Activated carbon fiber composites for gas phase ammonia adsorption

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ABSTRACT

Low-cost activated carbon fiber composites (ACFCs) were explored as the basis for a system to remove NH_3 from the gas phase. ACFCs were synthesized by chemically activating a phenolic precursor on a glass fiber substrate using ZnCl_2 as catalyst. Additionally, ACFCs were oxidized with concentrated nitric acid at both room temperature and 83 °C to increase the density of surface oxygen groups. Commercially available phenolic-based physically activated carbon fibers were also oxidized under the same condition as a benchmark. Both physical properties and surface chemical properties of these materials were characterized using SEM, BET, elemental analysis, FTIR, XPS, and Boehm titration. Dynamic flowthrough NH_3 adsorption was measured at 500 ppm, at both 0% and 50% relative humidity. Results suggest ACFCs exhibit high surface area, rich oxygen functional groups, with post-treatment further improving surface oxygen content. ACFCs displayed fast sorption kinetics and high NH_3 adsorption capacity up to 50 mg/g. Acidic oxygen groups at the surface are correlated with ammonia adsorption. A new anhydride-based reaction mechanism was identified and is proposed, collectively with carboxylic acid functional groups, as being primarily responsible for retaining NH_3 .

1. Introduction

Ammonia (NH_3) is a notoriously hazardous chemical that is harmful to both industrial processes and human beings. For example, in the 193 nm-lithography semiconductor manufacturing process, trace NH_3 levels as low as 1 ppb are capable of damage to optics in the range of \$5 million for equipment and \$10,000 per hour for cleaning[1]. Fuel cells using acidic electrolytes suffer performance decay when fed gases containing more than 1 ppm NH_3 [2]. In the international space station (ISS), NH_3 could be emitted from human or animal urine or refrigeration system leaks, posing a health risk to astronauts, and is thus regulated to below 7 ppm[3]. Beyond these hazards, NH_3 is also regarded as one of the most dangerous Toxic Industrial Chemicals (TICs) —a new concerns for military chemical defense [4]. Due to its wide availability, ease of acquisition in large quantities and high toxicity, NH_3 could be used by terrorist to cause catastrophic casualties and injuries to civilians and military personnel. In all scenarios mentioned above, there is significant interest and need in developing an air filtration unit that can adsorb NH_3 effectively, encompassing both ease of containment and tailored pressure drop compatible with existing air handling systems[4-7].

In the literature, several types of adsorbents have been previously investigated for ammonia adsorption including activated carbons, zeolites, alumina, silica, graphene oxides (GO)[8] and metal organic frameworks (MOFs)[9], with activated carbons emerging as the most effective solution due to their high surface area and low cost[10]. Since NH_3 is a small molecule (diameter $\sim 3 \text{ \AA}$) with very high vapor pressure (10 atm at 25 °C), physical adsorption by activated carbon is thermodynamically unfavorable[8]. Although only a limited amount of surface chemical functional groups are present on virgin activated carbon, chemisorption has been as the main factor—as opposed to physical adsorption—dictating NH_3

uptake[11]. Unmodified granular activated carbons (GAC) and powdered activated carbons (PAC) have reported adsorption capacities ranging from 0.25 to 5.7 mg/g at 5,000 to 10,000 ppm of NH_3 [11-13]. To improve capacity, one approach is to tailor surface chemistry by maximizing acidic functional groups—a factor often quantified by oxygen content as characterized by elemental analysis or XPS[14]. Methods to increase O content include AC surface oxidation by sulfuric acid[13, 15], nitric acid[12, 14, 15], air[15], hydrogen peroxide and sodium dichloroisocyanurate[16]. Another common approach to modify AC is through impregnation of metal chloride salts or oxides, including W, V, Mo, Zn, Cr, Cu, etc[17-22]. Through these modifications, acidic surface functional groups have been dramatically increased along with an accompanying adsorption capacity ranging from 10–80 mg/g[11-13, 16-21, 23, 24].

