

Chemically Treated Activated Carbon Cloths for Removal of Volatile Organic Carbons from Gas Streams: Evidence for Enhanced Physical Adsorption

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The micropore surfaces of activated carbon cloths (ACCs) have been chemically modified by introducing controlled amounts of nitrogen, oxygen, or chlorine on the surface of the micropores. The treatments with ammonia, oxidative reagents, or chlorine produce surfaces that are basic, acidic, and polar, respectively. The modified ACCs were evaluated for removal of several different volatile organic compounds (VOCs) in the 10–1000 ppmv concentration range. VOCs examined included acetaldehyde, acetone, and benzene. Acetaldehyde adsorption capacity increased by 500% with oxidized ACC surfaces as compared to untreated ACC surfaces. Acetone adsorption was also enhanced by 350% on oxidized surfaces. The level of benzene uptake was high with most all of the treated surfaces. Thermal regeneration of the ACCs at 100 °C was sufficient to desorb each of the three VOCs without any decrease in the adsorption capacity of the treated ACCs.

Introduction

The presence of VOCs in indoor and outdoor air is of concern because these gases promote photochemical formation of ozone and other contaminants (1) and may have adverse effects on human health (2–5). The Clean Air Act (1990) requires reductions in the emissions of toxic VOCs, hence some urgency exists to develop improved systems capable of removing such contaminants down to very low levels.

Typical indoor air quality control devices consist of a filter or electrostatic precipitator for particulate removal and infrequently a carbon adsorption bed of granular activated carbon (GAC) to remove some of the gaseous contaminants from the gas stream. Drawbacks to the use of GACs include relatively expensive containment and the need to be replaced or regenerated to prevent breakthrough and desorption of the gaseous contaminants (6).

Improved contact efficiency and higher adsorption capacities of ACC when compared to GAC was reported as early as the 1970s (7, 8). The potential for in situ electrical regeneration was also disclosed at that time. Very recently, it has been demonstrated that at high concentrations of contaminants, ACC with the highest surface area displays a higher adsorption capacity. However at low ppmv concentrations, lower surface area ACCs adsorbed the largest amount of contaminant (9–11). These observations are directly related to pore volume scaling with surface area, and smaller pores can display enhanced adsorbate-adsorbent interactions because of overlapping adsorption potentials between the walls of the pores (12, 13).

Recent work has described how the chemistry of the pore surface in ACC can be modified, and these modified surfaces may influence adsorption characteristics of various contaminants (14). In this paper, these studies are extended to describe the use of chemically modified ACCs on the removal of selected VOCs.

Experimental Procedures

The starting material, ACC-20, was obtained from Nippon Kynol Inc. Characteristics of the untreated ACC-20 sample are presented in Table 1.

Treatment of ACC-20 with NH₃ or Cl₂. About 1.0 g of ACC-20 was placed in a 5-cm i.d. quartz tube in a temperature-controlled 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 (reaction temperatures and times are discussed in the next section). After completion, the gas was replaced with nitrogen, and the sample was cooled to room temperature. The product was weighed and placed in closed vials for further characterization.

Oxidation of ACC-20. The oxidation reactions were carried out by immersing 1.45 g of ACC-20 in 100 mL of 1/1 (v/v) HNO₃/H₂SO₄ 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

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TABLE 1

Physical Characteristics and Elemental Composition of ACCs^a

ACC-20 with	BET (m ² g ⁻¹)	V _{t(N₂)} (mL g ⁻¹)	V _{m(N₂)} (mL g ⁻¹)	C (wt %)	H (wt %)	N (wt %)	O (wt %)	Cl (wt %)
(1) 3.9% O (untreated)	1550	0.74	0.61	95.40 95.97*	0.68	0.05	3.92 4.03*	
(2) 4.0% N (nitrided)	1738	0.84	0.59	91.96 94.34*	0.27	4.50 4.06*	3.23 1.60*	
(3) 7.8% Cl (chlorinated)	1523	0.73	0.54	87.71	0.06	0.27	4.15	7.8
(4) 16% Cl (chlorinated)	1374	0.66	0.51	77.93 88.94*	0.01	0.06	6.00 3.27*	16 7.8*
(5) 21% O (oxidized)	1409	0.66	0.55	76.26 85.53*	1.41	1.49	20.84 13.84*	
(6) 32% O (oxidized)	1105	0.47	0.35	64.76 76.60*	1.55	0.72	32.32 23.39*	

^a An asterisk (*) indicates the percent of element as determined by XPS. Bulk analyses are 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 Nature of Pore Structure and Nitrogen Isotherms, respectively.

