Tailoring of Surface Oxygen-Containing Functional Groups and Their Effect on Adsorptive Denitrogenation of Liquid Hydrocarbons Over Activated Carbon

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DOI 10.1002/aic.13886
Published online August 8, 2012 in Wiley Online Library (wileyonlinelibrary.com).

The objective of this study is to get a fundamental understanding of role of surface oxygen-contained functional groups (OCFG) in adsorptive denitrogenation (ADN) of liquid hydrocarbons over activated carbon, and thus to improve the ADN performance of activated carbon through modification of surface chemistry of activated carbon. A set of activated carbon samples with different amount and distribution of OCFG was prepared by oxidative modification and thermal treatment of a commercial activated carbon. The prepared activated carbons were characterized by the temperature-programmed desorption coupled with mass spectrometry for the concentration of various OCFG, and evaluated in a fixed-bed adsorption system using a model fuel containing aniline, indole, quinoline, carbazole, and ethyl-carbazole. The results indicate that OCFG, especially the strong carboxyls, weak carboxyls and anhydrides, play a crucial role in determining the adsorptive performance of activated carbon for selective removal of nitrogen compounds from liquid hydrocarbons. The adsorption mechanism of the nitrogen compounds over activated carbon was discussed on the basis of the structure-performance correlation and the molecular simulation. *AIChE J,* 59: 1236–1244, 2013
Keywords: adsorption, denitrogenation, activated carbon, oxygen-contained functional groups, liquid hydrocarbon

Introduction

Reducing sulfur content in various transportation fuels is crucial due to environmental concerns, which require the sulfur content in diesel fuel to be less than 15 ppmw.[1–7] Hydrodesulfurization (HDS) is a major process in current refineries to remove sulfur from various liquid hydrocarbon streams. However, it is well known that the presence of nitrogen compounds, such as pyridine, quinoline, acridine, indole, and carbazole, in the liquid hydrocarbon streams, even at very low concentration, strongly inhibits the ultra-deep HDS and poisons most of the catalysts used in the subsequent processes.[1,3,8–13] It has been reported in literature that the removal of these nitrogen compounds prior to HDS could remarkably improve the HDS performance.[1,11,14,15] The nitrogen compounds existing in fuels also cause odor and color, and reduce the thermal and oxidative stability of fuels.[12,16] Conversely, denitrogenation is one of the major tasks in upgrading of the coal liquids derived from coal direct liquefaction and coal pyrolysis, since nitrogen content in these coal liquids can be as high as more than 2000 ppmw, which is much higher than that in the petroleum-based hydrocarbon streams with the similar boiling rang.[17] Consequently, deep denitrogenation of liquid hydrocarbon streams for production of ultra-clean fuels is becoming a more and more important research subject worldwide.[11,14,16] Currently, removal of nitrogen compounds from various liquid hydrocarbon streams is performed via the catalytic hydrodenitrogenation (HDN) process in refineries. However, due to much stronger C—N bond than C—S bond, HDN is much more difficult than HDS, requiring severer reaction conditions and higher hydrogen consumption.[3,18–20]

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Alternatively, a great deal of attention has been paid to the adsorptive denitrogenation (ADN) of liquid hydrocarbon streams, as ADN can be conducted at ambient condition without using hydrogen gas.[11,14,21–23] Some investigations on ADN of liquid hydrocarbons have been reported recently in the literature.[11,16,21–24] Different types of adsorbents, including zeolites, activated carbon, activated alumina, silica gels and others, have been tested for ADN. Among them, it was found that activated carbon is a promising adsorbent material for selective removal of the nitrogen compounds, due to its wide source, easy for surface modification, high adsorption capacity and good selectivity.[11,21–23,25]

In general, adsorption behavior of carbon materials depends on their physical and chemical properties.[26,27] Many investigations of using activated carbon as an adsorbent for the gas-phase adsorption to separate and/or purify gases, and for the liquid-phase adsorption to separate organic compounds from aquatic solutions have been conducted widely. However, relatively fewer investigations on using activated carbon as an adsorbent to remove the polar compounds, such as sulfur/nitrogen-containing compounds, from liquid hydrocarbon streams have been performed. Seredych et al.[28] concluded that the micropore volume of carbon materials is a main factor governing the amount of the adsorbed dibenzothiophene (DBT) in adsorptive desulfurization, whereas Jiang et al.[29] believed that the significant increase in the DBT adsorption capacity of the modified activated carbon is mainly due to the increase of mesopore volume. However, Zhou et al.[25] reported that the significant improved adsorption capacity for sulfur compounds over the oxidation-modified activated carbon was mainly due to increase in the oxygen-containing functional groups (OCFG). It appears that the mechanisms proposed by different researchers are quite different. In our previous studies[21,22] in the structure-performance correlation, it was found that there was no satisfied correlation between the adsorption capacity for both quinoline and indole and the textural properties of the activated carbons, such as the total surface area, microporous surface area or mesoporous surface area. However, the surface chemistry, such as concentration of the OCFG of the activated carbons may play a more important role in determination of their adsorptive capacity and selectivity for the nitrogen compounds. Because of using the commercial activated carbon samples in our previous study, these activated carbon samples show the differences not only in the surface chemistry, but also in the textural structure, which make it is difficult to examine and distinguish the effect of the different factors on ADN performance and to get insight into the ADN mechanism of liquid hydrocarbon streams on activated carbon.