Besides adsorption capability, ease of containment and pressure drop are also critical factors for HVAC (heating, ventilation, and air conditioning) system design[25]. GAC has very slow kinetics due to the large geometry of granules; PAC has fast mass transfer, while extremely high pressure drop makes it impractical for air handling system. Fiber-form adsorbents, on the other hand, possess a unique combination of rapid kinetics, low pressure drop and simplified containment for HVAC applications [26, 27]. As a fabric forms of activated carbon, activated carbon fibers (ACFs) has been synthesized and studied for water and air purification ever since 1960s. The synthesis, development, and environmental applications of ACFs have been reviewed comprehensively by Suzuki[26], Economy[27], Le Cloirec[28], Cukierman[29], et al. For NH_3 adsorption, Kynol based ACFs have been studied, and showed extremely poor affinity towards NH_3 . After oxidation treatment by nitric acid and sulfuric acid, ACFs showed tremendous increase in both adsorption capacities and

breakthrough times[14]. Although the superior performance compared with GAC and PAC and extensive research activities [27], ACFs are only used in niche markets commercially due to its exceedingly high cost (~\$500/kg). If low cost ACFs were developed, it may raise great interests.

Objectives of the present study are to explore a low-cost activated carbon fibers system for NH₃ adsorption, and investigate the correlations between surface chemistry and adsorbent-adsorbate interactions. In the present study, chemically activated carbon (CAFs) based on glass fiber substrates were synthesized and modified with surface oxidation. The low cost is achieved through use of both glass fiber substrate and activation catalysts, which greatly reduce the cost for both materials and processing temperature at approximately 400 °C. More importantly, a primary advantage of these CAFs over ACFs is a rich distribution of surface functional groups originating from the precursor retained due to the low processing temperature[30]. This in turn proves effective for polar pollutants like NH₃. In this work, first, the synthesis of a variety of ACFs and surface modifications is described; this is followed by characterization of surface chemistry and physical properties; afterwards, NH₃ adsorption is evaluated in flowthrough configurations; at last, the mechanisms of ammonia adsorbate–adsorbent interactions are characterized and discussed.

2. Materials and methods

2.1 Materials

Novolac resin (Schenectady International Inc., HRJ-2190) was employed as a polymeric phenolic precursor, ZnCl₂ (Sigma-Aldrich, Cat. 208086, 99%) served as activation agent. Solvents include Ethanol (Decon, 200 proof) and DI Water. A non-woven glass fiber mat (Craneglas 230, Neenha Technical materials) with fiber diameter of 6.5 μm was used due to

ease of use and low cost. Commercial ACFs (Nippon Kynol[®], ACC-5092-20) were used as-received.

2.2 Synthesis

Phenolic based chemically activated carbon fibers (CAFs) were synthesized based on previous work with modifications[31]. 30 g Novolac was dissolved in 200 ml of ethanol at room temperature, followed by adding 30 g of ZnCl₂. Craneglas mat was then dip-coated into the solution and dry at room temperature. Afterwards, the fiber mat was placed into a convection oven wherein the temperature was slowly raised from 110 to 170 °C over 8 hr. Next, the sample was transferred to an enclosed Lindberg furnace under N₂ flow and heated to 400 °C at a rate of 30 °C min⁻¹ and held for 30 min to activate. Afterwards, the sample was allowed to cool down under flowing N₂. The sample was washed with 0.5 N HCl and rinsed with DIW. The composite was then placed in a vacuum oven and dried at 150 °C overnight.

To further improve surface acidity and thus ammonia uptake, Phenolic based ACFCs were also post-treated with concentrated HNO₃. 1 g of Phenolic CAF (labeled as Phenolic) was placed in concentrated HNO₃ at either room temperature (labeled as Ph-Nitric-RT) or 83 °C (Ph-Nitric-80). After the reaction, samples were washed with DIW several times to remove residual acid. Afterwards, samples were dried in a hood and then vacuum dried at 100 °C overnight. Kynol (ACF20) was used as received. ACF20 was also post-treated with concentrated HNO₃. Under the same condition described above, and labeled as A20-Nitric-RT and A20-Nitric-80, respectively.

