

Surface Chemical Functional Groups Modification of Porous Carbon

Wenzhong Shen^{*1}, Zhijie Li² and Yihong Liu¹

¹State Key Laboratory of Heavy Oil, China University of Petroleum, Dongying, Shandong, 257061, P. R. China

²Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu, Sichuan, 610054, P. R. China

Received: August 29, 2007; Accepted: September 11, 2007; Revised: November 2, 2007

Abstract: The surface chemistry and pore structure of porous carbons determine its application. The surface chemistry could be modified by various methods, such as, acid treatment, oxidization, ammonization, plasma, microwave treatment, and so on. In this paper, the modification methods were illustrated and compared, some new methods also reviewed. The surface chemical functional groups were determined by the treatment methods, the ammonization could increase its basic property while the oxidization commonly improved its acids. In the end, the commonly characterization methods were also mentioned. Some interesting patents are also discussed in this article.

Keywords: Porous carbon, surface chemical groups, modification, characterization.

1. INTRODUCTION

Porous carbons had been widely used as adsorbents, catalyst/catalyst supports, electronic material and energy storage material due to its higher surface area and larger pore volume.

The specific surface area, pore structure and surface chemical functional groups of porous carbon determined its applications [1-2]. The pore structure of porous carbon could be controlled by various routes, such as, activation conditions (activation agent, temperature and time), precursor, templates, etc. The surface chemical functional groups mainly derived from activation process, precursor, heat treatment and post chemical treatment.

The surface functional groups anchored on/within carbons were found to be responsible for the variety in physicochemical and catalytic properties of the matters considered [3-5]. So, many researchers focused on how to modify as well as to characterize the surface functional groups of carbon materials in order to improve or extend their practical applications [5-7]. Ljubisa R. Radovic reviewed the carbon materials as adsorbents in aqueous solution and pointed out that the control of chemical and physical conditions might be harnessed to produce carbon surfaces suitable for particular adsorption applications [8]. Carlos Moreno-Castilla compared the surface chemistry of the carbon has a great influence on both electrostatic and non-electrostatic interactions, and can be considered the main factor in the adsorption mechanism from dilute aqueous solutions [9].

Modification of the surface chemistry of porous carbons might be a viable attractive route toward novel applications of these materials. A modified activated carbon containing

different functional groups could be used for technological applications such as extracting metallic cations from aqueous and nonaqueous solutions, in catalysis, for treatment of waste and toxic effluents produced by a variety of chemical processes, and so on.

The heteroatoms on the surface of activated carbon took significant role on its application. The heteroatoms of porous carbon surface mainly contained oxygen, nitrogen, hydrogen, halogen, etc, which bonded to the edges of the carbon layers and governed the surface chemistry of activated carbon [10]. Among these heteroatoms, the oxygen-containing functional groups (also denoted as surface oxides) were the widely recognized and the most common species formed on the surface of carbons, which significantly influenced their performance in sensors [11], energy storage and conversion systems [12-14], catalytic reactions [15], and adsorptions [16-18]. The surface oxygen-containing functional groups could be introduced by mechanical [19, 20], chemical [21, 22], and electrochemical routes [23]. The employment of oxidizing agents in wet or dry methods was reported to generate three types of oxygen-containing groups: acidic, basic, and neutral [24-27]. Based on the above modifications, a continuous supply of suitable oxidizing agents into the pores of a carbon matrix was believed to be a key factor determining the successful introduction of reliable oxygen-containing functional groups onto the surface of carbon materials.

In addition, the nitrogen-containing groups generally provide basic property, which could enhance the interaction between porous carbon and acid molecules, such as, dipole-dipole, H-bonding, covalent bonding, and so on. The nitrogen groups were introduced by ammine treatment, nitric acid treatment and some containing nitrogen molecule reaction.

In this review, we focused on the introducing oxygen and nitrogen heteroatoms on traditional porous carbon (activated carbon and activated carbon fiber) by various methods; the improved application property of modified porous carbon

*Address correspondence to this author at the State Key Laboratory of Heavy Oil, China University of Petroleum, Dongying, Shandong, 257061, P. R. China; Tel: +86-546-8395341; Fax: +86-546-8395395; E-mail: shenwzh2000@yahoo.com

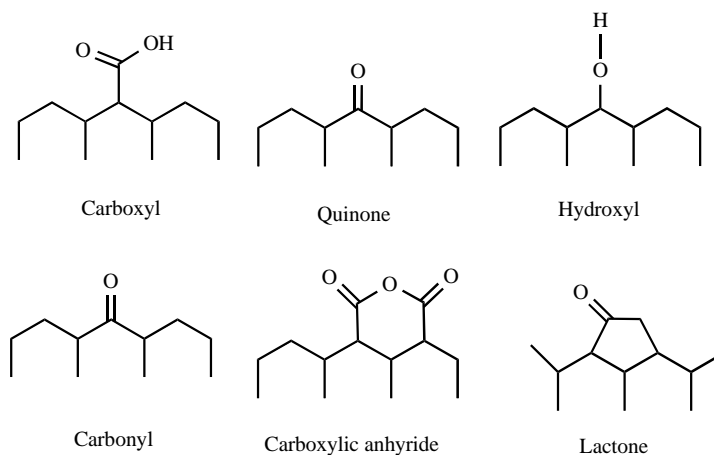


Fig. (1). Simplified schematic of some acidic surface groups bonded to aromatic rings on AC [28].

was also illustrated. In the end, the ordinary characterization means of oxygen and nitrogen groups were listed.

2. METHODS FOR SURFACE MODIFICATION

The nature and concentration of surface functional groups might be modified by suitable thermal or chemical post-treatments. Oxidation in the gas or liquid phase could be used to increase the concentration of surface oxygen groups; while heating under inert atmosphere might be used to selectively remove some of these functions. It was shown that gas phase oxidation of the carbon mainly increased the concentration of hydroxyl and carbonyl surface groups, while oxidations in the liquid phase increased especially the concentration of carboxylic acids [2]. Carboxyl, carbonyl, phenol, quinone and lactone groups on carbon surfaces were shown in Fig. (1) [28].

While, the ammonization could introduce the basic groups, such as, C-H, C=N groups, amino, cyclic amides, nitrile groups, pyrrole-like structure [29]; which were shown in Fig. (2) [30]. In addition, the halogen-containing groups could produce through porous carbon reacted with halogen at moderate temperature, this modified porous carbon showed potential application in electrochemistry or batteries [31].

