

THE EFFECT OF CHEMICAL MODIFICATION OF ACTIVATED CARBON CLOTH ON THE ADSORPTION CAPACITY OF ORGANICS AND WATER VAPOR

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Keywords: adsorption, activated carbon, chemical treatment.

INTRODUCTION

In an effort to maximize VOC adsorption, particularly in the case of compounds which are not readily adsorbed on activated carbon cloth (ACC), e.g., acetaldehyde, and to minimize the adsorption of water vapor, several chemical treatments were performed on virgin ACC-20. A sulfuric/nitric acid treatment produced a highly oxidized surface; chemical treatment with NH₃ produced a basic surface and increased the nitrogen content of the ACC; and finally, Cl₂ was used to produce a polar surface. Adsorption isotherms were measured for acetaldehyde, benzene, and water vapor to observe the effect on adsorption capacity for chemically treated ACC-20.

EXPERIMENTAL PROCEDURES

The starting material, ACC-20, was obtained from Nippon Kynol, Inc. Characteristics of the untreated and chemically modified ACC-20 samples are presented in Table 1. A brief summary of the experimental procedures used in this research is presented below. For a more detailed description of experimental procedures, please consult Dimotakis et al., 1995 and Cal, 1995.

Modification of ACC-20 with Ammonia or Chlorine

About 1.0 g of ACC-20 was placed in a 5-cm i.d. temperature-controlled quartz tubular furnace. The tube was purged with N₂ for 5 min, the temperature was increased to 180°C for 15 min, and then at the desired reaction temperature NH₃ or Cl₂ were introduced for the necessary reaction period. After completion, the gas was replaced with nitrogen, and the sample was cooled to room temperature. The samples were stored in closed vials prior to analysis.

Oxidation of ACC-20

The oxidations reactions were performed by immersing 1.45 g of ACC-20 in 100 ml of 1/1 (v/v) HNO₃/H₂SO₄ solution for two time periods: 10 min and 4 days. Gas evolution was observed during treatment. After the treatment, the product was washed with distilled water and left to dry overnight. Twelve hours later, it was dried at 150°C with N₂ for 30 min and then was stored in closed vials.

X-Ray Photoelectron Spectroscopy (XPS) Measurements

XPS was used to determine the elemental content (O, N, Cl and C) of the surface of the treated and untreated ACC samples (Briggs and Seah, 1983). 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-K α radiation and a power of 400 Watts 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 to 10⁻¹⁰ torr). To analyze for the surface groups the carbon region of the XPS spectrum was deconvoluted to individual peaks (Table 2). XPS techniques were used to characterize the chemical changes on the surface of the fiber down to about 30 Å to 100 Å which is the maximum depth that the emitted photoelectrons can escape and be detected (Briggs and Seah, 1983). XPS can identify the N, Cl or O groups present based on their binding energy values. It was assumed that the chemical nature of the surface is similar to that of the core of the sample. Table 2 describes the percent of 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 shake-up peaks) (Foster, 1993).

Organic and Water Vapor Adsorption Isotherms

Acetaldehyde, benzene, and water vapor adsorption isotherms for the ACC samples were measured gravimetrically using a Cahn microbalance (Model C-2000). The gas stream for the organic compound of interest was generated using a certified gas cylinder of known organic concentration, diluted with hydrocarbon-free air using mass flow controllers (Tylan Model FC-280) to obtain the desired concentrations. To generate gas streams with different relative humidities, a membrane humidifier was used in combination with a dew-point hygrometer (Cal, 1995). The adsorption isotherms were measured at 25°C and a total pressure of about 1 atm. ACC sample masses were between 10 and 20 mg and the total gas flow rate through the gravimetric balance was 0.1 to 0.25 L/min.