2.3 Ammonia adsorption

A dynamic breakthrough test has been used to evaluate the efficiency of the ACFC media for removing NH₃ from air in a flow-through configuration (Fig. 1). Influent NH₃ concentrations were adjusted using flow controllers and calibrated by effluent NH₃ sensor

(NH₃ electrochemical sensor, Industrial Scientific, iBrid MX6, 0-500 ppm with 1ppm resolution). Effluent NH₃ concentrations were monitored using the same electrochemical sensor. ACFCs were punched to form 2.4 cm diameter circles with sample weight ~ 0.3 g and bed depth ~ 1.4 mm. All ACFCs were tested under 250 mL/min flow rate, 500 ppm NH₃ inlet concentration and both 0% and 50% relative humidity (RH). Adsorption capacity of active media is calculated by integration of the flowthrough curve until $C/C_0 = 0.1$ (50 ppm). In order to study a special interaction mechanism, samples were thermally regenerated at 100-200 °C for 1 hr after breakthrough.

Fig. 1 Ammonia dynamic flowthrough test

2.4 Characterizations

SEM images were obtained using a Hitachi S-4700 with mixed field emission with a 10 kV–15 kV accelerating voltage. Samples were attached on an aluminum sample holder using a carbon tape. Sample conductivity was improved by coating with a thin layer of metal using a gold palladium plasma.

Surface area and pore size analysis was obtained using a Quantachrome Autosorb-1 pore surface analyzer. Samples were first dried at 110 °C under vacuum before measurement. These samples were degassed until the outgassing pressure change was below 5 µm Hg/min before analysis. N₂ adsorption isotherms at 77K were used to measure the surface area and pore volume. BET equation was used to calculate the surface area using P/P_0 range from

0.05 to 0.3; The Dubinin-Radushkevitch (DR) equation was used to deduce the total micropore volume; Total pore volume was estimated from the amount of nitrogen adsorbed at $P/P_0 = 0.95$. Mesopore volume was calculated by the difference of total pore volume and micropore volume.

Coating contents of samples were measured by TGA (Hi-Res TA Instruments 2950 Thermogravimetric Analyzer). The coating contents of ACFCs were measured by burning off carbon coating at 800°C in air. Sample's coating content was calculated by the following equation:

$$\text{Coating Content \%} = \frac{\text{Weight loss \% (from 110 °C to 800 °C)}}{1 - \text{moisture content \% (weight loss from RT to 110 °C)}}$$

Elemental analysis was used to quantify carbon, hydrogen, nitrogen and other heteroatoms presents in the carbon matrix. Chemical composition (C, H, and N) of samples was determined using a Model CE440 Elemental Analyzer. The detection limit for each element was 0.10% with errors 0.06%. Additionally, zinc (Zn) content was determined by ICP/MS with detection limits < 1 ppb. Oxygen content was determined indirectly by the following equation:

$$w[\text{O}] = w[\text{coating content\%}] - w[\text{C}] - w[\text{H}] - w[\text{N}] - w[\text{Zn}]$$

The zeta potential (ζ) of PANCAF and HACAX was measured at different equilibrium pH using Zetasizer Nano ZS (Malvern Instruments) to identify the isoelectric point (IEP). Samples (~ 10 mg) were grounded into powder, and mixed with 15 ml aqueous solution with pH between 2 and 12. pH of solution was adjusted by adding 0.5 N HCl or NaOH. After shaking for 24 hr, the zeta potential of adsorbent and final pH of suspension was measured.

The pH isotherm was measured to identify point of zero charge pH (PZC), which is the pH when the activated carbon materials have zero net charge as total; Above which, the

carbon is negatively charged and vice versa. This method is based on the work by Lopez-Raman et al.[32] with minor modifications. Samples (~ 10 mg) were ground into powder, and mixed with 15 ml aqueous solution with pH between 2 and 12. pH of solution was adjusted by adding 0.5M HCl or NaOH and measured by pH electrode. After shaking for 24 hrs, pH of the final suspension was measured by pH electrode. The pH at which $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$ or plateau is determined as PZC.

