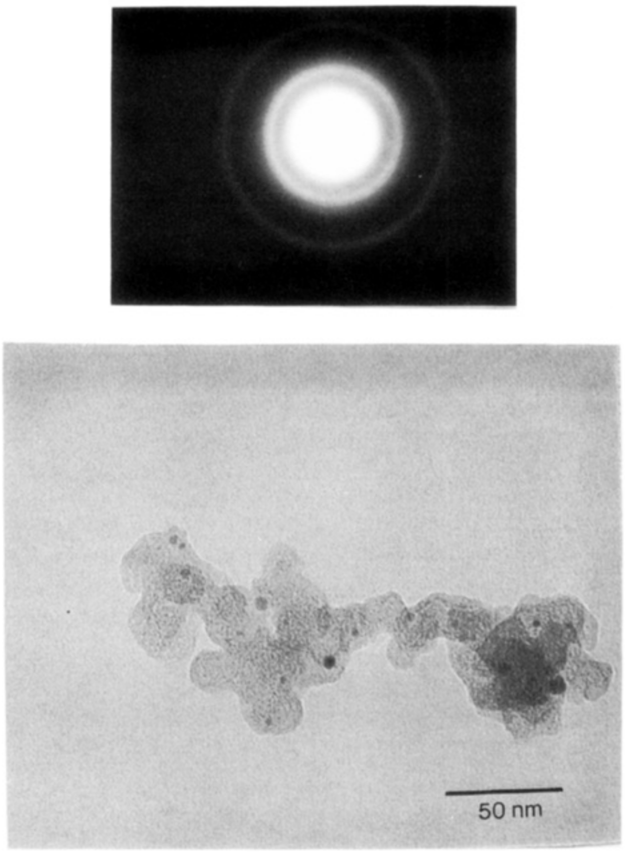

Figure 3. (a, top) Electron diffraction pattern of 3.4% Pd/C-HTT-H_2 after a 573 K reduction. (b, bottom) TEM micrograph of 3.4% Pd/C-HTT-H_2 after a 573 K reduction.

tion of crystallite sizes exist.[19] The crystallite height, L_c, was not changed significantly by HTT, but it increased noticeably after oxidation by HNO_3, as shown in Table 4. The crystallite width, L_a, was similar for all the carbons and consistent with values reported for other carbon blacks,[36] although the HTT decreased the crystallite width by about 10% compared to the C-AS IS sample. This value was regained after the HNO_3 treatment, thus indicating that surface oxygen groups in the C-AS IS and the C-HNO_3 samples may be responsible for the larger widths. Further, the d_{002} values indicate the HNO_3-treated sample has an interlayer spacing closest to graphitic carbon, while the other carbons have interlayer spacings larger than graphite, which is again consistent with previously reported results and the turbostratic nature of carbon black.[18,36] A typical diffraction pattern from a Pd catalyst made using C-HTT-H_2 as a support is shown in Figure 3a, and the corresponding micrograph is shown in Figure 3b. These are shown because the diffuse rings correspond to the (01) and (11) reflections of the small crystallites in the turbostratic carbon black.

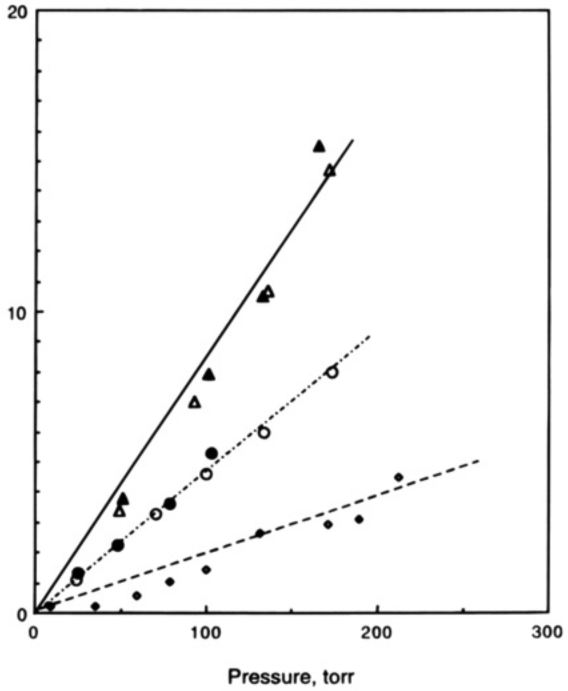

Figure 4. H_2 uptakes at 300 K on C-AS IS (△, ▲), C-HNO_3 (○, ●) and Grafoil (◇, ◆) after a 573 K reduction. (Open symbols represent first and closed symbols second isotherm).