2.1. Acid Treatment

Acid treatment was generally used to oxidize the porous carbon surface; it enhanced the acidic property, removed the mineral elements and improved the hydrophilic of surface. The acid used in this case should be oxidation in nature; the nitric acid and sulfuric acid were the most selected.

Liu *et al.* reported that coconut-based activated carbon was modified by nitric acid and sodium hydroxide; it showed excellent adsorption performance for Cr (VI) [32].

Modification caused specific surface area to decrease and the total number of surface oxygen acidic

groups to increase. Nitric acid oxidation produced positive acid groups, and subsequently sodium hydroxide treatment replaced H^+ of surface acid groups by Na^+ , and the acidity of activated carbon decreased. The adsorption capacity of Cr (VI) was increased from 7.61mg/g to 13.88mg/g due to the presence of more oxygen surface acidic groups and suitable surface acidity after modification.

Shim *et al.* also modified the pitch-based activated carbon fibers with nitric acid and sodium hydroxide [6]. The specific surface area of the activated carbon fibers decreased after oxidation with 1 M nitric acid, but the total acidity increased three times compared to the untreated activated carbon fibers, resulting in an improved ion-exchange capacity of the activated carbon fibers. The points of zero charge of the activated carbon fibers that affect the selectivity for the ionic species changed from pH 6 to pH 4 by 1 M nitric acid and to pH 10 by 1 M sodium hydroxide treatment. The carboxyl acid and quinone groups were introduced after nitric acid oxidation. The carboxyl groups of activated carbon fibers decreased, while the lactone and ketone groups increased after the sodium hydroxide treatment. The adsorption capacity of copper and nickel ion is mainly influenced by the lactone groups on the carbon surface, pH and by the total acidic groups.

Coal-based activated carbons were modified by chemical treatment with nitric acid and thermal treatment under nitrogen flow [33]. The treatment with nitric acid caused the introduction of a significant number of oxygenated acidic surface groups onto the carbon surface, while the heat treatment increases the basicity of carbon. The pore characteristics were not significantly changed after these

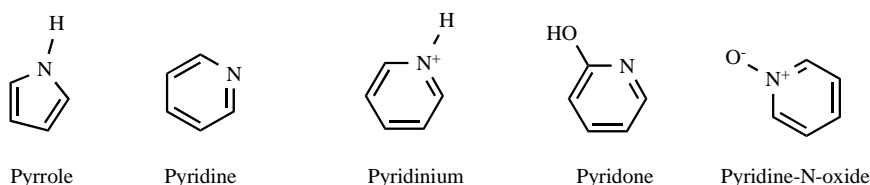


Fig. (2). The nitrogen functional forms possibly present in carbonaceous materials [30].

modifications. The dispersive interactions are the most important factor in this adsorption process. Activated carbon with low oxygenated acidic surface groups has the best adsorption capacity for benzene and toluene.

The coconut-based activated carbon was pretreated with different concentrations of nitric acid (from 0.5 to 67%) and was selected as palladium catalyst support [34], the result showed that the amount of oxygen-containing groups and the total acidity on the activated carbons, the Pd particle size and catalytic activity of Pd/C catalysts are highly dependent upon the nitric acid concentration used in the pretreatment. The pretreatment of activated carbon with a low concentration of nitric acid could increase the structure parameters due to removal of the impurities, would be beneficial to create an appropriate density of total acidity environment, and would further improve the Pd dispersion and the catalytic activity of Pd/C catalysts. Meanwhile, a too-large amount of oxygen-containing groups assembling densely on the activated carbon could influence the Pd dispersion on the activated carbon well.

Peach stone shells were pretreated by H_3PO_4 and pyrolysis at 500°C for 2 h, then, it was prepared by changing the gas atmosphere during thermal treatment (no external gas, flowing of nitrogen, carbon dioxide, steam or air [35]. High uptake of *p*-nitrophenol appears, affected to low extent with gaseous atmosphere except steam which raises adsorption considerably. Flowing air was the most effective in enhancing the adsorption of methylene blue, which was attributed to the formation of oxygen-functionalities with acidic nature, and to enhancement of wider microporosity. The removal of lead ions was considerably enhanced by running air during thermal treatment (two-fold increase) due to the formation of acidic oxygen-functionalities associated with metal exchange by the negatively charged carbon surface. Li describes the method of eliminating residual carbon from flow able oxide [36].

The activated carbon derived from poly(VDC/MA) was treated with $\text{HNO}_3/\text{H}_2\text{SO}_4$ solutions and heat-treatment in Ar [37]. Acid-treatment increased the adsorption of methyl mercaptan compared with the original activated carbon, and the adsorbed amounts increased with ratio of H_2SO_4 in $\text{HNO}_3/\text{H}_2\text{SO}_4$ solutions. Hydrogen bonding between acidic groups formed by acid-treatment and thiol-groups methyl mercaptan played a role in adsorption of methyl mercaptan on activated carbon. Hasenberg *et al.* shows a process and catalyst blend for selectively producing mercaptans and sulfides from alcohols [38].

Surface modification of a coal-based activated carbon was performed using thermal and chemical methods [39]. Nitric acid oxidation of the conventional sample produced samples with weakly acidic functional groups. There was a significant loss in microporosity of the oxidized samples which was caused by humic substances that were formed as a by-product during the oxidation process. However, thermal treatment produced a carbon with some basic character while amination of the thermally treated carbon gave a sample containing some amino ($-\text{NH}_2$) groups.

The formation of the weakly acidic functional groups on porous carbon surface were thought to be similar to the reaction involving the oxidation of 9,10-dihydrophen-

anthrene and diphenylmethane with nitric acid [40], and the mechanism was displayed in Fig. (3). The formation of the dicarboxylic group was thought to occur on the aliphatic side of the molecule especially if the side chains consisted of more than one carbon atom (reaction (a)). The reaction was initiated by the splitting of the C-C at the α -position of the benzylic carbon atom. Oxidation involving a methylene ($-\text{CH}_2^-$) group would result in the formation of a ketone as shown in reaction (b). Nitrogen could be added to the carbon by a similar reaction as in the nitration of benzene. The mechanism would involve the formation of the highly reactive nitronium ion (NO_2^+), which would ultimately form the nitrated product as shown in reaction (c).

The amination reaction was achieved via a two stage process. The first stage was the nitration stage where the nitric acid was mixed with concentrated sulphuric acid to form the nitronium ions which then reacted via electrophilic substitution of the hydrogen ion of the carbon matrix as shown in reaction (d). The formed nitro-species formed was reduced using a suitable reducing agent and in this case sodium dithionite was employed. This result then showed the effectiveness of the reduction reaction shown in reaction (e). This modification process was another example of the application of a classic organic reaction on activated carbon modification. The reaction was shown in the illustration of the amination of phenanthrene.