In this study, the oxidative modification and thermal tailoring of surface OCFG of a commercial activated carbon was conducted, and the ADN performance of the modified activated carbon samples were evaluated in a fixed-bed adsorption system using a simulated fuel, which contains typical nitrogen-containing compounds, including aniline, indole, quinoline, carbazole, and ethyl-carbazole, in liquid hydrocarbons. The activated carbon was first modified by the chemical oxidation using ammonium persulfate (APS) as an oxidant at the best oxidation conditions determined in our previous study[17] to maximize the number of OCFG on the surface, and then, heat treatment in N_2 and H_2, respectively, was conducted to tailor the OCFG on the sample surface to obtain carbon materials with totally different OCFG distribution on the surface, but similar textural structure. The study focused on examining the effect of the surface OCFG on the adsorption capacity and selectivity for different nitrogen compounds in liquid hydrocarbons. The modified and tailored activated carbon samples were characterized by the nitrogen adsorption at 77 K and the modified TPD-MS (temperature-programmed desorption coupled with mass spectrometry) method reported in detail in our previous paper.[30] The adsorption performance of these different activated carbons for the five nitrogen compounds was evaluated and the results were correlated with their surface chemical properties to build a relationship between the surface chemical structure of the activated carbons and their ADN performance. In addition, the adsorption mechanism of different nitrogen compounds on carbon surface was discussed in combination with the computational chemistry study.

Experiments

Carbon materials and surface modification

A commercial activated carbon, Maxsorb 1, denoted as PAC, was used as an original activated carbon. This carbon was prepared from petroleum coke by chemical activation. To maximize the number of OCFG on the surface, PAC was chemically modified by treating it with 2.0 mol/L APS solution (in 1 mol/L H_2SO_4, 1.0 g of PAC with 20 cm^3 of APS solution) at 60°C for 3 h, which is the best oxidation condition for introduction of the carboxylic acid groups according to our previous work.[30] The detailed preparation method has been reported in one of our previous papers.[30] The modified sample was dried under vacuum at 110°C overnight for removal of moisture and other adsorbed contaminants before use. This oxidatively modified sample was denoted as OPAC. A part of OPAC sample was further heated to 350 and 600°C, respectively, under a flow of N_2 (50 cm^3/min) in a horizontal tube furnace at a rate of 5°C/min, and held at the desired temperature for 2 h. These samples were denoted as OPACN-350 for the heat treatment at 350°C and OPACN-600 for the heat treatment at 600°C. Another part of OPAC sample was heated under a flow of H_2 (50 ml/min) to 600°C in a horizontal tube furnace at 5°C/min, and held at 600°C for 2h, which was denoted as OPACH-600.

Characterization of textural properties of activated carbons

The textural characterization of the materials was determined by adsorption/desorption of nitrogen at 77 K using ASAP2010 surface area and porosimetry analyzer. Standard BET and DR model were applied, respectively, to get surface area and pore volume. The pore size distribution was calculated according to density functional theory (DFT) method.

Characterization of OCFG on activated carbon samples

OCFG of the activated carbon samples were analyzed by the temperature-programmed desorption (AutoChem 2910) with a mass spectrometer (TPD-MS). The surface OCFG, including strongly acidic carboxylic groups (SA), weakly acidic carboxylic groups (WA), carboxylic anhydrides (CA), and two different lactones (LD, LC), CA, phenols (PHs), carbonyls plus quinones (CQ#1, CQ#2), and pyrones (PYs), were quantified. The detailed identification and quantification of these surface OCFG were conducted by a modified TPD-MS spectra deconvolution method, which was developed in our previous study[30] on the basis of the method reported by Figueiredo et al.[26,31,32]

Table 1. Composition of Model Fuel with Five Different Nitrogen Compounds

Compound	Purity (wt%)	Concentration (wt%)	*N* (ppmw)
Aniline (An)	99	0.055	82.5
Quinoline (Qu)	98	0.076	82.5
Indole (In)	99	0.069	82.5
Carbazole (Ca)	97	0.098	82.5
3-Ethyl carbazole (ECa)	97	0.115	82.5
Naphthalene (Nap)	99	0.076	82.5
Decane	99	49.7	–
Toluene	98	49.7	–
Total	–	100.0	–

Model fuel

A model fuel (MF) was prepared for evaluation of the adsorption performance of the carbon samples, which contained the same molar concentrations of aniline (An), quinolone (Qu), indole (In), carbazole (Ca), 3-ethylcarbazole, and naphthalene (Nap), in a mixture of decane and toluene (1:1 by volume). All of the compounds were obtained from Sigma-Aldrich Co. and used as received. The nitrogen concentration of each compound in fuel was 82.5 ppmw. The corresponding total nitrogen concentration was 412.5 ppmw. The detailed composition of MF is listed in Table 1. The chemical structures and some physical properties of these model compounds are shown in Table 2 for convenient comparison.

Adsorption experiment

ADN of MF over the activated carbon samples was performed in a fixed-bed flowing system. About 0.8–1.2 g activated carbon sample was packed in a stainless steel column with diameter of 4.6 mm and length of 150 mm. The packed column was pretreated by passing N_2 gas through the adsorbent bed at 150°C for 2 h for drying. After the pretreatment, the temperature of the column was reduced to room temperature, and MF was then fed into the column from the bottom by a HPLC pump. The adsorption conditions were controlled at a liquid hourly speed velocity of 4.8 h^{-1} and 25°C. The treated fuels were periodically sampled at an interval of 15–20 min for analysis, until the saturation point was reached.

