Water Vapor Adsorption on Chemically Treated Activated Carbon Cloths

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Water vapor adsorption on activated carbon cloth (ACC20) which has been oxidized to a level of 32% oxygen exhibits a unique isotherm with uniform hysteresis of small magnitude upon desorption. In contrast the adsorption on untreated ACC20 and chemically modified ACC20 (7.8% Cl), ACC20 (16% Cl), and ACC20 (4% N), exhibits sigmoidal isotherms with hysteresis loops of varying magnitudes. The latter ACCs display high capacity for moisture removal at relative humidities >50%. At saturation, all treated cloths exhibit high adsorption capacities for water (0.5–0.67 mL/g of fiber) and 100% desorption upon heating to 100 °C. The untreated and treated ACC20 samples exhibited no degradation upon heating to 100 °C. Total water adsorption volumes are lower than the total nitrogen pore volumes for all samples except for the ACC20 (32% O), which adsorbs similar volumes of both adsorbates.

Introduction

We have recently investigated activated carbon cloths (ACCs) and chemically treated ACCs for removal of toxic volatile organic compounds (VOCs) contaminants that have been detected in indoor air.[1,2] In general ACCs offer the advantages of superior contact efficiency and higher adsorption capacity over granular activated carbons (GACs).[3] Regeneration can be done easily by resistance heating.[3,4] To date there has been little[5] attention paid to the adsorption of water vapor by ACCs, other than to note that at low oxygen content the carbon cloths tend to be hydrophobic while at higher oxygen concentrations the carbon is more hydrophilic. To our knowledge there are no reports on the properties of ACCs containing much higher amounts of oxygen (32% O) other than our preliminary reports.[2] In view of the advantages that ACCs offer over conventional GACs and our recent success in enhancing VOCs' adsorption on chemically modified carbon cloths by 300–500% over untreated ACCs,[2] it appeared reasonable to determine whether we could greatly modify ACC moisture adsorption by chemical treatment.

Chemically modified ACCs with increased amounts of N, Cl, or O have micropore surfaces that exhibit basic (N), polar (Cl), or acidic (O) character.[2,3] Thus different interactions with water would be anticipated with such surfaces. One might ask whether these new systems could be designed to display enhanced removal of water as compared to currently used zeolites or other systems used for moisture removal such as P_2O_5 which is nonreversible.[6,7] It is also important to understand how the competitive adsorption of water affects the uptake of VOCs particularly at high relative humidities.

This paper describes how different chemical groups which are present at the micropore surface affect the adsorption as well as the desorption of water vapor over the range of 0–100% relative humidity (RH). The successful design of a new high-capacity adsorption system for water vapor is described. Implications of this work for improved moisture removal at low ppmv and VOC separation are also briefly discussed.

Experimental Section

Materials Synthesis and Characterization. Details of the conditions used to synthesize and characterize the chemically treated ACCs used in this study are described here for clarity.[2] The starting material, ACC20, was obtained from American Kynol, New York. Characteristics of the untreated ACC20 sample are presented in Table 1.

Treatment of ACC20 with NH_3 or Cl_2. About 1.0 g of ACC20 was placed in a 5 cm i.d. quartz tube in a temperature-controlled tubular furnace. The tube was purged with N_2 for 5 min and the temperature was increased to 180 °C for 15 min and then at the desired reaction temperature NH_3 or Cl_2 were introduced for the necessary reaction period (reaction temperatures and times are discussed in the next section). After completion the gas was replaced with nitrogen and the sample cooled to room temperature. The product was weighed and placed in closed vials for further characterization.

Oxidation of ACC20. The oxidation reactions were carried out by immersing 1.45 g of ACC20 in 100 mL of 1/1 (v/v) HNO_3/H_2SO_4 solution for two different time periods, 10 min and 4 days. Gas evolution was observed. After the reaction the product was washed with distilled water and left to dry overnight in a hood. It was dried 12 h later at 150 °C with N_2 for 30 min and then kept in closed vials.