Infrared spectrum was obtained by Thermo Nicolet Nexus 670 FTIR to identify chemical functional groups. As activated carbon samples are intrinsic absorbers, DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) mode is applied to maximize signal intensity. Fibrous samples were directly measured without KBr addition. Data acquisition was performed by Omnic[®] software with 32 scans at a resolution of 4 cm^{-1} .

Boehm titration with minor changes[33-36] was employed to quantify surface acidic oxygen functional groups into phenolic, lactonic, and carboxylic acid functional groups within activated carbon (the detailed procedure is described in **ESI**).

3. Results and discussion

3.1 Physical properties

SEM images presented in Fig. 2 show the textures of different samples. ACF20 has fiber diameter $\sim 13 \pm 5\text{ }\mu\text{m}$ densely packed in a woven pattern; HNO_3 treatment either at room temperature and $80\text{ }^\circ\text{C}$ did not cause noticeable changes at the micron scale. All ACFCs are composed of active coatings and glass fiber substrates. The original glass fiber is $\sim 6.5\text{ }\mu\text{m}$ in diameter and loosely packed. Activated layers are either coated uniformly on glass fiber or as bridging in-between fibers. Same as that for ACF20, there are no obvious geometry changes after HNO_3 treatment, suggesting that oxidation by HNO_3 will not affect mechanical integrity.

Fig. 2 SEM image of ACFCs and ACF and oxidation derivatives

Coating content and pore size analysis are summarized in Table 1. Compared with ACFs materials which are pure carbon, coating content of ACFCs are controlled between 30 to 50 %_{wt} to keep reasonable amount of active coating layers without introducing tremendous pressure drop. Coating content is essential to leveraging capacity, pressure drop and cost for specific applications; in light of that, most of the parameters are calculated and compared based on coating as opposed to the total materials. High surface area and porosity are essential to providing more accessible functional groups and thus adsorption efficiency[37]. Most ACFCs are microporous (> 90%), and have relatively high surface area values (> 1000 m²/g based on coating); micropores are critical for removal of trace contaminants due to the higher overlap in potential from the van der Waal forces of opposite pore walls[8]. Post-treatment with nitric acid has little effect on surface area of samples, except the phenolic based ACFCs treated with HNO₃ at 80 °C (Ph-Nitric-80C), where the material underwent degradation and/or blockage of the pore structure. It may be due to the incomplete carbonization of chemical activation, which leads to relatively unstable structure compared with materials obtained from physical activation[38].

Table 1 Coating Content, Surface Area and Pore Analysis

Material	Coating (% _{wt})	BET (m ² /g)	BET- Coating (m ² /g)	Micro-pore (cm ³ /g)	Meso-pore (cm ³ /g)	Micro- pore Ratio (%)
ACF20 [39]	>99	1843	1843	0.62	0.02	96
A20-Nitric-RT	>99	2375	2375	1.28	0.02	98
A20-Nitric-80C	>99	2428	2428	1.3	0.04	97
Phenolic	47	608	1294	0.33	0.04	89
Ph-Nitric-RT	53	688	1310	0.35	0.04	90
Ph-Nitric-80C	53	213	402	0.11	0.02	85

3.2 Surface chemistry properties

Surface chemistry—in particular the density and type of oxygen functional groups—is of paramount importance for NH₃ adsorption in activated carbons[8, 40]. One potential means of introducing oxygen groups including carboxylic, phenolic and lactonic sites is by oxidization of carbonaceous materials using nitric acid[15]. These functional groups can potentially greatly improve NH₃ adsorption capacity.

Given that the importance surface chemistry plays for successful adsorbents design for NH₃, several techniques, including elemental analysis, FTIR, pH isotherm, zeta potential and Boehm titration were employed to explore surface chemistry from different perspectives.