Analysis of treated MF samples

The total nitrogen concentration in the treated MF was analyzed by using ANTEK9000 series nitrogen analyzer with analysis limitation of 1 ppmw. The detailed analysis method was reported in our previous paper.[17] The concentration of various nitrogen compounds in the treated MF was quantitatively analyzed by Varian CP 3800 gas chromatography with a capillary column (30-m length, 0.25-mm internal diameter, and 0.25-μm film thickness) and a flame ionization detector, or a nitrogen/phosphorous detector, using *n*-tetradecane as an internal standard.

Computational method

All quantum chemical calculations were performed by applying the generalized gradient-corrected DFT using the DMol3 module in Materials Studios 4.4 package of Accelrys. A compound of 9-anthracene acid (9AA), which contains three ring conjugated system attached with one acidic carboxylic substitution at the ninth position, was used as a model in the molecular simulation to mimic carboxyl on activated carbon surface. The adsorption energy (E_{Ads}) was estimated by energy optimization of the 9AA-adsorbate complex. The calculation parameters of double-numeric quality basis set with polarization functions (DNP), spin-restricted and density functional semicorepseudopotentials were used. All SCF tolerances were set to fine, that is, the tolerance of energy, gradient and displacement were converged to 1.0E−5 Ha, 0.002 Ha/Å, and 0.005 Å, respectively.

Results and Discussion

Oxidative modification and thermal tailor of activated carbons

To study the effect of OCFG of activated carbons on their ADN performance, several samples with different concentration and distribution of OCFG were prepared. It should be noticed that within the APS oxidative modification process, almost no functional groups other than oxygen-containing groups or metal ions were introduced onto the carbon surface according to our previous work.[30]

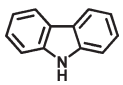
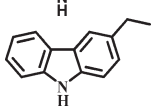
Textural properties of modified activated carbons

The adsorption–desorption isotherms of the original and modified samples are shown in Figure 1. OPAC shows a significant reduction in the N_2 uptake compared with the PAC, probably due to the part destruction or collapse of the porous structure of the carbon during its oxidation process.[30] OPAC, OPACN350, and OPACH600 show almost the same isotherms, and similar pore size distribution, as shown in Figure 2, indicating the heat treatment of OPAC at 350°C under N_2 and 600°C under H_2 caused almost no (or only slightly increase of pore volume, due to removal of OCFG in pores) change in the textural properties. These three samples provide a good sample set for examining the effect of OCFG on ADN performances. The measured textural parameters of the original carbon (PAC) and the modified carbon samples are summarized in Table 3.

Measurement of OCFGs on modified activated carbons

TPD-MS was used to monitor the released CO_2, CO, and H_2O during the temperature program. Figure 3 shows the

Table 2. Some Properties of Tested Nitrogen Compounds and Naphthalene

Name	Structure	Molecular Weight	p*K*a	Critical diameter* (Å)
Aniline (An)		93	4.62	5.9
Quinoline (Qu)		129	4.85	7.1
Indole (In)		117	16.2	6.7
Carbazole (Ca)		167	19.9	9.0
3-Ethyl-carbazole (ECa)		195	–	10.7
Naphthalene (Nap)		128	–	7.7

*Critical diameter is defined as "the smallest diameter of a cylinder through which the molecule can pass without distortion," which was calculated by the Material Studio 4.2 using DMol3 model.

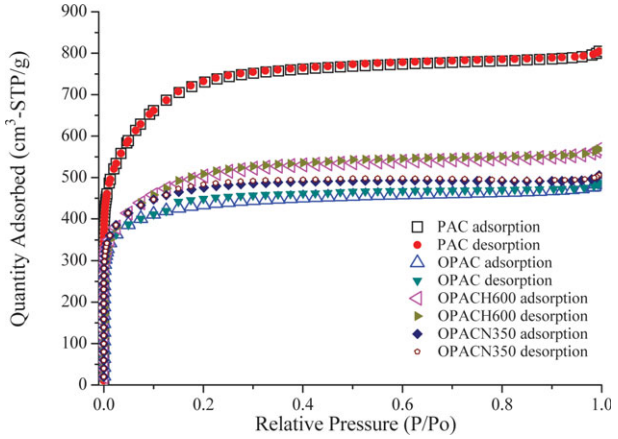


Figure 1. Nitrogen adsorption–desorption isotherms of the original and modified activated carbons.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

CO and CO_2 TPD profiles for PAC, OPAC, OPACN350, OPACN600, and OPACH600. It shows that there were significant amounts of released CO and CO_2 when the temperature was higher than 200°C due to the decomposition of the different OCFG. Some H_2O release was found for PAC and OPAC, while almost no H_2O release was observed for OPACN350, OPACN600, and OPACH600 (Table 4). The amounts of the released CO, CO_2, H_2O, and total oxygen content for the different samples are summarized in Table 4. Interestingly, OPAC, OPACN350, OPACN600, and OPACH600 have quite different oxygen contents, although they have similar textural structures. The oxidative modification by the APS solution increased the oxygen content by a factor of 4.2, for example, the amount of OCFG of OPAC is 4.2 times of that of PAC. The heat treatment modification at different temperature and atmosphere reduced the oxygen concentration of the oxidized sample to different levels. It should be mentioned that the OPACH600 showed much low concentration of OCFG in comparison with OPACN600, indicating that H_2 played a more effective role during the heat treatment process for removing OCFG than N_2. Some possible interactions of H_2 and OCFG in the thermal treatment has be discussed by Calo et al.[33]