X-ray Photoelectron Spectroscopy (XPS). XPS was used to determine the elemental content (O, N, Cl, and C) of the

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Table 1. Physical Characteristics and Elemental Composition of ACCS[a]

ACC20 with	BET [M² g⁻¹]	$V_t(N_2)$ [mL g⁻¹]	$V_m(N_2)$ [mL g⁻¹]	$V_t(H_2O)$ [mL g⁻¹]	C [wt %]	H [wt %]	N [wt %]	O [wt %]	Cl [wt %]
(1) 3.9 (untreated)	1550	0.74	0.61	0.61	95.40	0.68	0.05	3.92	
(2) 4.0% N (nitrided)	1738	0.84	0.59	0.67	91.96	0.27	4.50	3.23	
(3) 7.8% Cl	1523	0.73	0.54	0.59	87.71	0.06	0.27	4.15	7.8
(4) 16% Cl	1374	0.66	0.51	0.53	77.93	0.01	0.06	6.00	16
(5) 32% O	1105	0.47	0.35	0.49	64.76	1.55	0.72	32.32	

[a] The wt % element (C, H, N, O, Cl) was determined as described in the experimental section. V_t and V_m refer to the total pore and micropore volume. Their values were obtained as described in the Experimental Section. Nitrogen isotherms (volumetric measurements). $V_t(H_2O)$ refers to total water pore volume (see section I in Results and Discussion).
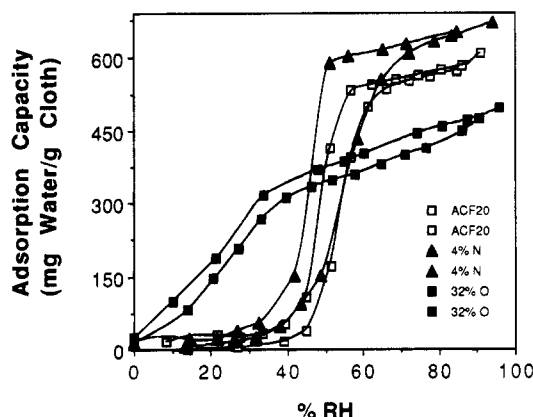

Figure 1. Water vapor adsorption–desorption isotherms of ACC20, ACC20 (4% N), and ACC20 (32% O).

surface of the treated and untreated ACC samples. The work was carried out at the Materials Research Laboratory of the University of Illinois at Urbana–Champaign, using a PHI 5400 (Perkin-Elmer, Physical Electronics Inc.) instrument. Mg Kα radiation and a power of 400 W at 15 kV were used. The samples were dried at 150 °C for 30–45 min prior to analysis since the technique requires ultrahigh vacuum (10^{-8}–10^{-10} Torr). To analyze for the surface groups, the carbon region of the XPS spectrum was deconvoluted to individual peaks. XPS techniques were used to characterize the chemical changes on the surface of the fiber down to 60 Å which is the maximum depth that the emitted photoelectrons can escape and be detected. XPS can identify the N, Cl, or O groups present based on their binding energy values. It is probable that the chemical nature of the surface is similar to that of the core of the sample. Figure 1 describes the percent total carbon area of each group as a function of the binding energy (variations within 0.7 eV are observed for the treated samples): phenol or ether (285 eV), carbonyl (287 eV), carboxylic (288.8 eV), and unsaturated bond transitions (291.1 eV also known as shakeup peaks).

Elemental Analysis. The elemental analysis was performed at the microanalysis lab of the University of Illinois at Urbana–Champaign, using inductive coupled plasma spectroscopy. The oxygen was determined by mass difference.

Nitrogen Isotherms (Volumetric Measurements). A Micrometrics (Norcross, GA) ASAP 2400 instrument was used to determine surface areas of the ACC samples. The samples were dried in vacuum at 200 °C for 24 h, and the adsorption measurements were carried out at liquid nitrogen temperatures. The BET equation was used to fit the adsorption data in the 0.05–0.25 relative pressure regime. Micropore volume values were determined from *t*-plot analysis. Critical factors in assessing the values reported here are the vacuum 10^{-3} Torr used to degas the samples while they were heated at 200 °C for 24 h and the regime of statistical thickness over which the least square fit of the data to the Jura–Harkins equation $t = [13.99/(0.034 - \log p/p_0)]^{0.5}$ was done (3–6 Å).

Their physical adsorption properties are summarized in Table 1. It should be noted that the nitrogen total pore volume was estimated at saturation P/P_0 values and the micropore volume determined using the Harkins–Jura equation with a statistical thickness value of 3.5–6 Å.