Calvo *et al.* reported that the surface chemistry of commercial activated carbon was one of the factors determining the metallic dispersion and the resistance to sintering, being relevant the role of surface oxygen groups [41]. The surface oxygen groups were considered to act as anchoring sites that interacted with metallic precursors and metals increasing the dispersion, with CO-evolving complexes significantly implied in this effect. On the other hand, CO_2 -evolving complexes, mainly carboxylic groups, seemed to decrease the hydrophobicity of the support improving the accessibility of the metal precursor during the impregnation step. The treatment of activated carbons with nitric acid led to a higher content in oxygen surface groups, whereas the porous structure was only slightly modified. As a result of oxidation, the dispersion of Pd on the surface of activated carbon was improved.

Santiago *et al.* compared several activated carbons for the catalytic wet air oxidation of phenol solutions [42]. Two commercial activated carbons were modified by HNO_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, or H_2O_2 and by demineralisation with HCl. The treatments increased the acidic sites, mostly creating lactones and carboxyls though some phenolic and carbonyl groups were also generated. Characterisation of the used activated carbon evidenced that chemisorbed phenolic polymers formed through oxidative coupling and oxygen radicals played a major role in the catalytic wet air oxidation over activated carbon.

Also, citric acid was used to modify a commercially available activated carbon to improve copper ion adsorption from aqueous solutions [25]. It was found that the surface modification by citric acid reduced the specific surface area by 34% and point of zero charge (pH) of the carbon by 0.5 units. But the modification did not change both external diffusion and intraparticle diffusion.

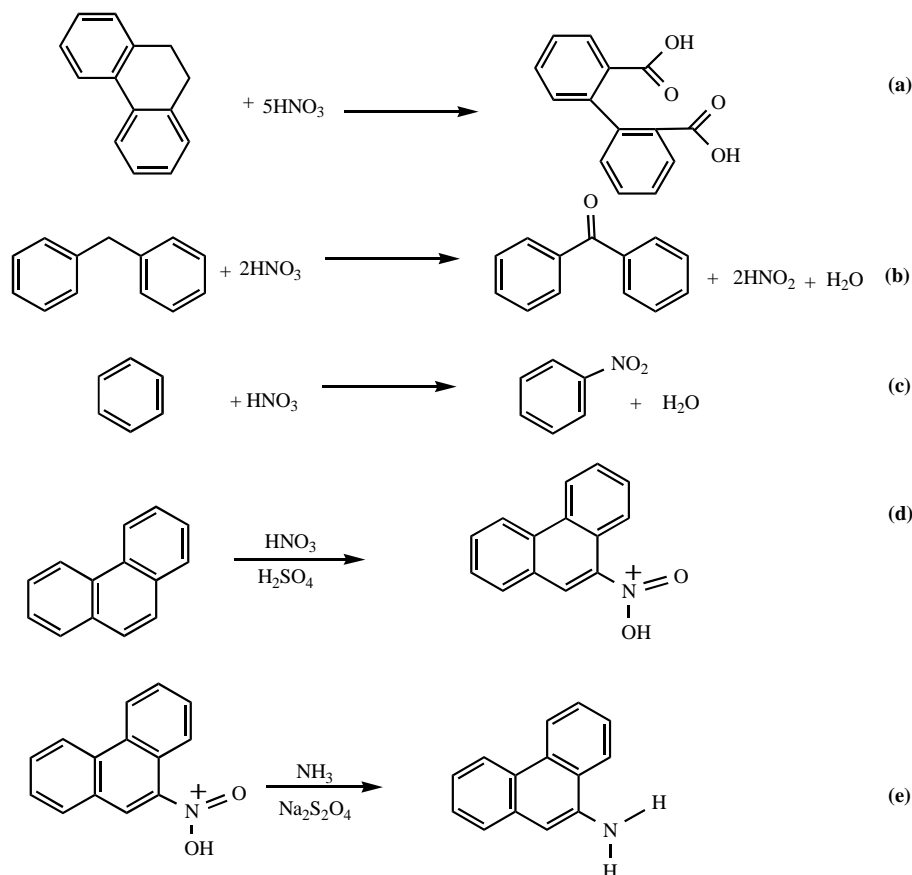


Fig. (3). The formation of acidic functional groups by nitric acid and amination reaction by thermal treatment [38].

2.2. Ammonia Treatment

It was well known that nitrogen-containing surface groups gave to activated carbons increased ability to adsorb acidic gases [43]. Practically, nitrogen was introduced into structure of activated carbon according to several procedures including treatment with ammonia or preparation of the adsorbent from nitrogen-containing polymers (Acrylic textile, polyaryamide or Nomex aramid fibers) [44-46]. Heating of phenol-formaldehyde-based activated carbon fiber in the atmosphere of dry ammonia at several temperatures ranged from 500°C to 800°C resulted in a formation of new nitrogen-containing groups in the structure of the fiber including C-N and C=N groups, cyclic amides, nitrile groups (C≡N) [47], and pyrrole-like surface structures with N-H groups [48]. Despite the changes in the surface chemistry, an outcome of heating of activated carbons in ammonia atmosphere might also be changed in porosity of the treated carbon. As it reported, extensive heat-treatment with gaseous ammonia might cause changes in the relative amounts of macropore, mesopore and micropores of commercial activated carbon [42].

In any case, since introducing of nitrogen-containing surface groups made activated carbon more alkaline and so increased adsorption of acidic agents is expected.

The commercial activated carbons were treated by gaseous NH₃ ranging from 400°C to 800°C for 2 h [49]. The CH and CN groups appeared after NH₃ treatment. It

demonstrated enhanced adsorption of phenol from water due to the formation of nitrogen-containing groups during ammonia-treated, which could form hydrogen bond with phenol.

A series of activated carbon fibers were produced by treatment with ammonia to yield a basic surface [47]. The adsorption isotherms of an acidic gas (HCl) showed a great improvement in capacity over an untreated acidic fiber. The adsorption was completely reversible and therefore involved the enhanced physical adsorption instead of chemisorption. This demonstrated that activated carbon fibers could be tailored to selectively remove a specific contaminant (acidic gas) based on the chemical modification of their pore surfaces.