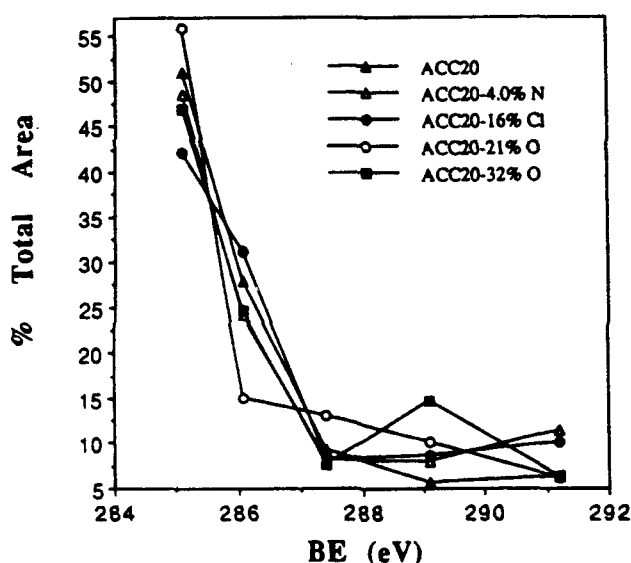


FIGURE 1. XPS data analysis: percentage contribution of each group in the total area of the carbon peak [phenol (285 eV), carbonyl (287 eV), carboxylic (288.8 eV), shake-up band (291.1 eV)].

left to dry overnight in a hood. Twelve hours later it was dried at 150 °C with N₂ 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 surface of the treated and untreated ACC samples (15). 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 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 (15). 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 shake-up peaks) (9).

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 (12). 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).

Organic Isotherms (Gravimetric Measurements). Acetone adsorption at concentrations of 25–1000 ppmv was determined as previously described (9). Acetaldehyde and benzene adsorption isotherms for the ACC samples were performed gravimetrically using a Cahn microbalance (Model C-2000). The gas stream for the VOC of interest was generated using a certified gas cylinder (Matheson Gas) of known VOC concentration, diluted with hydrocarbon-free air using mass flow controllers (Tylan Model FC-280) to obtain the desired concentrations. The adsorption isotherms were measured at 25 °C and a total pressure of 1 atm. ACC sample masses were between 10 and 20 mg, and the total gas flow rate through the gravimetric balance was 0.1 L/min.

Results and Discussion

Pore Surface Modification during Chemical Treatment.

Nitridation. Ammonia treatment of the ACC samples at 450–600 °C (for 12 h) yielded an increase in the N content from 0 to 1% by mass. At 800 °C (6 h) a 4% N content was achieved and about 5.8% N content in 12 h. The BET surface area decreased from 1600 m² g⁻¹ (ACC-20) to about 1400 m² g⁻¹ during nitridation at 700 °C (1.0–3.5% N content). At 800 °C, some etching of the pores is suggested since the

surface area increased to $1700 \text{ m}^2 \text{ g}^{-1}$ (at 4% N) and $\sim 2150 \text{ m}^2 \text{ g}^{-1}$ (at 5.8% N).

Nitridation of the ACC-20 samples results in N 1s peaks at 399 and 400–403 eV (broad, see Figure 1). The former can be assigned to amine and pyridine type groups while the latter can be assigned to pyrrolic nitrogen or amides or amino groups (literature values $\sim 400.2 \text{ eV}$) and ammonium derivatives (401.2 eV) (15, 16). Nitridation causes a minor decrease of the phenolic hydroxyl/ether peak. A slight increase of the shake-up peak at 291.1 eV relative to ACC-20 is also observed, indicative of the fact that nitrogen can be introduced in the carbon skeleton as pyridine nitrogen.

Oxidation. A 1/1 (v/v) mixture of $\text{H}_2\text{SO}_4/\text{HNO}_3$ acid was used to oxidize the pore surface to an oxygen content of $\sim 21\%$ after 10 min at ambient temperature ($T \sim 22^\circ\text{C}$). Longer treatments (≥ 4 days) resulted in a further increase in oxygen content to $\sim 32\%$. The N_2 BET surface area decreased with increasing degree of oxidation; e.g., $1400 \text{ m}^2 \text{ g}^{-1}$ (at 21% oxygen level) and $1150 \text{ m}^2 \text{ g}^{-1}$ (at 32% oxygen level) (Table 1).