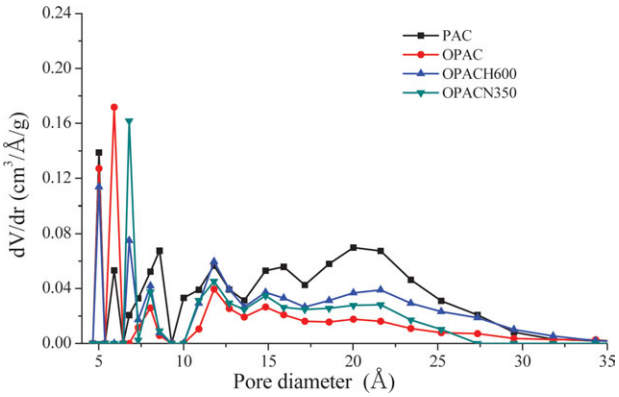


Figure 2. Pore distributions of the original and the modified activated carbon samples.

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Table 3. Pore Properties of Original and Modified Activated Carbons

Sample	S_{BET} (m^2/g)	S_{MES} (m^2/g)	S_{MIC} (m^2/g)	V_{total} (cm^3/g)	V_{MES} (cm^3/g)	V_{MIC} (cm^3/g)	Pore size (Å)
PAC	2311	1142	1168	1.18	0.62	0.56	20.5
OPAC	1438	538	900	0.74	0.26	0.49	21
OPACN350	1572	574	998	0.79	0.28	0.51	19.9
OPACH600	1677	788	890	0.89	0.45	0.43	21

To obtain the qualitative and quantitative information of various OCFG for different samples, the CO_2- and CO-evolution profiles were further deconvoluted by the method described in our previous work.[30] The deconvolution results of CO_2- and CO-evolution profiles for PAC, OPAC, OPACN350, OPACN600, and OPACH600 are shown in Figure 4. The deconvolution procedure fit, the data quite well for the CO_2 and CO profiles of all five samples. The obtained concentrations of strong acidic carboxyl, WA carboxyl, carboxylic anhydride, lactone (LD), lactone (LC), PH, carbonyl plus quinone, and PY are compiled in Figure 5. The oxidative modification using APS greatly increased the concentration of the strong carboxyl, weak carboxyl, anhydride, and PH, significantly increased the concentration of carbonyl and lactone groups, but only slightly increased the concentration of quinone groups. The heat treatment of OPAC at 350°C under the N_2 flow removed almost all of the strong carboxyl and weak carboxyl groups, and a half of the anhydride group, but almost did not cause any change in the concentration of the PH, carbonyl, quinone, and lactones-LD, and slightly increased the concentration of the lactones-LC. When the temperature increased to 600°C under the N_2 flow for 2 h, the thermal treatment removed almost all of the strong carboxyl, weak carboxyl, anhydride, PH, and lactone (LC) groups, whereas 81% of original carbonyl, 48% quinone, and 50% of Lactone-LD were remained. The thermal treatment of OPAC at 600°C under H_2 for 2 h could remove almost all OCFG other than carbonyl and quinone. Only 29% of original carbonyl and and 28% of original quinone were remained. The results indicate that it is possible to selectively tailor OCFG on the activated carbon surface by a combination of the oxidative modification and thermal treatment without significant changing the pore properties of activated carbon.

Adsorptive performance of different activated carbons

Adsorption Capacity. The adsorption performance of PAC, OPAC, OPACN350, and OPACH600 was evaluated in the fixed-bed adsorption system using MF, which contained the five typical nitrogen compounds. The breakthrough curves for total nitrogen and different nitrogen compounds over these four samples are shown in Figure 6. The breakthrough capacity and saturation capacity for each compounds and total nitrogen were calculated on the basis of the breakthrough curves. The results are summarized in Table 5. The breakthrough capacity for total nitrogen increases in the order of OPACH600 < PAC < OPACN350 < OPAC.

As shown in Figure 6, the breakthrough and saturation capacity of PAC for different compounds increased in the order of carbazole ≈ 3-ethyl-carbazole < quinoline < indole < aniline. Among five different nitrogen compounds, PAC had the highest capacity for carbazole and 3-ethyl carbazole, being 0.29 mmol-N/g-AC for both of them. Interestingly, the