Commercial activated carbon and activated carbon fiber were modified by high temperature helium or ammonia treatment, or iron impregnation followed by high temperature ammonia treatment [50]. Iron-impregnated and ammonia-treated activated carbons showed significantly higher dissolved organic matter uptakes than the virgin activated carbon. The enhanced dissolved organic matter uptake by iron-impregnated was due to the presence of iron species on the carbon surface. The higher uptake of ammonia treated was attributed to the enlarged carbon pores and basic surface created during ammonia treatment.

A commercial raw granular activated carbon was modified by polyaniline to improve arsenate adsorption [51].

It was found that the modification did not change the specific surface area. The content of the aromatic ring structures and nitrogen-containing functional groups on the modified granular activated carbon was increased. The surface positive charge density was dramatically increased in acidic solutions. The presence of humic acid did not have a great impact on the arsenic adsorption dynamics. The modification significantly enhanced the adsorption of humic acid onto the carbon. Meanwhile, the arsenate was reduced to arsenite during the process.

Lin *et al.* provided a method for minute deposition of polyaniline onto microporous activated carbon fabric could enhance the capacitance of the carbon serving as electrodes for electrochemical capacitors [52]. The result demonstrated that a capacitance enhancement of 50% in comparison with bare carbon could be achieved with minute polyaniline deposition (5wt%) using the deposition method, while only 22% was reached using the conventional method.

2.3. Heat Treatment

The nature and concentration of surface functional groups might be modified by suitable thermal or chemical post-treatments. Heating oxidation in the gas or liquid phase could be used to increase the concentration of surface oxygen groups, while heating under inert atmosphere might be used to selectively remove some of these functions. Thermal treatments had been used to produce activated carbons with basic character and such carbons were effective in the treatment of some organic hydrocarbons [53].

Heat treatment of carbon in an inert atmosphere or under inert atmospheres (hydrogen, nitrogen or argon) flow could increase carbon hydrophobicity by removing hydrophilic surface functionalities, particularly various acidic groups [54-57]. It had been shown that H₂ was more effective than inert atmospheres because it could also effectively stabilize the carbon surface by deactivation of active sites (i.e., forming stable C-H bonds and/or gasification of unstable and reactive carbon atoms) found at the edges of the crystallites. H₂ treatment at 900°C could produce highly stably and basic carbons [52, 55], and the presence of a platinum catalyst could considerably lower the treatment temperature [56]. H₂-treated carbons were expected to demonstrate much lower reactivity toward oxygen or chemical agents compared to carbons that were heat-treated in an inert atmosphere. The hydrophobic porous carbon effectively removed the non-polar organic molecules from aqueous solution. However, in order to prepare hydrophobic porous carbon, it needed high temperature and inert/reductive atmospheres to remove the heteroatoms on the surface of porous carbon.

The wood, coal-based activated carbons and a commercial activated carbon fiber with different physicochemical characteristics were subjected to heat treatment at 900°C under vacuum or hydrogen flow [58]. Oxygen sorption experiments showed lower amounts of oxygen uptake by the H₂-treated than by the vacuum-treated carbons, indicating that H₂ treatment effectively stabilized the surfaces of various carbons. At low pressures, from 0.001 mmHg to 5 mmHg, adsorption of oxygen was governed by irreversible chemisorption, which was well described by the Langmuir equation. At higher pressures oxygen uptake occurred as a

result of physisorption, which was in agreement with Henry's law. Kinetic studies showed that oxygen chemisorption was affected by both carbon surface chemistry and porosity. The results indicated that oxygen chemisorption initially started in the mesopore region from the high energetic sites without any mass transfer limitation; thus a constant oxygen uptake rate was observed. Once the majority of these sites were utilized, chemisorption proceeded toward the less energetic sites in mesopores as well as all the sites located in micropores. As a result, an exponential decrease in the oxygen uptake rate was observed.

Different precursors resulted in various elemental compositions and imposed diverse influence upon surface functionalities after heat treatment. The surface of heat-treated activated carbon fibers became more graphitic and hydrophobic. Polyacrylonitrile- and rayon-based activated carbon fibers subjected to heat treatment [59]. The presence of nitride-like species, aromatic nitrogen-imines, or chemisorbed nitrogen oxides was found to be of great advantage to adsorption of water vapor or benzene, but the pyridine-N was not. Unstable complexes on the surface would hinder the fibers from adsorption of carbon tetrachloride. The rise in total ash content or hydrogen composition was of benefit to the access of water vapor.

2.4. Microwave Treatment

The main advantage of using microwave heating was that the treatment time could be considerably reduced, which in many cases represented a reduction in the energy consumption. It was reported that microwave energy was derived from electrical energy with a conversion efficiency of approximately 50% for 2450 MHz and 85% for 915 MHz [60].

Thermal treatment of polyacrylonitrile activated carbon fibers had been carried out using a microwave device [61]. Microwave treatment affected the porosity of the activated carbon fibers, causing a reduction in micropore volume and micropore size. Moreover, the microwave treatment was a very effective method for modifying the surface chemistry of the activated carbon fibers with the production of pyrone groups. As a result very basic carbons, with points of zero charge approximately equal to 11, were obtained.

Microwave heating offered apparent advantages for activated carbon regeneration, including rapid and precise temperature control, small space requirements and greater efficiency in intermittent use [62]. Quan *et al.* investigated the adsorption property of acid orange 7 by microwave regeneration coconut-based activated carbons [63]. It was found that after several adsorption-microwave regeneration cycles, the adsorption rates and capacities of granular activated carbons could maintain relatively high levels, even higher than those of virgin Granular activated carbons. The improvement of granular activated carbons adsorption properties resulted from the modification of pore size distribution and surface chemistry by microwave irradiation.

2.5. Ozone Treatment

Ozone as a strong oxidization agent was widely applied in organic degradation; it could also oxidize the carbon material surface to introduce oxygen-containing groups. The

ozone dose and oxidization time affected the resultant oxygen-containing groups and the oxygen concentration on the carbon surface. The result of bituminous origin-based activated carbon oxidization with ozone showed that the higher the ozone dose, the higher was the oxidation of the carbon and the greater was the number of acid groups present on the carbon surface, especially carboxylic groups, whereas the pH of the point of zero charge decreased [64]. The surface area, micropore volume, and methylene blue adsorption all reduced with higher doses. These results were explained by the ozone attack on the carbon and the fixation of oxygen groups on its surface. Jackson introduces a method for supercritical ozone treatment of a substrate [65].