Oxidation results in a peak at 534 eV in the XPS spectrum at 534 eV and appears to be associated with an increase in the number of carboxylic groups. At 21% oxygen content versus 32% oxygen, the ether and phenolic hydroxyls are somewhat lower.

Chlorination. Chlorination of the samples was investigated at various temperatures for different times. A 16% Cl content was achieved at 450°C within 12 h presumably by ring substitution. The BET surface area decreased modestly with degree of chlorination. Samples with 7.8% Cl content showed very little change in BET surface area, but the samples with 12.3% Cl had a BET surface area of $1440 \text{ m}^2 \text{ g}^{-1}$, and the sample with 16% Cl had a surface area of $1437 \text{ m}^2 \text{ g}^{-1}$.

Chlorination at 450°C (ACC-20, 16% Cl) results in appearance of a Cl 2p peak at 201 eV of the XPS spectrum. Also chlorination causes an increase of the shake-up band at 291.1 eV (presumably associated with changes in charge transfer upon chlorination) as well as of the carboxylic and phenolic hydroxyl/ether bands relative to ACC-20 (17).

Nature of Pore Structure in the Chemically Treated ACC. The adsorption–desorption isotherms of the chemically treated ACC-20's for N_2 gas at liquid N_2 temperature are shown in Figure 2. All of the isotherms have two characteristic regions; one below the relative pressure, $P/P_0 = 0.2$, where a substantial increase of the adsorbate uptake is observed with increasing relative pressure. This is indicative of microporosity in all three treated fibers. At P/P_0 values larger than about 0.2, very little gas uptake with increased relative pressure is observed for nitrated and chlorinated samples. This is indicative of minimal meso- or macroporosity in the samples. No hysteresis is observed for those two samples upon desorption. For the oxidized sample, adsorption seems to be constant between $P/P_0 = 0.2-1.0$ (P/P_0 values). However, there is some hysteresis upon desorption indicative of slit-shaped pores, where the hysteresis curve is parallel to the relative pressure axis (ref 12, p 287).

Values for the total pore volumes of the treated ACC samples were obtained from the initial plateau of adsorption–desorption isotherms and at higher P/P_0 values ($0.7 < P/P_0 \leq 0.99$) where the maximum amount of N_2 gas has been adsorbed (Table 1). The gas volume was converted to liquid N_2 volume using the density of liquid N_2 at 77 K. There was practically no difference (less than 2%) in the

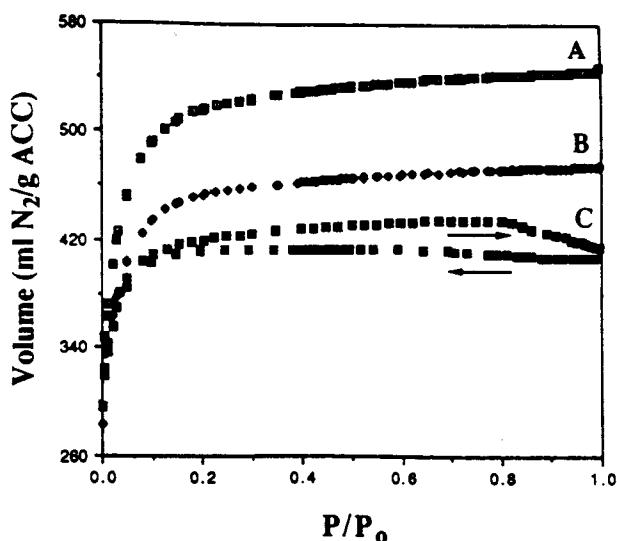


FIGURE 2. Nitrogen adsorption–desorption isotherms of the following: (A) ACC-20 (4% N), (B) ACC-20 (7.8% Cl), (C) ACC-20 (21% O).

volume of the adsorbed N_2 gas at $P/P_0 = 0.8$ compared to that at $P/P_0 = 0.95-0.99$ for each of the three treated fibers, indicating that there is no increase in the meso- or macroporosity. It is apparent that the nitrated ACC sample has the highest pore volume for N_2 gas, the chlorinated an intermediate one, and the oxidized the lowest one (in fact the highly oxidized has an even lower adsorption capacity). The capacity of the as-received ACC-20 falls between that of the nitrated and chlorinated samples.