According to previous literature, a critical design parameter for high capacity adsorbents is the O/C ratio[12], which is indirectly related to the number of acidic groups present in the pore structure. Higher oxygen content is also commonly regarded as the major reason for high NH₃ adsorption capacity[12, 13]. Key ACFC elemental analysis results are shown in Table 2. While original ACF20 showed only 5% O/C, nitric acid treatment greatly increased oxygen content on the surface, with 3-fold and 10-fold increases for room temperature and high temperature treatment, respectively. Original Phenolic ACFCs have more oxygen on

surface than ACF20 due to incomplete carbonization during chemical activation, and post-treatment improves O/C to 35% and 61%, which are each higher than ACFs treated under the same conditions, respectively.

Table 2 Elemental Analysis Results based on coating (%wt)

Materials	C	H	N	O	Zn	O/C
ACF20	94%	0.4%	0.3%	5%	-	5%
A20-Nitric-RT	84%	0.4%	1.0%	14%	-	17%
A20-Nitric-80C	66%	1.2%	0.7%	32%	-	49%
Phenolic	88%	2.0%	0.0%	10%	1%	12%
Ph-Nitric-RT	71%	1.3%	1.9%	26%	0%	36%
Ph-Nitric-80C	60%	1.6%	2.4%	36%	-	61%

FTIR in DRIFTS mode was used to further study surface functional groups[38, 41]. FTIR spectra of ACFs are shown in Fig. 3. The peaks at $\sim 1600\text{ cm}^{-1}$ could be assigned to C=C in the skeletal carbon matrix[42] for the original ACF20; however, peak position shifts towards higher frequency (i.e., towards 1650 cm^{-1}) upon oxidation by nitric acid at both RT and $80\text{ }^{\circ}\text{C}$, possibly suggesting the formation of more conjugated C=O due to carbonyl[43] or quinone[44] functional groups. Small peaks from $1740\text{-}1680\text{ cm}^{-1}$ suggest the presence of C=O related to lactone and/or carboxylic acid structures[45, 46]. A prominent peak at 1772 cm^{-1} for A20-Nitric-80 may suggest the presence of a significant amount of carbonyl groups including a mixture of carboxylic acid, lactone, and especially anhydride functional groups[47]. Peaks from $1390\text{-}1340\text{ cm}^{-1}$ might be due to phenol or nitro groups [13, 45, 46, 48]. These peaks are more pronounced in the more oxidized samples. The FTIR spectra confirmed the presence of acidic groups on the surface of these carbon fibers.

Fig. 3 FTIR of ACFs Series samples

Phenolic ACFCs FTIR spectra are shown in Fig. 4. Peaks at $\sim 1600\text{ cm}^{-1}$ suggest stable polyaromatic C=C[42]. Upon nitric acid oxidation, the peak near 1700 cm^{-1} both increased in intensity and broadened from 1706 cm^{-1} to $1760\text{--}1694\text{ cm}^{-1}$, and $1773\text{--}1697\text{ cm}^{-1}$ for original, RT treatment, and $80\text{ }^{\circ}\text{C}$ treatment respectively. This suggests the introduction of a variety of functional groups including carboxylic acid, lactonic[49], carbonyl or quinones[13], etc. Especially with the $80\text{ }^{\circ}\text{C}$ treatment, peaks above 1750 cm^{-1} may suggest the formation of anhydrides[13, 47]. Additionally, more pronounced peaks at 3400 cm^{-1} and 1040 cm^{-1} suggest a greatly increased amount of carboxylic acid groups integrated in the matrix.

Fig. 4 FTIR of ACFCs

Boehm titration was employed in order to quantify distribution of surface acidic functional groups amongst 3 main types: phenolic-, lactonic- and carboxylic acid-class groups (Fig. 5). Original ACF20 has a very limited amount of total surface acidic functional groups (0.2 mmol/g). RT treatment in nitric acid introduces phenolic, lactonic and carboxylic acid functional groups, while increasing total acidic functional groups 4.5-fold. Upon high temperature nitric acid treatment, most phenolic and lactonic functional groups have disappeared, while many more carboxylic acid functional groups (1.2 mmol/g) are introduced. It should be noted that Boehm titration method cannot distinguish anhydride with carboxylic acid, thus 1.2 mmol/g includes both since FTIR suggests the presence of anhydrides.