The impact of ozonation on textural and chemical surface characteristics of two coal-based activated carbons and their ability to adsorb phenol, *p*-nitrophenol, and *p*-chlorophenol from aqueous solutions had been investigated by Alvarez *et al.* [66]. The porous structure of the ozone-treated carbons remained practically unchanged with regard to the virgin activated carbon. At 25°C primarily carboxylic acids were formed while a more homogeneous distribution of carboxylic, lactonic, hydroxyl, and carbonyl groups was obtained at 100°C.

2.6. Plasma Treatment

The plasma treatment was regarded as a promising technique to modify the surface chemical property of porous carbon since it produced chemically active species affecting the adsorbability. During the plasma treatment, the slower chemical reaction by chemically active species took place only on the surface of activated carbon without changing its bulk properties at low pressure by long time treatments. It was possible to create any ambience for oxidative, reductive, or inactive reaction by changing the plasma gas [67]. Plasma could introduce basic and acid functional groups that were determined by the gaseous resource. The semi-quantitative analysis of the surface acidic functional groups showed that a difference in treatment conditions affected the quality and quantity of the functional groups [68].

Some experimental efforts had been reported on activated carbon treatment with oxygen-included plasmas. The negative charge of activated carbon was brought after the plasma treatment was due to dissociation of newly formed acidic groups. The hydrophilicity of plasma-treated carbons did not change significantly. The oxygen plasma appeared not to reach the smallest micropores of the carbon, indicating that the reaction took place only near the external surfaces of

the particles [69, 70]. The surface area of activated carbon that was treated by oxygen non-thermal plasma was decreased, and the concentrations of acidic functional groups at the surface were increased and the saturated adsorption amount of copper and zinc ion was considerably increased [71-74]. Oxygen species produced during the discharge react on the activated carbon surface resulting in the creation of weakly acidic functional groups that played an important role in adsorbing metal cations. Improvement in the adsorbability was attributed to the change in the surface chemical structure of the commercial activated carbon rather than the modification of the surface physical structure [75]. For example, the CF₄ plasma treatment could effectively improve the hydrophobic property, polarization and power density of the activated carbon fibers [76]. The activation of the carbon-surface by the nitrogen radio frequency plasma yielded a significant increase in adhesion for Cu-coatings [77]. The submicron vapor grown carbon fibers preserved their general smoothness upon plasma oxidation and the structural changes brought about by this treatment essentially took place only at the atomic scale [78]. The vapor grown carbon fibers were modified using NH₃, O₂, CO₂, H₂O and HCOOH plasma gases to increase the wettability and the results show that the oxidation strength was O₂>CO₂>H₂O>HCOOH [79]. The polyacrylonitrile fibers were treated with the nitrogen glow discharge plasma and the hydrophilic groups (N-H, C=N) were introduced on the fiber surfaces [80]. The air and nitrogen glow discharge were used to modify the activated carbon fibers, their surface became rough and several types of polar oxygen groups were introduced into the carbon fiber surface [81]. The invention by Miller *et al.* induces the steps of evaporation for regeneration of commercial activated carbon [82].

Viscose-based activated carbon fibers were treated by a dielectric-barrier discharge plasma and nitrogen as feed gas at different conditions [83]. It showed that the nitrogen plasma modification could remarkably change the distribution of the oxygen functional groups on the activated carbon fibers surface and there were more nitrogen atoms incorporated into the aromatic ring.

Different plasma treatment and the changes of related chemical functional groups were listed in Table 1.

In addition, space charge density could be improved by nitrogen plasma surface treatment of carbon materials [84].

Recently, atmospheric pressure plasma could treat various materials even those which were low temperature

Table 1. The Related Chemical Groups Change at Different Plasma Treatment Conditions

Plasma gaseous	Increased chemical groups	Decreased chemical groups
O ₂	- C-OOH, C=O	- C-OH, C-O-C [72]
N ₂	- C-OH, C-O-C-, O=C-O, pyridine and quaternary nitrogen	- C=O (aromatic ring) [79]
NH ₃	N-H [70]	
CO ₂	- C-OOH, C=O [76]	
H ₂ O	- C-OOH, C=O [76]	

degradable because it was realized in air with no vacuum system [85]. The surface activation remained stable over a quite long period: treated substrates could thus be stored.

2.7. Other Modification Methods

Air and steam activation was the commonly method to form pore and introduce oxygen-containing functional groups. Air oxidation can increase the amount of surface oxygen-containing functional groups (carboxylic acids and quinines) of rayon activated carbon fiber [86].

Furfural-based porous carbon showed basic and acidic characters after it was activated by steam and air, and it was proved as an efficient adsorbent material for mercury removal from aquatic solutions [87]. Different oxygen containing groups of acidic character (carboxylic groups, carboxylic groups involved in lactone binding, and phenolic hydroxyl and carbonyl groups) were present in all carbons. The amount of oxygen groups with different acidities on the surface of oxidized furfural adsorbent was considerably higher than that of the carbon activated with water vapor which had an alkaline character of the surface. Basic groups were not detected on the surfaces of the oxidized carbons. This did not mean, however, that such groups did not exist; more probably, it suggested that their reactivity toward HCl was diminished either through internal neutralization by acidic groups located on some aromatic system or by different electron distributions caused by the presence of acidic groups. The concentrations of the carboxylic and lactone oxygen containing groups on the surface of the samples obtained in the presence of steam were lower because steam was a weaker oxidant. The contents of carbonyl, phenolic, oxygen containing groups with basic character were nearly the same for both samples activated with steam.

When the commercial activated carbon was loaded sodium and potassium, it could efficiently remove NO and SO₂ from waste gases by adsorption [88].

Activated carbon from coconut shell was modified by sodium acetate, its adsorption for copper ion could be increased 2.2 times, after it was regenerated with NaOH, the adsorption capacity increased 3 times [89].

Pitch-based ordered carbon with fluorine could be fluorinated at room temperature or moderately elevated temperature, which has great potential applications in electrochemistry or batteries [90]. When the rayon activated carbon fiber was modified by chlorine or bromine, its surface hydrophilic property was increased and the adsorption capacity of dimethyl sulfide was increased [91].

Recently, we modified rayon activated carbon fiber with nitrocellulose combustion, the nitrogen and oxygen groups could be increased, and it showed excellent adsorption for ammine and carbon disulfide [92].

Tannic acid was employed in the modification of the surface properties of granulated commercial activated carbon [93]. Tannic acid was found effective to enhance the metal adsorption capacity of activated carbon surfaces.