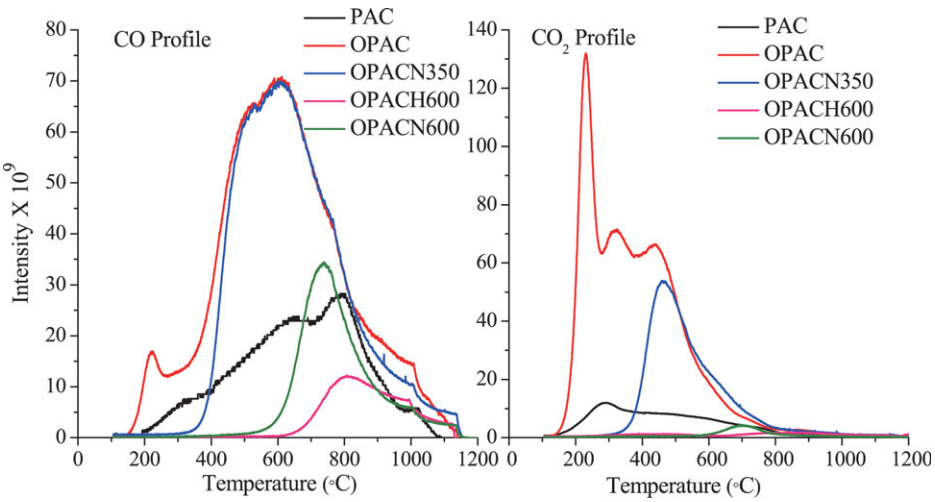

Figure 3. TPD-CO and TPD-CO_2 profiles of different activated carbons (PAC: original activated carbon, OPAC: oxidatively modified activated carbon at 60°C for 3 h; OPACN350 and OPACN600: After heat treatment of OPAC at 350 and 600°C, respectively, under a N_2 flow at 50 cm^3/min; OPACH600: heat treatment of OPAC at 600°C under a H_2 flow at 50 cm^3/min).

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breakthrough capacity and saturation capacity of OPAC for various nitrogen compounds increased in the order of quinoline < aniline < 3-ethyl-carbazole < carbazole < indole, which is quite different from that observed for PAC. It is noticed that after the oxidative modification, the capacity for quinoline, aniline, and indole increased from 0.202, 0.047, and 0.071 to 0.587, 0.553, and 0.184 mmol-N/g-AC, respectively. However, the oxidative modification made no increase in the adsorption capacity for carbazole and 3-ethyl-carbazole, and even slightly reduced their adsorption capacity. For OPACN350, the breakthrough and saturation capacity increased in the order of quinoline < carbazole < aniline ≈ 3-ethyl-carbazole < indole. It can be seen that heat treatment of OPAC at 350°C under N_2 decreased the capacity for all these nitrogen compounds. Moreover, when OPAC was heated at 600°C under H_2, the sample had almost no adsorption ability for all the nitrogen compounds. Considering that OPAC, OPACN350, and OPACH600 have almost same porous structure, as discussed before, it is reasonably considered that the significant difference in their adsorption capacity can be from the contribution of the different concentration of OCFG on the samples.

Adsorption Selectivity. To facilitate a quantitative discussion of the adsorption selectivity, a concept of the relative selectivity factor was used, which is defined as a value of the breakthrough capacity for the compound divided by the breakthrough capacity for the reference compounds (naphthalene).[23] The relative selectivity factors were calculated according to the breakthrough curves and the results are summarized in Table 6. It is clear that the selectivity factors for quinoline and aniline increased significantly after oxidative modification, while also a noticeable decrease was observed after the heat treatment. Moreover, it was found that the oxidative modification improved the selectivity for the basic nitrogen compounds by a factor of 15.5 and 4.4 for aniline and quinoline, respectively, which are much higher than those for the neutral nitrogen compounds, indole and carbazole. These results indicate clearly that the surface modification not only changes the adsorption capacity, but also significantly changes the adsorption selectivity for different compounds.

Correlation between surface OCFG and adsorption performance

To clarify the roles of OCFG in determination of the ADN performance of activated carbon, the measured ADN capacity of the activated carbon samples was correlated with the total oxygen concentrations. A relationship between the total oxygen concentrations in the carbon samples and the breakthrough adsorption capacities of the samples for total nitrogen is shown in Figure 7. It shows clearly that the adsorption capacity of the carbon samples for the total nitrogen increases linearly with increasing the oxygen concentration of the carbon samples. More interestingly, when extrapolating this trend to the zero oxygen concentration, the corresponding adsorption capacity is almost the zero, indicating that OCFG play a crucial role in determination of the ADN performance. Furthermore, the three samples of OPAC, OPACN350, and OPACH600 have similar pore structure, whereas OPAC has the highest adsorption capacity in the all examined samples, and OPACH600 has almost the zero capacity. All these results confirm that the concentration of OCFG is crucial in determining the adsorption capacity of activated carbon for ADN.

In further correlation between the various OCFG of the carbon samples with the same or similar pore structure and their adsorption capacity for different nitrogen compounds, it was found that the type of OCFG has also a strong effect on

Table 4. Amount of Released CO, CO_2, and H_2O on the Basis of TPD Profiles

Sample	Total CO_2 (mmol/g)	Total CO (mmol/g)	Total H_2O (mmol/g)*	CO_2+CO (mmol/g)	CO/CO_2 ratio	Total O (mmol/g)**
PAC	0.6	2.9	0.4	3.5	4.5	4.5
OPAC	4.4	8.2	1.8	12.6	1.9	18.7
OPACN350	1.7	5.9	0.0	7.6	3.5	9.3
OPACN600	0.1	1.8	0.0	1.9	18.2	2.0
OPACH600	0.0	0.8	0.0	0.8	0.0	0.8

*Amount of H_2O was estimated on the basis of TPD-H_2O profiles.
**Total O = CO + CO_2 × 2 + H_2O