Total pore volume values after chemical treatment follow the trends of the nitrogen BET surface area values. Micropore volume values follow the same patterns as total pore volumes and were determined (to a first approximation) from a t -plot analysis of the adsorption–desorption isotherm using the Jura–Harkins equation: $t = [13.99 / (0.034 - \log P/P_0)]^{0.5}$ (ref 12, pp 94–100).

Evaluation of the Chemically Modified ACCs for VOC Adsorption. Acetone. The adsorption isotherms of acetone (at 25°C) with virgin and chemically treated ACC-20 are shown in Figure 3. Over the range of concentrations examined (25–1000 ppmv acetone in N_2), one observes the highest adsorption capacity with the highly oxidized sample, ACC-20 (32% O). At 1000 ppmv acetone, the adsorption capacity of the oxidized ACC for acetone maximizes at about 23 wt %. This represents a 53% improvement over the untreated ACC-20 (3.9% O) sample, which shows only ~ 15 wt % acetone uptake. At 25 ppmv, there is a 350% improvement with the ACC-20 (32% O). Since the oxidized fiber is less porous (0.47 mL of liquid N_2/g) than the untreated ACC-20 (3.9%) sample (0.74 mL/g) the increased adsorption can only be due to chemical interactions at low adsorbate concentration. Surface oxygen groups are known to affect adsorption (18–20).

The chlorinated ACC-20 (16% Cl) sample shows a decrease in acetone adsorption throughout the concentration regime examined (Figure 4). Since chlorination of the fiber results in a slightly (13%) reduced surface area over the original ACC-20 (3.9%), one can conclude that the chlorine groups are not as effective in promoting adsorption of acetone. This comparison is even more pronounced with ACC-20 (21% O), which has very similar surface area ($1409 \text{ m}^2 \text{ g}^{-1}$), or ACC-20 (32% O) with a surface area of only $1105 \text{ m}^2 \text{ g}^{-1}$. Clearly oxidation produces surface groups

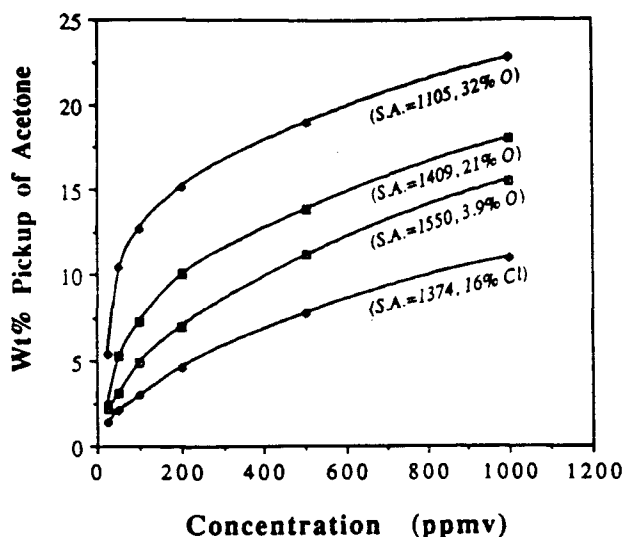


FIGURE 3. Acetone adsorption by chemically treated ACC-20 at 25–1000 ppmv in nitrogen (at 25 °C). The numbers on the curves correspond to those in Table 1.

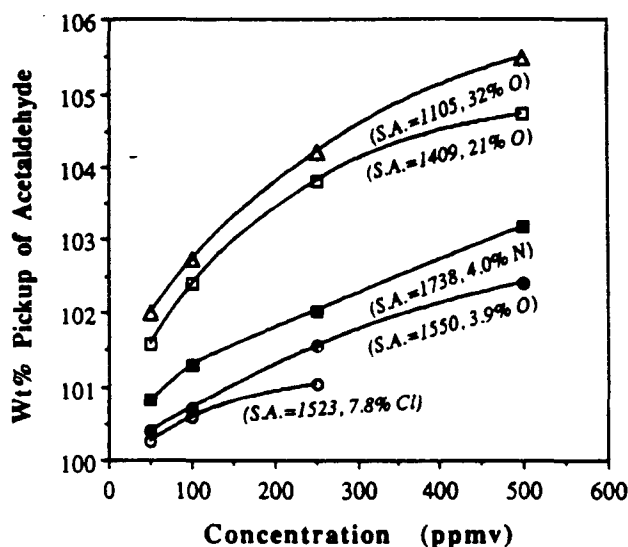


FIGURE 4. Acetaldehyde adsorption by chemically treated ACC-20 at 50–500 ppmv in nitrogen (at 25 °C). The numbers on the curves correspond to those in Table 1.

that enhance adsorption via dipole interactions and hydrogen bonding. It is important to mention that in all cases acetone is completely desorbed on heating to 80–100 °C, permitting complete recovery of the adsorption capacity.