Experimental Procedure for Measurement of Water Vapor Adsorption Isotherms. Measurement of adsorption isotherms for the ACC samples was performed gravimetrically using a Cahn microbalance (Model C-2000). The humidified gas stream was generated by passing a hydrocarbon-free air stream through two Erlenmeyer flasks in series containing distilled and deionized water and gas dispersion tubes and then diluted with hydrocarbon-free air using mass flow controllers (Tylan Model FC-280) to obtain the desired relative humidities. The adsorption isotherms were measured at 25 °C and a total pressure of 1 atm. Dry ACC samples were between 10 and 20 mg, and the total gas flow rate through the gravimetric balance was 0.15 L/min.

Results and Discussion

I. Properties of Chemically Treated ACCs. The adsorption properties and elemental composition of ACCs are summarized in Table 1. To summarize briefly: oxidation or chlorination decreases the pore volumes and surface areas, while nitridation increases pore volumes and surface areas. There is a further decrease in the pore volume and surface area with a progressive degree of chlorination (at the same temperature). This is also true for various levels of oxidation.[2]

The water vapor pore volumes were estimated from the adsorption isotherms at saturation P/P_0 values ($p/p_0 = 0.95$) and their importance in $H_2O(g)$ adsorption is discussed at the end of section II.

II. Water Adsorption–Desorption Isotherms. The adsorption–desorption interactions of water vapor with microporous and nonporous carbons have been studied extensively.[5,8-11] They are influenced by at least two factors: the oxygen sites (or so-called surface oxides) and the pore dimensions of the micropore system. Although surface oxides can promote adsorption they may limit the pore dimensions and therefore the total capacity of the system.

The adsorption of water on zeolites has also been studied extensively.[6,7] It is known that aluminum-rich zeolites show high affinity for H_2O vapor adsorption (their saturation capacity is about 25 mL of H_2O/g of sample) and are used as desiccants and for drying gases. The disadvantage of these adsorbents is the high regeneration temperature necessary.[12]

In this work the adsorption isotherm of a highly oxidized ACC is compared to isotherms of nitrided (Figure 1) and chlorinated ACCs (Figure 2). For reference purposes the adsorption isotherm on untreated ACC20 is presented in both figures.

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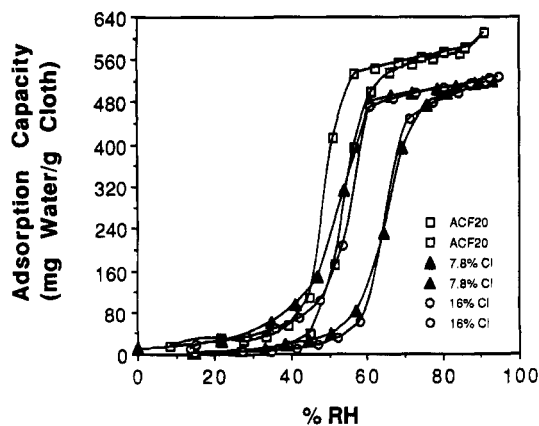(12) Breck, D. W. *Zeolite Mol. Sci.* **1974**, 412–415.

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Figure 2. Water vapor adsorption–desorption isotherms of ACC20 ACC20 (7.8% Cl) and ACC20 (16% Cl).

Highly Oxidized ACC20. ACC20 (32% O) has a highly hydrophilic surface and displays unique adsorption and desorption behavior (Figure 1). Following the adsorption branch we see that there is a large enhancement on the amount of adsorbed H_2O vapor at 10% Rh in comparison to untreated ACC20. The enhancement is much more dramatic (1700%) at 33% RH. Such overall improvement of moisture adsorption over the range of concentrations examined can only be explained through enhanced H bonding. A sample with 32% O is expected to have a much higher number of hydrophilic sites than any of the other samples tested, all of which had 6% oxygen content (Table 1). From X-ray photoelectron spectroscopy the surface oxygen appears mainly as carboxylic (288.8 eV) and some ketonic (287 eV), ether and hydroxyl (285 eV).[2] The number of hydroxyl groups of ACC20 is similar to that on the highly oxidized sample. However the number of carboxylic groups increases upon oxidation. It is therefore clear that −COOH groups are mainly responsible for the enhanced adsorption of water at low RH.[3-13] Enhanced H bonding and dipole–dipole interactions facilitate accessibility of the micropore volume available for water adsorption. It has been suggested that water molecules are initially adsorbed on hydrophilic or defect surface sites to form clusters of molecules.[5,16] The water clusters continually increase in size with small changes in RH. At some point the clusters achieve a critical proximity to a monolayer or multilayer of adsorbed water through enhanced water–water interactions. Thus the hydrophilic surfaces provided by ACC20 (32% O) are very efficient for moisture removal below 50% RH.[15] In fact they enhance $H_2O(g)$ adsorption by 1700% over untreated ACC20 at 33% RH.