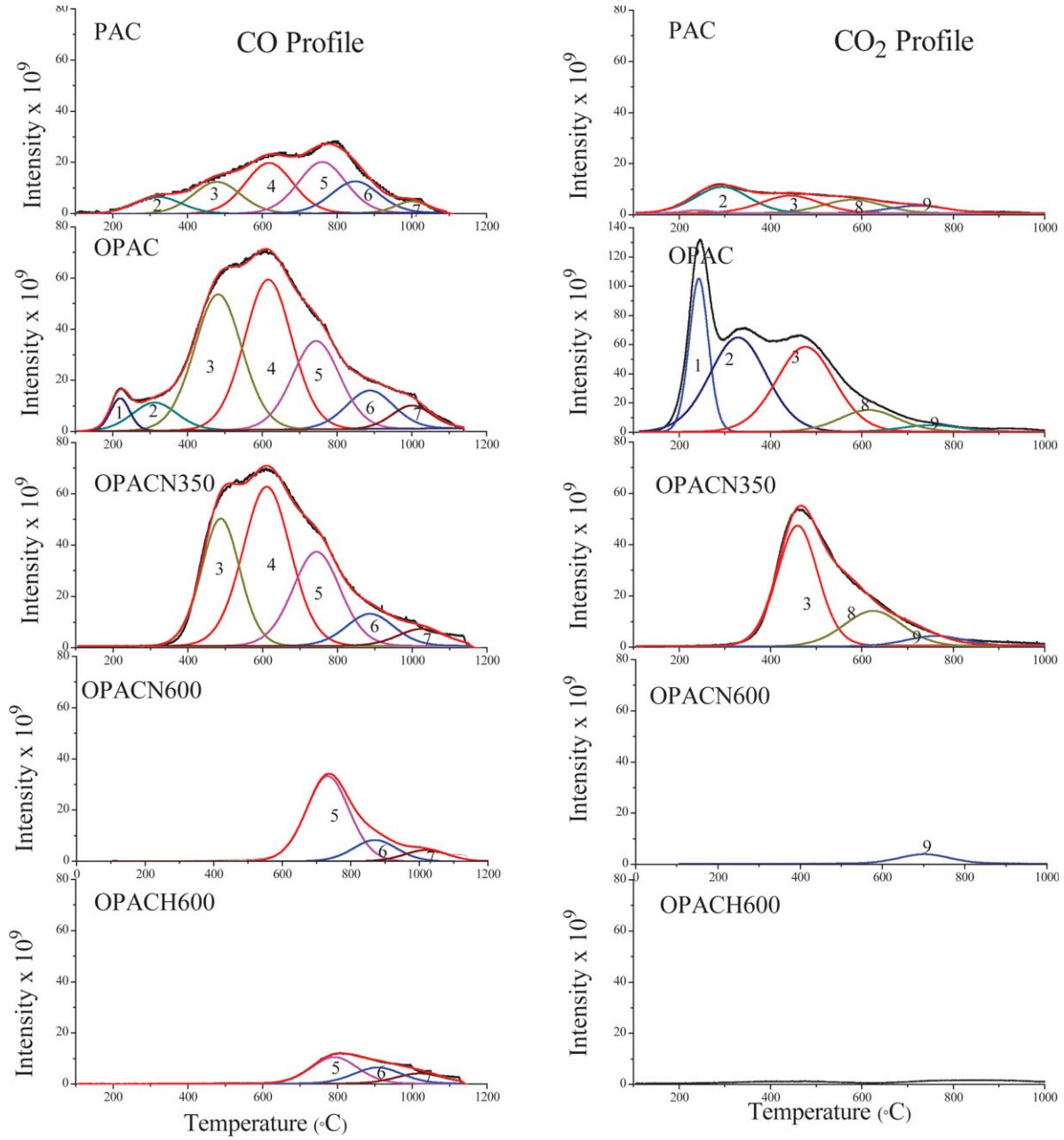

Figure 4. Deconvolution of TPD-CO and TPD-CO_2 profiles of original and modified activated carbons (Peak 1: SA carboxyls; peak 2: WA carboxyls; peak 4: PHs; peak 5 and 6: carbonyls-and/or-quinones 1 (CQ#1) and carbonyls-and/or-quinones 2 (CQ#2); peak 7: PYs; peak 8: lactones at lower temperature (LD) and peak 9: lactones at higher temperature (LC).

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the adsorption capacity for different nitrogen compounds. In comparison of OPAC and OPACN350, the major difference is that the former contains about 1.9, 1.2, and 1.6 mmol/g of strong carboxyls, weak carboxyls, and anhydrides, respectively, while the latter contains almost no strong carboxyls, no weak carboxyls and only 0.8 mmol/g of anhydrides. The adsorption capacity of OPACN350 decreased by 74.3, 64.6, 51.6, 47.8, and 41.7% for aniline, quinoline, indole, 3-ethylcarbazole, and carbazole, respectively. The results imply that the strong carboxyls, weak carboxyls and anhydrides have a major contribution to the adsorption of the basic nitrogen compounds, probably through an acid–base interaction, and also have a certain contribution to the neutral nitrogen compounds, probably through the hydrogen bond interaction. OPACN350, which contains no strong carboxyls and no weak carboxyls, also showed a certain adsorption capacity for the nitrogen compounds, indicating that the OCFG other than carboxyls also work for adsorption of the basic nitrogen compounds, although their affinity for the basic nitrogen compounds may be weaker. OPACH600, which has almost no OCFG, showed a very low, but certain, saturation capacity for the neutral nitrogen compounds and quinoline (Table 6). It indicates that the adsorption of these nitrogen compounds may be conducted through a π–π interaction, although this interaction is much weaker in comparison with the acid–base interaction and the hydrogen bond interaction.