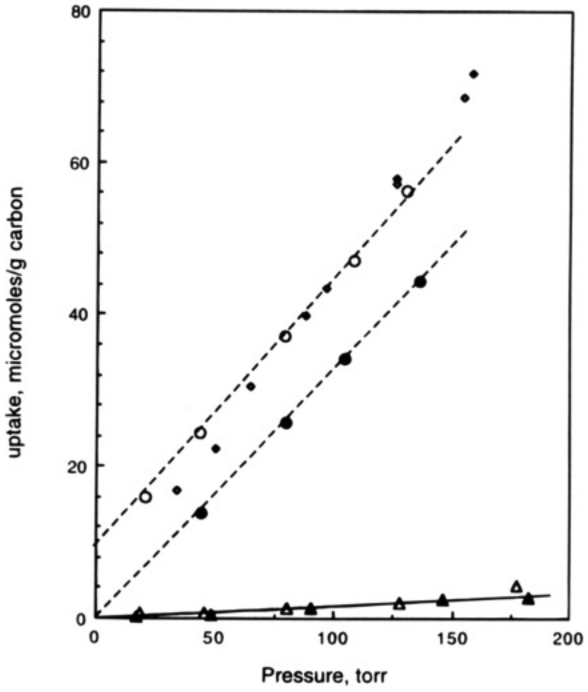

Figure 5. O_2 uptakes at 300 K on C-AS IS (◇, ◆), C-HNO_3 (○, ●) and Grafoil (△, ▲) after a 573 K reduction. (Open symbols represent first and closed symbols second isotherm).

H_2, O_2, and CO Adsorption. Typical H_2, O_2, and CO isotherms for these carbons are shown in Figures 4–6, and the uptakes are listed in Table 5. Only the C-HNO_3 sample exhibited any significant irreversible H_2, CO, or O_2 uptake at 300 K after a typical pretreatment procedure as it irreversibly adsorbed 11 μmol of O_2/g. All the carbon blacks had the highest adsorption capacity for CO, followed by O_2 and then H_2; however, the Grafoil sample had a larger reversible uptake of H_2 compared to O_2. The reversible O_2 and CO uptakes on the HTT- and HNO_3-treated carbons were less than on the C-AS IS sample, while the reversible H_2 adsorption was unchanged by pretreatment.

Heats of Adsorption. The heats of reversible H_2, O_2, and CO adsorption on the four carbons as well as the Q_{ad} value for irreversible oxygen adsorption are listed in Table 5. The integral heat of H_2 adsorption was similar on the carbon blacks (4.0 ± 0.5 kcal/mole H_2) but slightly lower on Grafoil (2.9 kcal/mol of H_2).

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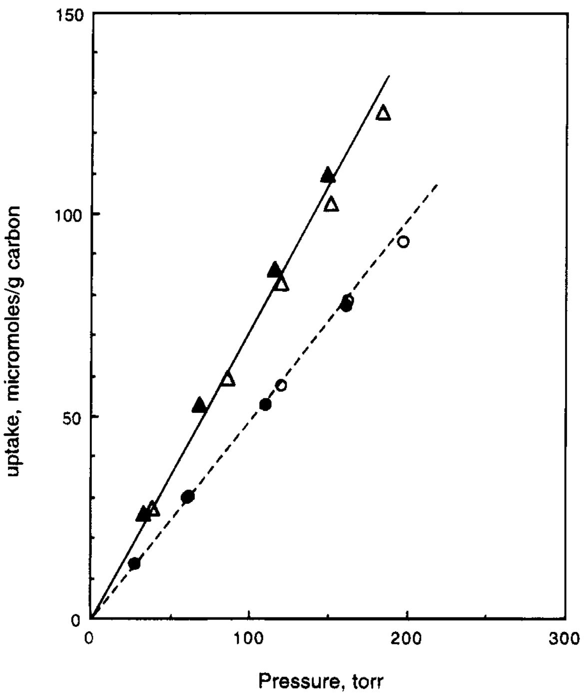

Figure 6. CO uptakes at 300 K on C-AS IS (△, ▲) and C-HNO_3 (○, ●) after a 573 K reduction. (Open symbols represent first and closed symbols second isotherm).