Another characteristic of the isotherm for ACC20 (32% O) is the appearance of a very small hysteresis loop. Hysteresis is not as profound compared to other treated or untreated ACC20 samples. Adsorption theories have suggested that the origin of that loop finds its most simplistic explanation in that the desorption branch represents a thermodynamically stable equilibrium and that changes have occurred in the adsorbed

phase so that the part of the phase formed at low relative humidity is no longer at equilibrium at the same RH value on desorption.[17] Following the suggested scheme from adsorption (clusters that transform to a continuous liquid H_2O phase), hysteresis will be observed up to the point where the adsorbed phase breaks into clusters centered on hydrophilic sites. At that point the desorption curve rejoins the adsorption, and the process is reversible.

Untreated, Nitrided, and Chlorinated ACC20. Water vapor adsorption on the hydrophobic surfaces of untreated, nitrided and chlorinated ACC20 exhibits sigmoidal isotherms (Figures 1 and 2).

For ACC20 the maximum water adsorption is less than 16 mg g^{-1} up to about 40% RH (Figure 1). The surface of the original ACC20 is hydrophobic and contains about 95.4% carbon and 3.92% O (Table 1). It starts to significantly pick up moisture at about 45% RH. In contrast to highly oxidized ACC20, there is a critical RH value (approximately 30% RH) above which water clusters form and then increased adsorption occurs.[18,19] Now adsorbate–adsorbate forces will promote the adsorption of further water molecules so that the isotherm will become convex to the relative humidity axis. Finally saturation occurs at about 60% RH.

ACC20 (4% N) adsorbs about 15 mg g^{-1} $H_2O(g)$ below 25% RH (Figure 1). Its capacity starts to increase above 35% RH (earlier than ACC20) due to enhanced hydrophilicity of its surface. In fact it adsorbs water vapor to its maximum capacity at about 55% RH and also exhibits hysteresis upon desorption. With NH_3 treatment the surface becomes basic with amine or pyridine and pyrrolic groups as revealed by the N 1s XPS peaks at 399 and 400–403 eV, respectively. Amine surface groups as well as micropore widening are expected to slightly favor H_2O adsorption compared to original ACC20 (Figure 1).[2] For ACC20 (7.8% Cl) and ACC20 (16% Cl) the maximum water adsorption is less than 16 mg g^{-1} up to about 40% RH (Figure 2) due to surface hydrophobicity.[2] Notice here that BET surface areas and total pore volumes progressively decrease with increasing chlorine content as determined by nitrogen adsorption. ACC20 (7.8% Cl) or ACC20 (16% Cl) starts picking up moisture at about 55% RH. It thus appears that the critical value of RH for water adsorption is shifted to higher values with progressive treatment, and we see a clear difference for differently treated ACCs. Saturation occurs at about 70% RH for both the chlorinated samples.

Summary and Conclusions

We have designed an ACC20 (32% O) system that is very efficient for moisture removal below 50% RH. It provides a high-capacity moisture adsorbent with improved removal in the low relative pressure regime (1700% enhancement over untreated or otherwise modified ACC20 at 33% relative humidity). For moisture removal at low ppmv, further optimization of pore

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geometry (size and shape) and chemistry is necessary. At the same time some of the systems we examined displayed minimal adsorption of water vapor at a typical indoor air environment (40−70% RH) and outdoor environment (0−100% RH). These modified ACCs have recently been shown to enhance adsorption of individual toxic VOCs, at low ppmv, by 300−400%. Thus we can predictably tailor the micropore surface chemistry to enhance adsorption of toxic VOCs and at the same time minimize water vapor adsorption from indoor and outdoor air environments over the whole range of relative humidity values.

Finally oxidized ACCs adsorb water at capacities much higher than those exhibited by zeolites, and the oxidized ACCs are easy to regenerate at low temperatures. Optimization of pore size and shape could further improve the efficiency of water adsorption at low RH by the oxidized ACCs.