Acetaldehyde Adsorption

Acetaldehyde typically has a low adsorption capacity on activated carbons, including ACC. Therefore, any chemical treatment that could substantially enhance the adsorption of acetaldehyde (and similar compounds, such as formaldehyde) could be potentially useful. Comparison of the adsorption capacities (at 25°C and 1 atm total pressure) for a series of chemically modified ACC-20 samples that were untreated, oxidized, nitrated and chlorinated as described by Table 2 are presented in Figure 1.

The largest gas-phase acetaldehyde concentration in air examined was 500 ppmv, while 1000 ppmv was the highest concentration of acetone and benzene studied. It was observed that acetaldehyde undergoes conversion to acetic acid at higher concentrations, making the adsorption capacity measurements invalid (Venugopal et al., 1967; Matheson Gas, 1993). The highly oxidized sample, ACC20-(32% O), exhibits a much higher adsorption capacity for

acetaldehyde in the 50 to 500 ppmv concentration range when compared to untreated ACC-20. At 50 ppmv ACC20-(32% O) adsorbs 400% more acetaldehyde than untreated ACC-20 and at 500 ppmv it adsorbs 130% more acetaldehyde. The less oxidized sample, ACC20-(21% O), also shows enhanced acetaldehyde adsorption similar to that of ACC20-(32% O).

The increase in acetaldehyde adsorption capacity on oxidized ACC is theorized to be due to an increase in dipole interactions and hydrogen bonding that occurs between the acetaldehyde molecules and the additional carboxylic groups present on the oxidized ACC-20 (Table 1). This effect appears to most pronounced at lower adsorbate concentrations, and diminishes at higher adsorbate concentrations, when the larger adsorbent pores begin to fill. It has been reported in the literature that surface oxygen groups can affect adsorption (Zawadzki, 1981; Boehm, 1966; Szymanski and Rychlicki, 1991).

Nitrated ACC20-(4% N) shows improved acetaldehyde adsorption capacity over untreated ACC-20 of 51% at 50 ppmv and 9% at 500 ppmv. This increase in adsorption capacity may be due to interaction with the basic surface or may be due to the change in pore structure of the ACC. Finally, in the case of the chlorinated ACC20-(7.8% Cl) a slight decrease in the adsorption capacity is observed compared to the untreated ACC. The decrease in adsorption capacity appears to be related to the ACC surface chemistry instead of physical properties because the pore volume is similar to that of ACC20-(21% O) (Table 1).

Benzene Adsorption

Adsorption isotherms for benzene and the series of chemically modified ACC are presented in Figure 2. Since benzene is nonpolar and essentially immiscible in H₂O, a hydrophilic surface should result in decreased adsorption (Puri et al., 1973). Oxidation of the ACC resulted in a 34% decrease in adsorption capacity for 1000 ppmv benzene in air, which is the same as the observed decrease in surface area (Figure 2 and Table 1). Therefore, oxidation had little or no effect on benzene adsorption, but rather the difference in adsorption capacity is due to changes in surface area and/or pore volume between ACC20-(3.9% O) and ACC20-(32% O). The nitrated (basic) surface shows a slight increase in benzene adsorption capacity, while the chlorinated ACC20-(7.8% Cl) showed a slight decrease in adsorption capacity as compared to ACC20-(3.9% O). This decrease in adsorption capacity may be attributable to the decrease in micropore volume observed on the chlorinated ACC samples or may also be attributed to experimental error in the measurements (Table 1).

Water Vapor Adsorption on Chemically Modified ACC

The adsorption of water vapor on ACC20-(32% O) differs significantly from the usually observed type V isotherm, and more closely resembles a type II isotherm (Figure 3). ACC20-(32% O) is expected to have many more oxygenated or hydrophilic sites than any of the other ACC due to its high oxygen content. The XPS data in Table 2 shows a higher number of carboxylic bonds than the untreated ACC-20, confirming that some of the hydroxyl and carbonyl bonds were oxidized to carboxylic bonds. The XPS data also shows that more carbon-oxygen (hydrophilic) bonds were formed during oxidation compared to untreated ACC-20. The increase in carboxylic groups may be responsible for the enhanced water vapor adsorption at low relative humidities (RHs). From Table 2 and the adsorption isotherm data, it appears that carboxylic groups have the most influence on water vapor adsorption at low RH. The difference between the adsorption and desorption curves (hysteresis) is not as pronounced here, as it is for the untreated ACC. This may be due to the increase in hydrogen-bonding between water and the oxidized carbon, allowing removal of water molecules in a more continuous manner.