The weakly bonded O_2 had a low heat of adsorption near 0.6 ± 0.3 kcal/mol of O_2, while that for reversible CO chemisorption was about 1.4 kcal/mol. This latter value is comparable to values of 1.9–2.9 kcal/mol obtained by Martin-Martinez and Vannice for activated carbons.[34]

Thermogravimetric Analysis. The thermogravimetric trace during linear TPD of the C-HNO_3 sample is shown in Figure 7. The broad weight loss peaks near 750 and 950 K correspond to those expected for decomposition of CO_2- and CO-evolving surface complexes, respectively.[2,37] The weight loss was monitored only from 573 K, and the initial weight loss is attributed to the evolution of H_2O.[37]

Discussion

Reactive S impurities should be removed from carbon prior to its use to prepare supported metal catalysts, and a high temperature treatment (HTT) can accomplish this;[2,12] however, this is routinely not done. The influence of such a HTT step on the adsorption behavior of high surface area carbons such as carbon black is therefore of interest, particularly since few, if any, heat of adsorption values have been reported for clean C surfaces after a typical catalyst pretreatment procedure. It is also important to determine if any significant changes in the physical properties of a carbon black occur as a consequence of a HTT step or as a result of a subsequent oxidation by HNO_3. The TEM micrographs of the carbon black samples revealed random orientation of crystallites within a carbon black particle, which is typically observed,[36] and diffraction lines corresponding to graphitic layers could be seen, as shown in Figure 3. The HTT in H_2 or Ar removed almost all the sulfur from the carbon black, as shown in Table 2, and it also removed surface oxygen-containing groups as observed previously.[1,11,14,38] However, the HTT step had no major effect on nitrogen adsorption, consistent with previous work on a carbon black by Chen et al.,[38] although a HTT step in H_2 did decrease nitrogen uptakes on activated carbons made from olive pits.[34]

The HNO_3 treatment decreased the surface area of the carbon black, contrary to results obtained by Papirer et al.[33] but in agreement with the results of Suh et al. for activated carbons.[4] This inconsistency has also been observed previously by Heal and Mkayula, who found that a HNO_3 treatment slightly increased the surface area of wood-based activated carbons but slightly decreased it for peat-based activated carbons.[32] The HTT step, which also eliminated oxygen groups, slightly decreased the size of the crystallites compared to the C-AS IS and C-HNO_3 samples, both of which contained oxygen groups. We could find no previous mention of the effect of oxygen functional groups on crystallite size in the literature. The increased crystallite height, L_c, in the presence of oxygen-containing surface groups is accompanied by a decreased interlayer spacing, d_{002}, in the case of the C-HNO_3 sample, which reflects a physical modification of the carbon during HNO_3 oxidation. Oxidation of carbon by HNO_3 is thought to be accompanied by some carbon gasification,[2] and the decreased micropore and total pore volumes for the C-HNO_3 sample have been attributed previously to both the breakup of micropore walls by oxidation to form oxygenated terminal groups and the mechanical destruction of pores by the surface tension of the oxidizing solution;[39] these effects in turn can decrease the surface area after an HNO_3 treatment. The low 1.4 wt % loss during HNO_3 oxidation suggests that any loss of carbon by a gasification reaction was compensated by addition of oxygen-containing groups. As seen in Table 2, the 8.5 wt % unaccounted for in the composition of the C-HNO_3 sample may be attributed to the presence of oxygen-containing groups on the surface.

Thus the HTT step modified the chemical composition of the carbon black by removing S and oxygen-containing groups (and providing chemisorbed hydrogen in the C-HTT-H_2 sample) while leaving the surface area, pore size distribution, crystallite size, and interlayer spacing relatively unchanged. On the other hand, the oxidation treatment with HNO_3 was more destructive and changed the structure of the carbon black, causing a decrease in surface area and pore volume, an increase in crystallite size, and a decrease in interlayer spacing. A DRIFTS study of this carbon black showed that the HNO_3 treatment changes the carbon black surface chemically by introducing oxygen-containing surface groups such as cyclic anhydrides, lactones, and phenols; no evidence for the introduction of nitrogen-containing groups was seen.[11] The presence of cyclic anhydrides and the absence of nitrogen-containing groups indicate a high degree of oxidation of the carbon by HNO_3.[40,41]

The presence of oxygen-containing surface groups is consistent with the weight change that occurs during thermogravimetric analysis of the C-HNO_3 sample.