The surface of activated carbon was modified with KOH, its adsorption and desorption behaviors for NO_x and the

accompanied surface reaction mechanism as well as the distribution of molecular ions on the surface were illustrated [94]. NO desorption occurs at the earliest stage as chemical adsorption occurs earlier, in a sort of competition, than physical adsorption due to strong basic OH⁻ ion of surface. The potassium that existed on the surface remained without being consumed even with complete desorption of NO_x.

2.8. Modification Porous Carbon for Electrode Materials

Porous carbon was generally used as electric double-layer capacitance electrodes material. It was well known that the electric capacity of an electrode was affected by its physical and chemical properties [95-103]. The effects of oxygen-containing functional groups on electric characteristics had been investigated qualitatively in terms of temperature-programmed desorption [102-104]; and the result indicated that the presence of oxygenated groups on the surface of the activated carbon most probably affected the capacitance of the materials mainly in improving the wettability of the material, increasing the capacitance; and producing pseudo capacitance effects.

Oda *et al.* compared the effect of surface chemical property of commercial porous carbon on its application in electrolyte [105]. In the case of the aqueous electrolyte, the electric capacity depended more on oxygen functional groups than on BET surface area. It was considered that a larger number of functional group promoted not only the wettability of electrodes but also the negative charge of electrodes leading to an increase in capacity. In the case of the organic electrolyte, pore structure seemed to be a more dominant factor than functional group. A significant increase in phenolic hydroxyl group was confirmed on the positive electrode. A mild oxidation of activated carbon fiber increased the number of phenolic hydroxyl groups and caused a severe oxidation carboxyl group mainly.

Fang *et al.* developed carbon electrode material through surface modification by vinyltrimethoxysilane and sodium oleate to enhance the hydrophobisation of Norit activated carbon and the affinity toward propylene carbonate solvent [106, 107], which improved the wettability of activated carbon in the electrolyte solution based on propylene carbonate solvent, resulting in not only a lower resistance to the transport of electrolyte ions within micropores of activated carbon but also more usable surface area for the formation of electric double layer, and accordingly, higher specific capacitance, energy density, and power capability available from the capacitor based on modified carbon. Especially, the effects from surface modification became superior at higher discharge rate, at which much better electric double-layer capacitance performance (i.e., much higher energy density and power capability) had been achieved by the modified carbon, suggesting that the modified carbon was a novel and very promising electrode material of electric double-layer capacitance for large current applications where both high energy density and power capability were required.

Variety in surface chemical character was achieved through modification of Row 0.8 activated carbons by heat treatment in vacuum, ammonia and ammonia-oxygen atmospheres, as well as by oxidation in moist air and with

concentrated nitric acid [108]. The importance of the surface chemistry of the carbon electrode materials was the adsorbed lead species exhibited different electrochemical activities due to its different existing states on the carbon surface.

The oxidation treatment mainly increased the oxygen-containing groups, which changed the surface acidic property of porous carbon. The efficient method to increase the oxygen-containing groups was the nitric acid or sulfuric acid oxygen, but it needed concentration acid and post-treatment to remove the residue acid; the plasma treatment took long time and the air oxidation required appropriate temperature (400-500°C). The pore structure was affected during oxidation in less or more degree. The nitrogen-containing groups introduced required higher temperature and increased the surface basic property of porous carbon. The heat treatment decreased the surface groups and narrowed the pore diameter. Although the microwave treatment took shorter time than others methods, the introduced chemical functional groups were less and determined by the atmospheres and carbon precursor. It was difficult to control the oxidation degree of ozone oxidation process. The introduced chemical functional groups should be considered its application and the simpler route.

3. ANALYSIS OF SURFACE FUNCTIONAL GROUPS

Elemental analysis was the primary method to obtain the elemental kinds and its amount, but it could not give the functional groups. A variety of experimental techniques had been used to characterize these functional groups of porous carbon, such as chemical titration methods, temperature-programmed desorption (TPD), X-ray photoelectron

spectroscopy (XPS), infra-red spectroscopy methods (FTIR, DRIFTS) and nuclear magnetic resonance (NMR) spectrum.

3.1. Chemical Titration

The chemical titration methods, such as proposed by Boehm [109, 110], were especially useful when it was used in combination with other techniques [111]. The amount of oxygen-containing groups (carboxyl, lactonic, and phenol) on the activated carbon was determined by adsorption neutralization with NaHCO_3 , Na_2CO_3 , and NaOH solutions, respectively [112, 113]. The basic group contents of the activated carbons were determined with 0.05 M HCl [114].

The traditional Boehm titration method, present several drawbacks, such as: the equilibrium times were very long for microporous materials; there were problems of reproducibility when dealing with small amounts of sample; and this technique only could determine about 50% of the total oxygen available in activated carbons [115].

3.2. TPD Decomposition

TPD was a thermal analysis method that was becoming more popular for the characterization of the oxygen-containing groups of activated carbons [116-128]. In this technique, all of the surface groups were thermally decomposed releasing CO and/or CO_2 and in some cases H_2O and H_2 , at different temperatures. The nature of the groups could be assessed by the decomposition temperature and type of gas released, and their respective amounts by the areas of the peaks. In this technique, all of the oxygen present was released and determined as CO , CO_2 , and H_2O , as confirmed by comparing the oxygen obtained by TPD and by elemental analysis. The major problem was the difficulty

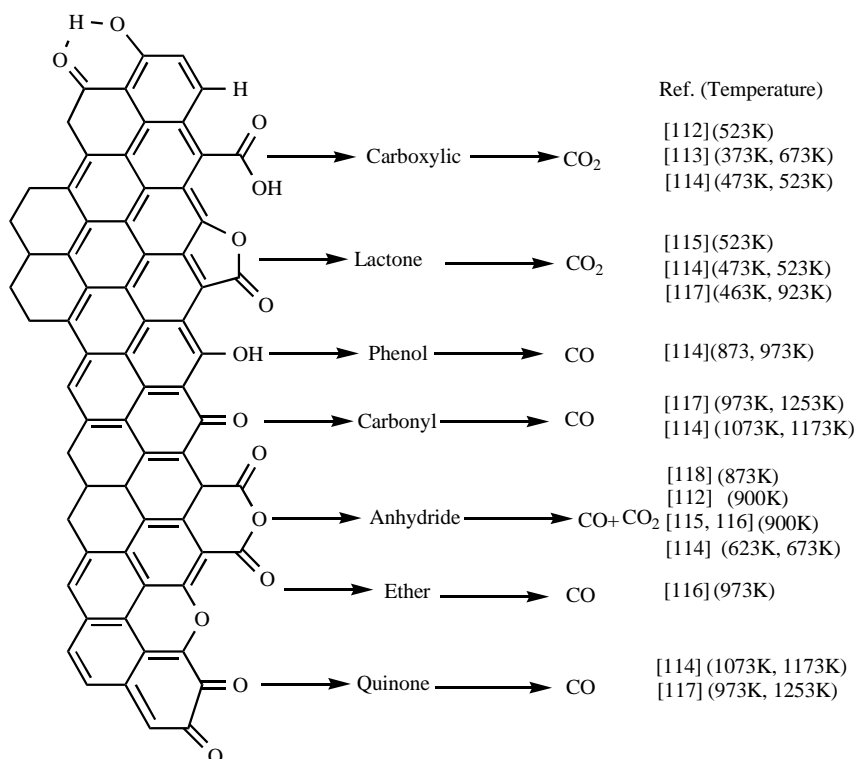


Fig. (4). Surface oxygen-containing groups on carbon and their decomposition by TPD [115-121].