Fig. 5 Surface acidic functional groups identified by Boehm titration

Original phenolic ACFCs showed improved concentration of acid functional groups compared with ACF20 but are still limited to ~ 0.4 mmol/g. RT treatment in nitric acid primarily introduces phenolic and carboxylic acid groups while increasing total acidic functional groups 3-fold. After high temperature nitric acid treatment, carboxylic acid functional groups including anhydrides increase to 2 mmol/g. Complete speciation of surface oxygen cannot be achieved through Boehm titration as it is limited in that it cannot probe neutral oxygen functionalities: ketones, aldehydes, esters, ethers, etc. Additionally, wet

chemistry may not be able to probe functionalities in ultra-small pores where hydrated ions cannot enter, such as the present case where hydrated Na^+ cannot get into pores smaller than 7.4 Å[50].

IEP and PZC are important measurements of the pH associated with net neutral surface and total charge, respectively. At $\text{pH} < \text{IEP}$ or PZC , sample surfaces and bulk are positively charged; conversely, at $\text{pH} > \text{IEP}$ or PZC , surface and bulk are negatively charged. IEP or PZC values each depend on the type and amount of functional groups. IEP or PZC lower than 7 tends to indicate activated carbons rich in acidic functional groups[41]. Lower values indicate increasing acidic functional groups/strength on surface[51]. Compared with IEP which only represents external surface, PZC represents the whole surface both internally and externally. Thus, differences between PZC and IEP reveal the distribution of charge and thus functional groups on the internal and external surface of porous carbons[41]. PZC and IEP of the ACFCs and ACFs are summarized in Table 3. For both ACF20 and phenolics, $\text{PZC} \sim 7$ of the original samples suggests the original materials are almost neutral as a bulk. After HNO_3 oxidation treatment, both PZC and IEP are decreased, suggesting that acidic functional groups were preferentially introduced on the surface. The difference between PZC and IEP shows non-uniformity between internal and external surfaces; the present results suggest external surfaces are more oxidized for all samples, which in turn suggests XPS may not be appropriate for quantification of functional groups of all samples. Higher temperature nitric acid treatment not only introduced more acidic functional groups but also showed more uniform oxidation compared with RT oxidation.

Table 3 pH of point of zero charge and pH of isoelectric point

	Sample	pH _{PZC}	pH _{IEP}	pH _{PZC} - pH _{IEP}
ACFs Series	ACF20	7.2	3.6	3.6
	A20-Nitric-RT	6.5	2.7	3.8
	A20-Nitric-80	4.5	1	3.5
ACFCs Series	Phenolic	7.2	2.8	4.4
	Ph-Nitric-RT	6.6	1.8	4.8
	Ph-Nitric-80	4.9	<1	>3.9

3.3 Ammonia adsorption

Dynamic breakthrough tests were employed to evaluate the efficiency of the ACFCs media for removing NH₃ from air in a flow-through configuration. The results are summarized in Fig. 6, with breakthrough curves in supplementary information (**ESI**). For ACFs samples, unmodified ACF20 has a capacity of only ~ 1 mg/g. A20-Nitric-RT has an adsorption capacity of ~ 10 mg/g due to increased surface acidic groups introduced by oxidation; 80 °C HNO₃ treatment exhibited more than double the sorption capacity at both 0% and 50% RH conditions, relative to RT treatment. Moisture plays an important role in adsorption capacity—either positive or negative depending on the circumstances. A20-Nitric-RT showed 66% more capacity under humid conditions compared with 0% RH conditions. This increase could be caused by improved surface acidity and thus hydrophilicity of materials, which increases moisture adsorption; thin layers of adsorbed water are known to promote adsorption of NH₃ by dissolution effects[8]. As for A20-Nitric-80, on the contrary, capacities under humid conditions are 40% lower than dry conditions. This may be due to excessive water adsorbed on the highly acidic surface under humid condition, which could clog the pores and prohibit diffusion of ammonia to active sites [10]. Another possibility is

that hydrated NH_3 ($\sim 5.3 \text{ \AA}$ [50]) is too large to access the ultrafine pores, or is simply limited by kinetics when a large amount of water has accumulated on the surface.