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Table 5. Gas Uptakes on Carbons and Heats of Adsorption after Treatment in H_2 and Evacuation at 573 K

carbon	irreversible gas uptake (mol/g) H_2	O_2	CO	Q_{irrev} kcal/mol of O_2	reversible gas uptake (mol/g) H_2[a]	O_2[b]	CO[b]	Q_{rev}, kcal/mol H_2[a]	O_2[b]	CO[b]
C-AS IS	0	0	0		6	34	58	4.3	0.33	
C-HTT-Ar	ca. 1	0	0		6	25	40	4.6	0.53	1.3
C-HNO_3	0	11	0	27[c]	6	24	36	3.5,3.5[c]	0.50, 1.1[c]	1.4, 1.4[c]
Grafoil	0	0			2	1.2		2.9		

[a] At 123 Torr [b] At 75 Torr. [c] Values obtained on a fresh C-HNO_3 not previously used for chemisorption.

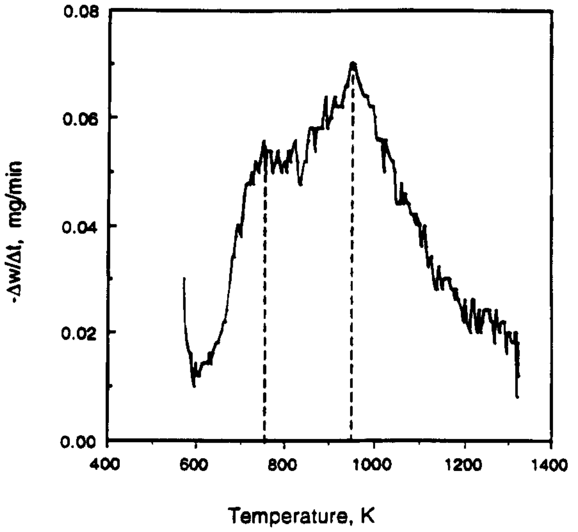

Figure 7. Rate of weight change upon heating C-HNO_3 in He.

Carbon–oxygen surface complexes in HNO_3-treated carbon blacks are thought to be stable up to 523 K, at which temperature evolution of CO_2 begins and gives a maximum in the rate of weight loss between 773 and 873 K; in contrast, CO evolution occurs from 673 to 1073 K and gives a rate maximum between 873 and 973 K.[1,37] Water evolution is seen between 400 and 773 K, while H_2 evolution may be seen above 973 K.[1,37] The evolution of CO_2 is associated with carboxylic groups and their derivatives, such as lactones and carboxylic anhydrides, while CO evolution is attributed to decomposition of quinones, hydroquinones, and phenols, and water loss is due to hydroquinones and phenols.[1,37] The sharp increase in weight loss for the C-HNO_3 sample starting near 600 K and peaking near 750 K is consistent with the observed decomposition of lactones in a DRIFTS study of this C-HNO_3 sample after heating to 673 K in Ar,[11] as well as the evolution of CO_2 at 650 K in a previous study of a HNO_3-treated char.[37] The broad peak at 950 K can be attributed to both decomposition of CO-evolving groups such as phenols as well as the high temperature evolution of CO_2 from carboxylic anhydride groups which were observed on these carbons by FTIR.[11,37] The initial weight loss below 600 K is consistent with the previously observed evolution of H_2O between 400 and 600 K.[37]