in identifying each surface group individually, because TPD spectra showed composite CO and CO₂ peaks.

The mainly surface oxygen-containing groups on activated carbon and their decomposition by TPD were shown in Fig. (4) [116-121].

Boudou JP *et al.* investigated the nitrogen in aramid-based activated carbon fibers by TPD [122]. The nitrogen bonding structure varied with the activation agents of H₃PO₄, H₃PO₄-CO₂, CO₂ or steam. The nitrogen group distribution was controlled by two simultaneous reactions: strong aromatization, and surface oxidative denitrogenation due a secondary activation triggered by gases released at high temperature. There were three kinds of nitrogen groups of pyridinic nitrogen, condensed pyridinic nitrogen and an unknown intermediate component during TPD process. The largest part of nitrogen evolves as molecular nitrogen in two steps: the first one below 870°C and the second one between 930°C and 1380°C. HCN evolved from 880°C to 1230°C. When the ACF was activated by H₃PO₄, HCN co-evolves with NO were formed during TPD process. The TPD products of N₂ and a small amount of nitrile groups should be rather related to a pyridinic cycle bearing oxygen substituents or intracyclic oxygen atoms making the cycle more prone to be open by thermal cracking. This opening would occur during TPD by releasing both HCN and N₂ at lower temperature, instead of pure N₂ formed by surface or gas phase radical recombination as a result of hydrogen starvation at higher temperature.

3.3. X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was a frequently technique for investigation of the surface functionalities of carbon materials as illustrated by a number of studies [99, 123, 124]. Valence band XPS had the ability to distinguish some subtle chemical differences, and the combination of XPS data from different regions could indicate differences in chemical composition with depth into the surface [125]. The sampling depth for an XPS

measurement on carbon fibers was reported to be only about 10-15 nm [126]. The XPS spectra of C_{1s} and O_{1s} indicated that carbonyl groups were introduced to the surface at low oxidation potentials, and the concentration of alcohol-ether groups increased at high oxidation potentials [127]. However, the OH and C-O oxygen atoms in the carboxyl groups could not be easily distinguished if the XPS experiments were carried out at room temperature [118]. Moreover, addition of a defect peak to the pristine C_{1s} profile appeared imperative in the fitting when the treatment destroyed the crystalline order of the carbonaceous materials [128]. This spectroscopic method had been extensively employed to study the surface carbon-oxygen complexes and elemental composition before and after surface treatments.

When applied to porous carbons for the determination of the oxygen surface groups, XPS had the following drawbacks: (i) the external surface area was only a small fraction of the total surface area and it was not representative of all of the material; (ii) the holes in the surface could affect the final results because the surface was not flat; (iii) the analysis was made in high-vacuum, that was, under conditions quite different from those usually used in the applications of the carbon catalyst, and a rearrangement of the surface can occur; and (iv) deconvolution of the O_{1s} and C_{1s} peaks was not straightforward, and it was still a matter of discussion.

The bonding energy and their assignment of C_{1s}, O_{1s}, and N_{1s} deduced from XPS spectra for modified Norit ROW 0.8 were list in Table 2 [99].

3.4. FT-IR (Fourier Transform-Infrared Spectroscopy)

The FT-IR method had been widely used to characterize the surface groups of different oxides, and also applied to various types of carbon and carbonaceous materials. Since IR transmission spectra had peaked shapes where the specific chemical bonds existed, it was possible to know which functionalities were created on the surface of activated carbon by comparing locations and depths of the peak lines.

Table 2. The C_{1s}, O_{1s}, and N_{1s} Deduced from XPS Spectra for Modified Norit ROW 0.8

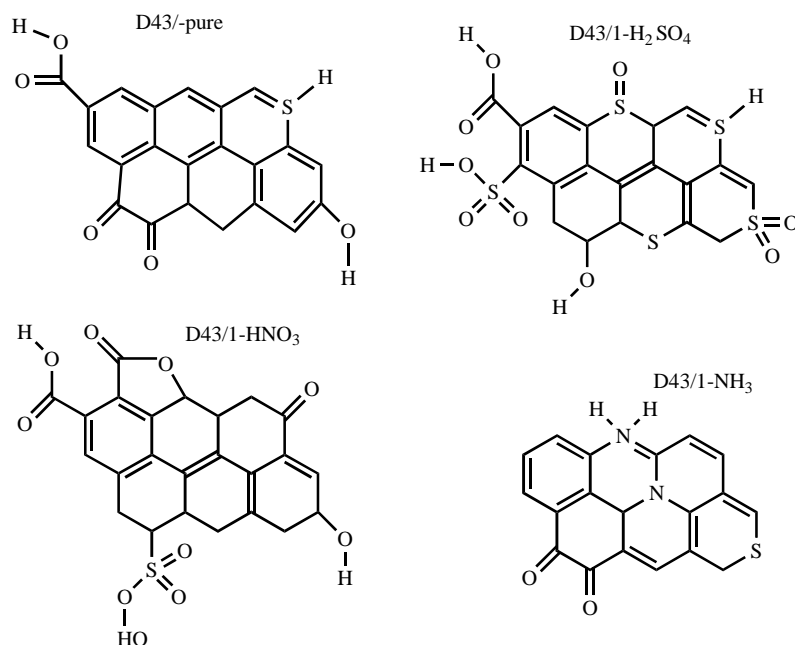
C _{1s}		O _{1s}		N _{1s}	
B.E. (eV)	Assignment	B.E. (eV)	Assignment	B.E. (eV)	Assignment
284.5 ± 0.1	- C=C-, non-functionalised sp ² C	530.6 ± 0.2	C=O (carboxyl)	398.6 ± 0.3	Pyridinic nitrogen, Ar-N-Ar
286.1 ± 0.1	- C-OH, .C-O-C≡, C-O-R	532.3 ± 0.3	C=O (ester, amides)	399.4 ± 0.3	-N-H Pyrrolic nitrogen Pyridine nitrogen
287.4 ± 0.2	- C-N, C=O	533.5 ± 0.2	C-O-C≡ (ester oxygen)	400.2 ± 0.1	-O-C=N Pyridine pyrrole
288.7 ± 0.2	- C=N, -N=C-O-, COOC-	534.3 ± 0.2	COH, COOH, N-O-C	401.3 ± 0.2	N, quaternary
289.3 ± 0.1	- COOH (carboxyl acid)	536.3 ± 0.4	H ₂ O _{ads} , O _{2ads}	402.5-403.8	Pyridine-N-oxide
290.4 ± 0.4	π→π* shake-up satellite			404.5 ± 0.4	NO _x , oxidized, N-O-C
292.0 ± 0.4	Plasmon				