Fig. 6 Ammonia dynamic adsorption capacity under 0% and 50% relative humidity

For phenolic ACFCs, the original sample shows slightly better capacity ($\sim 2 \text{ mg/g}$) compared with ACF20. This could be explained by the incomplete carbonization of phenolic ACFCs which provide residual acidic functional groups at a level 4 times higher than ACF20 as suggested by Boehm titration. Ph-Nitric-RT has a sorption capacity of $\sim 10 \text{ mg/g}$; 80°C HNO_3 treatment exhibited at least double the sorption capacity at both 0% and 50% RH conditions relative to RT treatment. The effect of humidity on capacity follows the same trend as with the series of ACFs samples.

ACFCs and ACFs series each follow similar trends, with acid treatment greatly improving adsorption capacity. RT-nitric acid treatment increased capacity by 4-fold to 6-fold; high temperature nitric acid treatment increased capacity by an order of magnitude; moreover, the trends coincide with the amount surface acidic functional groups determined by Boehm titration and elemental analysis.

3.4 Mechanism of anhydride-ammonia interaction

Mechanisms of interaction between NH_3 and various surface functional groups merit specific evaluation. NH_3 can be adsorbed on and interact with the surface through various mechanisms, roughly categorized into: non-specific van der Waals force, dissolution in water film adsorbed on surface, hydrogen bonding, Brønsted acid-base interactions (mainly carboxylic acid sites via ammonium ions)[12, 13]. In this study, another distinct mechanism was discovered, involving Brønsted acid-base interactions and contributing a higher amount of adsorbed NH_3 .

Both Ph-Nitric-80 and A20-Nitric-80 showed a broad range of acidic functional groups in their FTIR spectra. The peak at $1750\text{-}1800\text{ cm}^{-1}$ suggests the formation of anhydride due to aggressive oxidation by HNO_3 at high temperature. In order to further explore the interactions with NH_3 , FTIR of original samples and samples treated with NH_3 were compared.

For A20-Nitric-80, as shown in Fig. 7, the original sample has an intense peak at 1773 cm^{-1} suggesting the presence of anhydride functional groups. After treatment with NH_3 , the peak at 1773 cm^{-1} shifted to 1734 cm^{-1} indicating the possible formation of COOH from the anhydride. Increased intensity at 1635 cm^{-1} may imply the formation of amide bonds[52]; peaks at 1535 cm^{-1} and 1370 cm^{-1} suggest the formation of COO^- [12]. After thermal regeneration, the peak at 1774 cm^{-1} reappeared, along with a small peak at 1717 cm^{-1} , implying the possible formation of imide bonds[52].

Fig. 7 FTIR of A20-Nitric-80, loaded with NH₃ and regenerated

For Ph-Nitric-80, the same trend is also observed by FTIR. As shown in Fig.8, after treatment with NH₃, the increased intensity at 1439 and 1400 cm⁻¹ suggests the presence of NH₄⁺, and a peak shift from 1773-1684 to 1710-1650 cm⁻¹ suggests a change from COOH and O=C-O-C=O into COO⁻. Peaks at 1657 and 1562 cm⁻¹ suggest the formation of amide bonds. After regeneration, the peak at 1774 cm⁻¹ reappeared, along with a new peak at 1722 cm⁻¹, which may also suggest the formation of imide bonds. In the absence of strong acid or base, neither imides nor amides are generally regenerable under the mild heating conditions tested[53].

Fig. 8 FTIR of original Ph-Nitric-80, treated with NH_3 and regenerated sample

The interactions between anhydride functional group and ammonia are illustrated in Fig.