Adsorption-desorption isotherms for nitrated ACC20-(4.1% N) are presented in Figure 3. ACC20-(4.1% N) exhibits an increase in water vapor adsorption capacity (200 to 600%, depending upon the RH) in the lower RH range (RH < 50%). This may be due to the increase in carboxylic sites compared to untreated ACC20-(3.9% O), as represented in the XPS data in Table 2. It has also been suggested that nitrogen can also constitute polar sites for H₂O_(g) adsorption (Bradley and Rand, 1993; Tomlinson, et al., 1993), thereby increasing H₂O_(g) adsorption at low RH. ACC20-(4.1% N) exhibits about a 10% higher water vapor adsorption capacity than ACC20-(3.9% O) at high RHs. This is due to the increased total pore volume of ACC20-(4.1% N) observed in Table 1. The widening in the adsorption hysteresis curve in for ACC20-(4.1% N) in Figure 3 is most likely due to a change in pore size distribution.

Adsorption isotherms for water vapor and chlorinated ACC are presented in Figure 4. Table 1 shows a decrease in BET surface area, a decrease in carbon content (in wt%), and a slight increase in oxygen content with increasing chlorination. The decrease in surface area may be due to chlorine atoms limiting or closing off access to the smaller micropores present on the ACC. Water vapor adsorption was decreased at RHs < 60% and where capillary condensation occurred (the step rise in the adsorption curve) was shifted to higher RHs for the chlorinated ACCs. The amount of water vapor adsorbed at saturation was decreased to a due to a decrease in pore volume (Table 1). While chlorination increases the amount of polar sites present on the ACC due to the addition of chlorine atoms, these sites do not appear to be favorable for water adsorption, as are carboxylic sites. Chlorination appears to increase the hydrophobicity of ACC.

SUMMARY

ACC-20 was chemically modified, producing oxidized, chlorinated, and nitrated samples. Adsorption capacities for VOCs in the 10 to 1000 ppmv concentration and water vapor from 0 to 95% RH were measured. Oxidized ACC-20 showed an enhanced physical adsorption for acetaldehyde and water vapor, probably due to increased dipole-dipole interactions and hydrogen bonding. Oxidation of ACC-20 changed the shape of the water vapor adsorption isotherm, so that it no longer resembles a Brunauer type V. Benzene showed a decreased adsorption capacity (about 20 to 30% less, depending upon concentration) on oxidized ACC-20, which may be due to and increase in hydrophilicity of ACC-20, or a change in pore size distribution. Nitridation of ACC showed little effect on organic adsorption capacity, but increased the saturation adsorption capacity for water vapor by 10% on ACC-20 and increased the breadth of its hysteresis loop. These changes were the result of changes in the pore size distribution of ACC-20.

ACKNOWLEDGEMENTS

This research was supported through grants from the Center for Indoor Air Research (Grant 91-03), the Hazardous Waste Research and Information Center (Grant ENR HWR 94-115), and the Advanced Environmental

Control Technology Research Center (Grant EPA CR 812582). We would also like to thank Richard T. Haasch of the Materials Research Laboratory of the University of Illinois at Urbana-Champaign for his assistance in analyzing the XPS data.

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Table 1. Physical Characteristics and Elemental Composition of ACCs.