The effect of different pretreatments on adsorption properties is discussed next. No irreversible CO adsorption at 300 K was observed on any of these carbon samples after a typical catalyst pretreatment procedure, which agrees with previous work.[34] Dissociative H_2 adsorption on clean carbon surfaces is activated, with an activation energy between 13 and 30 kcal/mol depending on the type of active sites on a carbon surface; consequently, significant irreversible H adsorption is expected only at high temperatures.[42] The absence of irreversible hydrogen adsorption on all these carbon blacks is thus consistent with the expected slow rate of dissociative adsorption at room temperature. Significant adsorption of hydrogen has been reported previously to occur at 300 K on an activated carbon oxidized first in air and then with a NaClO solution,[43] but the role of residual Na atoms in increasing the rate of hydrogen adsorption is unclear. Once formed, C–H surface complexes are more stable than C–O surface complexes, though chemisorption of H_2 and O_2 is thought to take place on the same set of active sites.[2,42,44] Dissociative O_2 adsorption is known to occur irreversibly on clean carbon surfaces above 200 K,[45,46] and activation energies of 3–12 kcal/mole on graphon,[47] 7–12 kcal/mol on a saran char,[48] 13–25 kcal/mol at different oxygen surface coverages on a cellulose char,[49] and 6–15 kcal/mol on carbon films[50] have been reported. A large variation in irreversible oxygen uptakes by different carbons has been observed previously, though the reasons for the differences are not always mentioned. Irreversible O_2 chemisorption at 300 K on cellulose chars which were heat treated in N_2 at 573 K was negligible;[49] however, irreversible oxygen chemisorption at 300 K, which produced C–O and C=O bonds, was observed with a carbon sample containing 21% H after exposure to air for several days.[51] Cellulosic chars prepared at 1273 K did not chemisorb oxygen at 373–473 K while chars prepared at 723 K did, which perhaps reflects differences in active surface area or chemical composition of the surface.[52] In the current study, the pretreatment was found to alter the irreversible oxygen uptake on these carbon blacks at 300 K, a temperature at which no carbon gasification occurs.[1] The absence of irreversible O_2 adsorption on the C-AS IS sample is consistent with the reported inhibition of carbon oxidation in the presence of sulfur,[6] while the absence of O-containing surface species on C-HTT-H_2, even after oxidation at 673 K, accompanied by a decreased rate of oxidation, is consistent with the reported suppression of oxygen chemisorption in the presence of chemisorbed H_2.[11,43] The reason for the lack of irreversible O_2 uptake

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at 300 K on C-HTT-Ar is not clear at this time, especially since it can rapidly oxidize at 673 K in O_2,[11] but it is attributed to an activated adsorption process.

It may be suggested that the pretreatment in H_2 at 573 K was responsible for the suppression of subsequent irreversible H_2 and O_2 chemisoption. However, the C-HNO_3 sample, which already possessed a high concentration of oxygen-containing groups, irreversibly chemisorbed a significant amount of oxygen at 300 K after a typical catalyst pretreatment procedure of reduction and evacuation at 573 K in H_2. No previous study of oxygen adsorption at 300 K on HNO_3-treated carbons after such a pretreatment has been found. The thermogravimetric analysis of this carbon sample indicates that significant weight loss, attributed to the decomposition of oxygen-containing groups on the surface, occurs above 600 K. It is not known if the pretreatment in H_2 at 573 K can accelerate the decomposition of these groups and thus create additional sites for O_2 adsorption; however, such sites would also be expected to adsorb H_2[42,43] and no irreversible H_2 adsorption was seen. It is known that exposure of carbons which have been outgassed at high temperatures to oxygen at 300 K creates basic oxygen groups, while the base adsorption capacity of HNO_3-treated acidic carbons is high.[2,37] The HNO_3 treatment introduces large quantities of acidic groups and creates a polar surface,[2,37] and the presence of these groups appears to enhance oxygen adsorption. The HNO_3 treatment creates more CO_2-containing groups on the carbon, while air oxidation at 673 K creates more CO-yielding complexes, especially in the early stages of air oxidation, with further oxidation causing an increase in CO_2-yielding complexes.[37] Thus the presence of CO_2-evolving groups on the carbon surface may be creating new sites which can chemisorb O_2 at 300 K and form CO-evolving groups.[2,37] This hypothesis is consistent with the observation of the further development of oxygen groups corresponding to carboxyl carbonates, quinones, and C—O single bonds, such as those in alcohols and cyclic ethers, upon exposure of the C-HNO_3 sample to oxygen at 673 K; such groups were not created on the HTT carbon black samples.[11] The modification of adsorption behavior and reactivity of HNO_3-treated carbons and other carbons with acidic groups has been observed previously, and it resulted in an increased rate of H_2 gasification at 1048 K, which was attributed to the creation of nascent sites by O_2 desorption,[53] and enhanced gasification of glassy carbon by steam and CO_2 due to an increase in active sites which could dissociatively chemisorb O_2 and CO_2.[54] The presence of surface complexes that decompose to give CO_2 is known to increase the H_2O adsorption capacity of charcoal, and the presence of O-containing complexes increases adsorption of SO_2.[2] A DRIFTS study of the C-HNO_3 sample found no evidence for the presence of N-containing groups,[11] which is consistent with its low N_2 content, as shown in Table 2; hence, the enhanced O_2 uptake is not attributed to the presence of N-containing groups as proposed for the enhancement of carbon oxidation in the presence of nitrogen.[6]