Acetaldehyde. Very little data have been reported on the adsorption of acetaldehyde on porous materials (21). Comparisons of the adsorption characteristics for a series of ACC-20 samples that were untreated, oxidized, nitrated, and chlorinated are presented in Figure 4. The highly oxidized sample (32%) shows a much better uptake of acetaldehyde in the 50–500 ppmv concentration regime as compared to untreated ACC-20. In fact at 50 ppmv it adsorbs 2.0% by weight acetaldehyde whereas the ACC-20 adsorbs only 0.4%. The less oxidized sample (21% O) also shows enhanced acetaldehyde adsorption to a degree similar to that of the ACC-20 (32% O). The ACC samples could be completely regenerated below 100 °C. Nitrated ACC cloths with 4% N show an improved acetaldehyde uptake, indicating that the basic pore surface does interact somewhat with acetaldehyde. Finally in the case of the

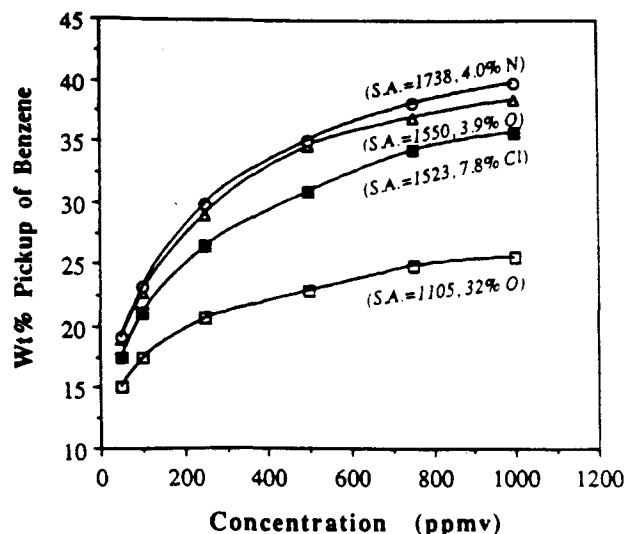


FIGURE 5. Benzene adsorption by chemically treated ACC-20 at 50–1000 ppmv in nitrogen (at 25 °C). The numbers on the curves correspond to those in Table 1.

chlorinated ACC sample (~7.8% Cl), a slight decrease in the adsorption capacity is observed compared to the as-received ACC. The decrease in adsorption capacity appeared to be related to the sample's surface chemistry instead of physical properties because the pore volume is similar to that of ACC-20 (21% O) (Table 1).

Benzene. Since benzene (nonpolar) is not miscible with H₂O, a hydrophilic surface should result in decreased adsorption (22). However, benzene adsorption on ACC-20 (32% O) at 1000 ppmv results in a 23% weight increase (see Figure 5).

The differences between ACC-20 (32% O) versus ACC-20 (3.9% O) can be interpreted based on surface area differences (see Figure 5 and Table 1). It is apparent that benzene adsorption decreases with BET surface area. The nitrated or basic surface shows a slightly increased benzene adsorption, while more polar surfaces ACC-20 (7.8% Cl) show slightly decreased uptake as compared to ACC-20 (3.9% O).

Summary and Conclusions

Conditions for the chemical modification of high surface area carbon fibers have been established that allow various chemical elements (N, O, Cl) to be chemically bound to the activated carbon cloths' carbonaceous structure at various levels. Both chlorination and oxidation lead to decreased surface area, total pore volume, and micropore volume, while treatment with ammonia results in somewhat higher values of porosity.

The oxidized surfaces displayed greatly enhanced adsorption of acetone (by 350%) and acetaldehyde (by 500%) at 25 and 50 ppmv, respectively, over untreated ACCs. They also exhibited enhanced adsorption of acetone (by 75%) and acetaldehyde (by 130%) at 1000 and 500 ppmv, respectively. Such an increase can best be interpreted as arising from strong hydrogen bonding. The chemically modified fibers all displayed 100% reversibility under relatively mild reactivation conditions.

The role of pore surface chemistry on the design of new and improved adsorbents for the removal of toxic VOCs from indoor air environments was assessed in the low ppmv regime. It was shown that micropore surface chemistry

can be modified, leading to a significant increase in adsorption of toxic VOCs from indoor air.

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