ACC-20 Chemical Treatment	BET Surface Area [m ² /g]	Total Pore Volume [cm ³ /g]	Micropore Volume [cm ³ /g]	C [wt%]	H [wt%]	N [wt%]	O [wt%]	Cl [wt%]
3.9% O/untreated	1550	0.74	0.61	95.40 95.97 ^a	0.68	0.05	3.92 4.03 ^a	0
4.1% N (nitridated)	1738	0.84	0.59	91.96 94.34 ^a	0.27	4.50 4.06 ^a	3.23 1.60 ^a	0
7.8% Cl (chlorinated)	1523	0.73	0.54	87.71	0.06	0.27	4.15	7.8
16% Cl (chlorinated)	1374	0.66	0.51	77.93 88.94 ^a	0.01	0.06	6.00 3.27 ^a	16 7.8 ^a
21% O (oxidized)	1409	0.66	0.55	76.26 85.53 ^a	1.41	1.49	20.84 13.84 ^a	0
32% O (oxidized)	1105	0.47	0.35	64.76 76.60 ^a	1.55	0.72	32.32 23.39 ^a	0

a. % Elemental as determined by XPS. Difference in Cl values between the two methods may be due to uncertainty in the calibration standard used.

Table 2. XPS Deconvolution of the Carbon 1s Peak Area for Chemically Modified ACC-20.

Binding Energy [eV]	Percentage of Total Area of Carbon Peak					
	3.9% O (untreated)	21% O	32% O	12.3% Cl	16% Cl	4.1% N
285 (C-C, C-H)	50.94	55.9	46.86	57.28	42.08	48.43
286 (phenol, hydroxyl, C-OH)	27.87	14.92	24.68	21.00	31.12	24.20
287 (carbonyl, C=O)	9.29	13.03	7.64	8.12	8.23	8.14
289 (carboxylic, C=OOH)	5.58	9.99	14.59	7.16	8.56	7.90
291 (shake-up band, π → π*)	6.32	6.15	6.23	6.43	10.00	11.35

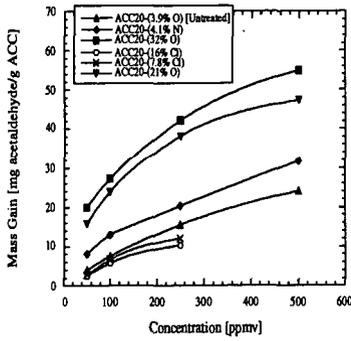


Figure 1. Adsorption of Acetaldehyde on Chemically Modified ACC.

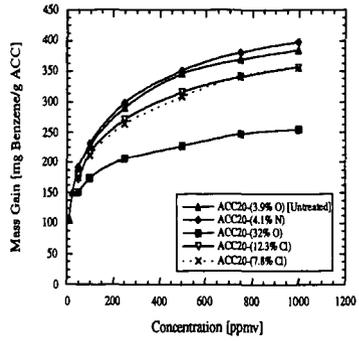


Figure 2. Adsorption of Benzene on Chemically Modified ACC.

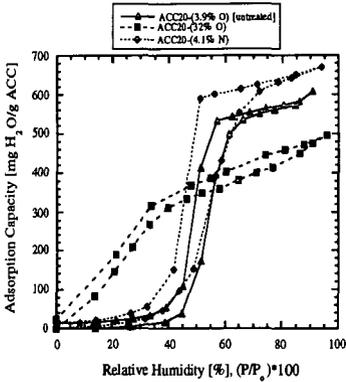


Figure 3. Adsorption and Desorption of Water Vapor on Oxidized and Nitrated ACC-20.

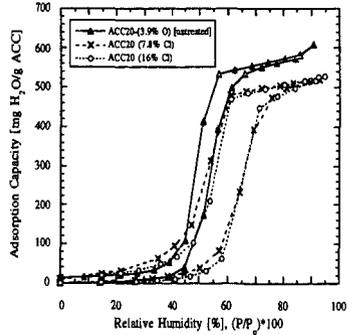


Figure 4. Adsorption and Desorption of Water Vapor on Chlorinated ACC-20.