9. Whether the final product stays in amide or imide form is greatly influenced by the presence of water. In the absence of water, reactions should be driven more towards formation of imide bond; conversely, with water present in more humid conditions, the reactions would tend towards formation of amide and carboxylate anion—ammonium cation pairs. Typically, Brønsted acid-base interactions are reversible, while amide or imide bonds are irreversible in the absence of a catalyst. Humid conditions should favor amide and COONH_4 pair formation, in which case 50% of initial capacity could be recovered after regeneration by heating; on the other hand, sorption at 0% RH should tend to yield more imides—which would be completely irreversible and necessarily lead to < 50% regeneration efficiency. Indeed, we see this pattern (i.e., 50% regeneration efficiency at 50% RH, and < 50% at 0% RH condition[54]) in the regeneration tests for the samples anticipated to have the highest anhydride content: A20-Nitric-80 and Phenolic-Nitric-80. Collectively, these results support the FTIR finding of anhydrides upon high temperature nitric acid treatment.

Fig. 9 Mechanism of NH_3 interaction with anhydride functional group

3.5 Correlation between surface functional groups and capacity

In order to analyze which functional group(s) play the key role in adsorption capacity, the sample capacity and measured amount of functional groups have been summarized and converted to equivalent units (mmol/g), as shown in Table 4.

Table 4 Summary of surface functional groups vs. adsorption capacities and regenerated capacities

Sample	x mmol/g			y mmol/g	
	Phenolic	Lactonic	Carboxylic Acid	Capacity 0% RH	Capacity 50% RH
ACF20	0.06	0.12	0.00	0.1	0.1
A20-Nitric-RT	0.32	0.33	0.27	0.3	0.5
A20-Nitric-80	0.00	0.00	1.19	2.7	1.5
Phenolic	0.13	0.26	0.00	0.1	0.2
Ph-Nitric-RT	0.33	0.44	0.53	0.7	0.7
Ph-Nitric-80	0.05	0.86	2.00	3.0	1.4

Correlation coefficient r and significance testing p -value were computed using Matlab (Table 5). The correlation coefficient r is a measurement of linear dependence between two variables X and Y . The p -value is employed for testing the hypothesis of no correlation against the alternative that there is a nonzero correlation. If the p -value is less than 0.05, or more strictly 0.01, then the correlation between X and Y is significant.

Table 5 Correlation coefficient r and p -value of different surface functional groups and capacities

	Dry-Capacity		Wet-Capacity	
	r	p	r	p
Phenolic	-0.551	0.257	-0.375	0.464
Lactonic	0.355	0.490	0.299	0.565
Carboxylic	0.961 ^{**}	0.002	0.921 ^{**}	0.009

The results demonstrate that phenolic- and lactonic-class functional groups are less correlated with dynamic adsorption capacity. On the other hand, carboxylic acid-class groups—anhydrides included therein—are strongly correlated with high adsorption capacity. Results suggest that carboxylic acid-class functional groups exhibit a significant influence on high dynamic adsorption capacity. Conversely, phenolic- and lactonic-class functional groups are less significant for adsorption capacity.

4. Conclusions

In this work, activated carbon fiber composites (ACFCs) were developed for removal of ammonia from air. Kynol based ACFs modified by oxidation, and both original and oxidized ACFCs possess a large density of surface acidic functional groups and thus high NH_3 adsorption capacity. High surface area $> 1000 \text{ m}^2/\text{g}$ observed in all ACFCs is essential to providing more accessible surface functional groups and consequently adsorption efficiency. Surface characterization showed that surface acidic oxygen groups, in particular carboxylic acid and/or anhydrides, play the key role in both adsorption capacity and regeneration efficiency. Reaction of anhydrides with ammonia results in formation of non-regenerable amide and/or imide units, indicating the possibility for high temperature ammonia adsorption.

Compared with traditional physical activation, where harsh activating conditions result in a low number of heteroatoms and fewer surface functionalities[30], chemical activation may serve to retain a rich distribution of surface functional groups originated from a precursor, which could in turn prove effective for polar pollutants like NH_3 .

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