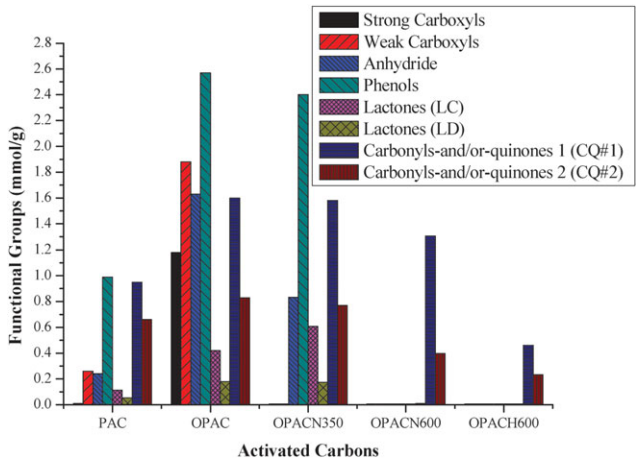

Figure 5. Concentrations of various functional groups in different activated carbon samples, which were determined by the deconvolution of the TPD-CO, TPD-CO_2, and TPD-H_2O profiles.

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Multiple mechanisms may work together to determine the adsorption performance of activated carbons for various nitrogen compounds in liquid hydrocarbon streams. The increase of the oxygen functional groups may more significantly enhance the adsorption ability of activated carbons than other factors. The acid–base and the H bonding interactions may play a more important role in the adsorption mechanism over the surface oxygen-rich activated carbon, while the π–π interaction may be dominant in the adsorption over the surface oxygen-poor activated carbon.

It should be pointed out that the average pore size of the activated carbon samples used in this study is about 20 Å, while the critical diameter of the adsorbate molecules is less than 11 Å. Thus, the diffusion limitation of the adsorbate molecules in the pores in this study is not important. By comparison of the adsorption selectivity and capacity of the activated carbons for various adsorbates with the critical diameters of the adsorbates, it is clear that the pore size of the activated carbons is not a critical factor in determination of their ADN performance in this study.

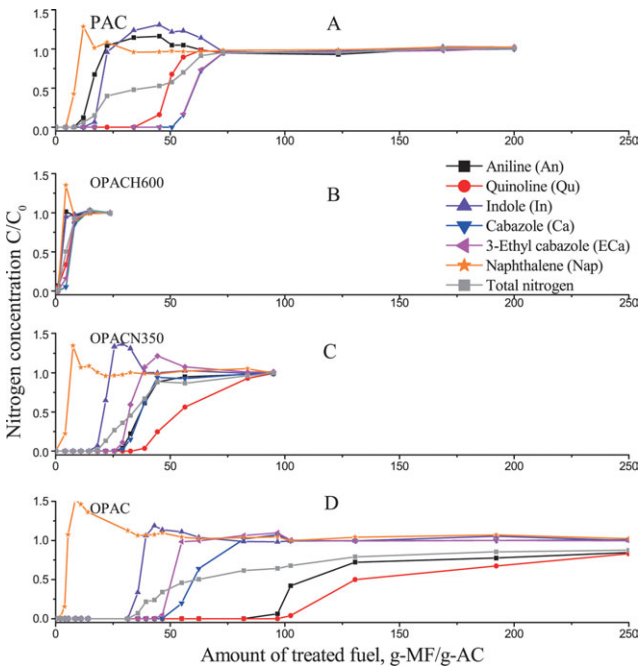

Figure 6. Adsorption breakthrough curves of different compounds on different activated carbon samples.

[Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

Table 5. Relative Adsorption Selectivity of the Original and Modified Carbons for Different Compounds

Sample	Naphthalene	Aniline	Indole	Quinoline	Cabazole	2-Ethyl cabazole
PAC	1	1.6	2.4	6.8	9.8	9.8
OPAC	1	24.9	9.4	30.0	14.6	13.9
OPACN350	1	9.6	6.0	14.0	11.2	9.6
OPACH600	1	0.6	2.0	0.80	4.0	3.0

Estimation of adsorption energies and correlation with adsorption capacity

To further examine how the nitrogen compounds interact with OCFG and get into insight of the ADN mechanism, a molecular simulation was conducted using the DFT method.[34] The E_{Ads} of the model compounds including aniline, quinoline, indole, carbazole, 3-ethyl carbazole, and naphthalene on the carboxyl group in 9-anthracene acid was estimated. The results are summarized in Table 7. According to these results, E_{Ads} for nitrogen containing compounds on the carboxyl can be classified into two groups. For the basic nitrogen containing compounds, such as aniline and quinolone, E_{Ads} value is 7.32–7.38 KJ/mol, whereas for the neutral nitrogen containing compounds, such as indole, carbazole, and 3-ethyl-carbazole, E_{Ads} value is around 4.28–4.83 KJ/mol. E_{Ads} value for naphthalene is the lowest, about 3.12 KJ/mol, due to a weak interaction. These values reflect the adsorption affinity, which includes the acid–base interaction, hydrogen bond along with the steric hindrance.