The integral Q_{ad} value for irreversible oxygen adsorption on the HNO_3 treated carbon was ~27 kcal/mol after heating in H_2 and evacuating at 573 K. High values have been reported for oxygen adsorption on freshly ground graphite, i.e., initial values of 100 kcal/mol at low coverage dropped to 50 kcal/mol at higher coverages.[46] Ward and Rideal reported O_2 heats of adsorption at 273 K to be 40 kcal/mol or lower on charcoals with ash contents of 0.2–10% which had been baked for 2–3 days at a low temperature of 693 K.[55] Higher heats of O_2 adsorption between 60 and 84 kcal/mol at 273 to 298 K have been reported for charcoals with 0.3% ash content which were heated under vacuum for 2–60 h at higher temperatures of 1223–1273 K.[56,57] A high initial heat of 84 kcal/mol on charcoal, which was attributed to adsorption on sites of highest activity, decreased with increasing coverage to a constant value of 4.3 kcal/mol.[56] Ismail and Walker[58] reported a Q_{ad} value of 42 kcal/mol at 373 K on a clean Saran char after a HTT at 1173 K. High initial heats of 60–100 kcal/mol have been reported for O_2 adsorption at 298 K on Ambersorb, an amorphous carbon with 3.5% S, as well as on a char derived from phenol–formaldehyde copolymer.[59,60] These initial heats decreased rapidly with increasing coverage, and the integrated Q_{ad} value for "chemisorbed O_2 ($\Delta H > 12$ kcal/g mol)" was calculated to be 30 kcal/mol after a HNO_3 treatment followed by evacuation at 1173 K at 10^{-3} Torr.[60] The value of 27 kcal/mol for the present C-HNO_3 sample at 300 K is near this integral value, despite the difference in pretreatments. These previous studies have shown that the heat of adsorption is a strong function of oxygen coverage of the carbon surface[55–60] and that the pretreatment given to the carbon prior to the oxygen adsorption experiments as well as the impurities in the carbon can affect the value of heats of adsorption of O_2.[58] Specifically, higher heats of O_2 adsorption were obtained when higher temperatures of evacuation and desorption were used prior to heat measurement.[58] The integral value of 27 kcal/mol in the current study is consistent with the initial presence of oxygen functional groups on the surface, indicating that the sites with the highest binding energies are already associated with oxygen-containing groups and are unavailable for further oxygen chemisorption. Alternatively, this heat of adsorption may be more similar to a heat of reaction attributable to the formation of a new carbon–oxygen species on the surface. Such a phenomenon would be similar to the creation of basic species such as pyrone (a heterocycle containing a carbonyl and an ether group) which are known to form on HTT carbons after exposure to oxygen at 300 K.[61,62] These pyrone groups are thought to form by the combination of a heat resistant oxygen-containing group, which stays on the surface even at 1073 K, with another O group created during air exposure.[61,62]

The pretreatment of the carbons did not significantly affect the heats of reversible adsorption of H_2, O_2 and CO at 300 K. The integral Q_{ad} values for reversible CO

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adsorption on all the carbon samples was around 1.4 kcal/mol, which is consistent with previous values of 1.9–2.9 kcal/mol reported for CO adsorption on activated carbons.[34] The Q_{ad} values for reversible H_2 adsorption on the turbostratic carbon surfaces did not vary significantly as it was 4.0 ± 0.5 kcal/mol but a lower value of 2.9 kcal/mol was obtained for the graphitic surface. The heat of reversible O_2 adsorption was very low on all surfaces, varying from 0.3 to 1.1 kcal/mol, which is near the value of 2.8 kcal/mol reported previously for a HTT Saran char.[48] No Q_{ad} values for H_2 after a similar pretreatment could be found in the literature for comparison.

Summary

A high temperature treatment (HTT) at 1223 K of a turbostratic carbon black decreased its sulfur content and removed oxygen-containing surface groups, but it did not significantly alter the N_2 BET area, pore size distribution, or adsorption behavior. However, a subsequent oxidation by HNO_3 caused a decrease in surface area, micropore volume, and total pore volume and increased the apparent interlayer spacings. An important finding was that this latter treatment induced significant irreversible O_2 adsorption at 300 K while H_2 and CO adsorption capabilities were not noticeably affected. The irreversibly adsorbed oxygen had a relatively low heat of adsorption of 27 kcal/mol, which is attributed to adsorption on a carbon surface already containing a high coverage of oxygen, and this value might be associated with the heat of the formation of basic oxygen groups on this carbon surface. The different pretreatments had little effect on the heats of reversible adsorption of H_2, O_2, and CO at 300 K, and similar values for each adsorbate were obtained for all the carbon black samples.

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