The correlation between the estimated E_{Ads} values for different compounds on the carboxyl group and the measured breakthrough and saturation capacities of OPAC for these

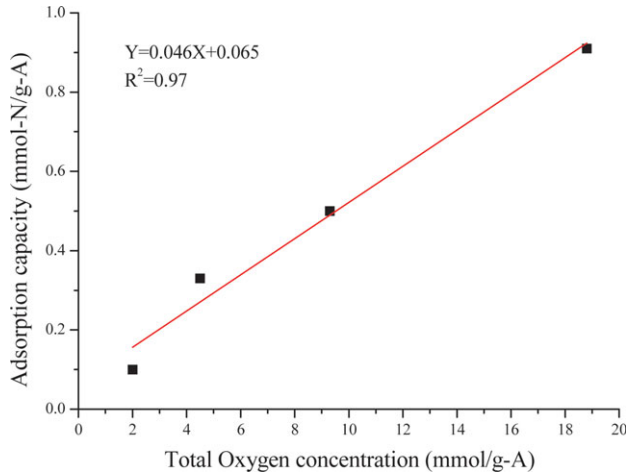

Figure 7. Correlation between the surface oxygen concentration and adsorption capacity of different activated carbon samples.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 6. Adsorption Capacities of ACs on the Basis of the Test in the Fixed-Bed Flow System

Sample	Adsorption capacity Q (mmol-N/g-A)					Total *N*	Total O (mmol/g-A)
	Aniline	Indole	Quinoline	Cabazole	2-Ethyl cabazole		
PAC							
Breakthrough	0.047	0.071	0.202	0.291	0.291	0.333	4.5
Saturation	0.097	0.110	0.280	0.337	0.334	1.036	
OPAC							
Breakthrough	0.553	0.184	0.587	0.285	0.273	0.910	18.7
Saturation	0.887	0.207	0.960	0.374	0.300	2.847	
OPACN350							
Breakthrough	0.142	0.089	0.208	0.166	0.142	0.504	9.3
Decrease* (%)	74.3%	51.6%	64.6%	41.7%	47.8%	44.8%	
Saturation	0.205	0.122	0.321	0.215	0.189	0.991	
OPACH600							
Breakthrough	0.004	0.012	0.005	0.024	0.018	0.090	2.0
Saturation	0.015	0.016	0.031	0.040	0.036	0.140	

*The decrease percent was obtained by comparing the breakthrough capacity between OPAC and OPACN350.

Table 7. Estimated Adsorption Energy of Different Nitrogen-Containing Compounds on the Carboxyl Group in 9-Anthracene Acid, Calculated by Material Studio 4.2 Using DMol3 Model

Compounds	ΔE_{ads} (KJ/mol)
Aniline (An)	7.32
Quinoline (Qu)	7.38
Indole (In)	4.28
Carbazole (Ca)	4.83
3-Ethyl carbazole (ECa)	4.63
Naphthalene (Nap)	3.18

compounds is shown in Figure 8. A pretty good linear relationship is found. This result further confirms that the carboxyl groups on the carbon surface play a crucial role in the selective adsorption of the nitrogen compounds from liquid hydrocarbon streams, and the adsorption affinity is dominantly based on the acid–base interaction and hydrogen-bond interaction.

Conclusions

The APS oxidative modification of the activated carbon can increase the ADN capacity of the activated carbon by about three times. The dramatic improvement of adsorption performance of the activated carbon is ascribed to the significant increase of OCFG on the carbon surface during the oxidative modification. The amount and distribution of OCFG on the activated carbon surface can be further tailored by the thermal treatment at different temperatures and environments without significant change in the textural properties of the activated carbon, which changes the ADN capacity and selectivity of the activated carbon greatly. The evaluation, characterization and correlation of the modified activated carbon samples together with the molecular simulation indicate that OCFG, especially the strong carboxyls, weak carboxyls anhydrides, and PHs play a crucial role in determining the adsorption performance of activated carbon for selective removal of the nitrogen compounds from liquid hydrocarbons.

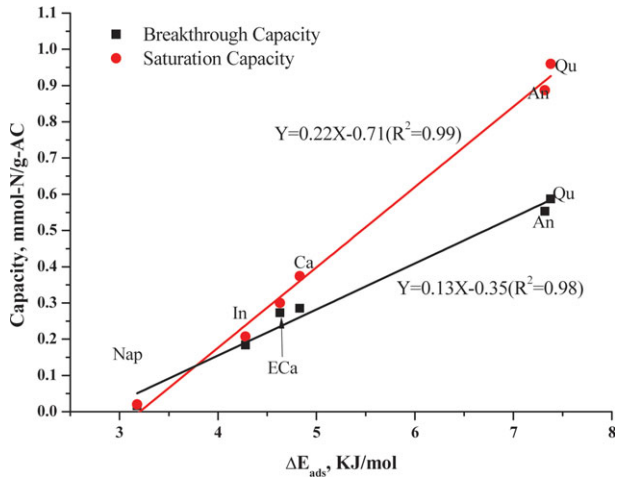

Figure 8. The relationship between the estimated E_{Ads} for different compounds on the carboxyl group and the measured adsorption capacities of OPAC for them.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Acknowledgments

This work was supported by the US Department of Energy through CPCPC (DE-FC26-03NT41874) and the Chinese state key laboratory of heavy oil processing project (SKLVP201102008). The China Scholarship Council is gratefully acknowledged for a scholarship to support Na Li at the Pennsylvania State University for this study.

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Manuscript received Jan. 31, 2012, and revision received Jun. 20, 2012.