Table 3. IR Assignments of Functional Groups on Carbon Surfaces (Adapted from: 46, 63,130-133)

Group or functionality	Assignment regions (cm ⁻¹)	Group or functionality	Assignment regions (cm ⁻¹)
C-O in ethers (stretching)	1000-1300	N-H, C=N	1560-1570
Alcohols	1049-1276, 3200-3640	Cyclic amides	646,1461,1546,1685
Phenolic groups		C-N aromatic ring	1000, 1250, 1355
-C-OH (stretching)	1000-1220	C-N	1190
O-H	1160-1200, 2500-3620	C=C=N	2070-2040
Carbonates; carboxyl-carbonates	1100-1500, 1590-1600	N-O-	1300-1000
-C-C aromatic (stretching)	1585-1600		
Quinones	1550-1680		
Carboxylic acids	1120-1200, 1665-1760, 2500-3300		
Lactones	1160-1370, 1675-1790		
Carboxylic anhydrides	980-1300, 1740-1880		
C-H (stretching)	2600-3000		

FTIR was mainly used as a qualitative technique for the evaluation of the chemical structure of carbon materials. It was not easy to get good spectra because carbons are black materials that absorbed almost all of the radiation in the visible spectrum, and the peaks obtained were usually a sum of the interactions of different types of groups [129]. Some FT-IR assignments of chemical functional groups were listed in Table 3 [46, 63, 130-133].

In order to completely understand the chemical function groups, it should simultaneous use these methods to analyze the chemical composition. Terzyk illustrated the chemical groups of activated carbon with HNO₃, H₂SO₄ and NH₃ by applying the following techniques: TPD, FTIR, XPS, thermal analysis, resistance, and enthalpy of immersion, the related surface function groups were drawn in Fig. (5) [134].

**Fig. (5).** The proposed structure of surface functionalities of the studied carbons [134].

3.5. NMR Spectrum

The ^{13}C NMR spectra could determine the chemical functionalities of porous carbons [135]. The peaks near 30 ppm, 80 ppm and 127 ppm could be assigned to the sp^3 -hybridized carbon [136], sp -hybridized carbon and sp^2 -hybridized carbon in graphite or graphite-like domains [137-140], respectively.

The peak near 175 ppm might be due to alkoxy and OH substituted carbon. The peak at 40 ppm could be attributed to the presence of $-\text{CH}$ and $-\text{CH}_2$ groups and the signal at 39 ppm were the crosslinked methylene groups [141, 142]. The olefinic carbon atoms with a broad signal between 120 and 140 ppm were clearly detectable in the solid-state ^{13}C NMR spectrum [141].

4. CURRENT & FUTURE DEVELOPMENTS

In this review, various methods of porous carbon surface modification were presented. Modification of porous carbon via acidic, thermal treatment were not by far, the most studied technique, might be attributed to its simplicity, availability of oxidization process. Generally, oxidization treatment of porous carbon was favorable for enhancing its adsorption for polar molecules while thermal treatment was desired for adsorption for non-polar molecules. The nitrogen functional groups could improve its adsorption for odor gases and acidic molecules. These methods could change the pore structure of porous carbon in little or large degree.

Many novel or simpler technology is still developing to meet new application demands. The quantity of surface chemical functional groups control and certain group introducing are still challenge for porous carbon surface modification.

REFERENCES

- Rodriguez-Reinoso F, Molina-Sabio M. Textural and chemical characterization of microporous carbons. *Adv Colloid Interface Sci* 1998; 76-77: 271-294.
- Figueiredo JL, Pereira MFR, Freitas MMA, Orfao JJM. Modification of the surface chemistry of activated carbons. *Carbon* 1999; 37: 1379-1389.
- Biniak S, Szymanski G, Siedlewski J, Swiatkowski A. The characterization of activated carbons with oxygen and nitrogen surface groups. *Carbon* 1997; 35: 1799-1810.
- Szymanski GS, Karpinski Z, Biniak S, Swiatkowski A. The effect of the gradual thermal decomposition of surface oxygen species on the chemical and catalytic properties of oxidized activated carbon. *Carbon* 2002; 40: 2627-2639.
- Izquierdo MT, Rubio B, Mayoral C, Andre's JM. Modifications to the surface chemistry of low-rank coal-based carbon catalysts to improve flue gas nitric oxide removal. *Appl Catal B Environ* 2001; 33: 315-324.
- Shim JW, Park SJ, Ryu SK. Effect of modification with hno_3 and naoh on metal adsorption by pitch-based activated carbon fibers. *Carbon* 2001; 39: 1635-1642.
- Yin CY, Aroua MK, Daud WMAW. Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. *Sep Purif Technol* 2007; 52: 403-415.
- Radovic LR, Moreno-Castilla C, Rivera-Utrilla J. Carbon materials as adsorbents in aqueous solution in "Chemistry and Physics of carbon", radovic Jr, Ed. Marcel Dekker: New York, 2001; 27: 227-405.
- Carlos M-C. Adsorption of Organic Molecules from Aqueous Solutions on Carbon Materials. *Carbon* 2004; 42: 83-94.
- El-Sayed Y, Bandosz TJ. Adsorption of valeric acid from aqueous solution onto activated carbons: role of surface basic Sites. *J Colloid Interf Sci* 2004; 273: 64-72.
- Lukaszewicz JP. Carbon-film-based humidity sensor containing sodium or potassium. recovery effect. *Sens Actuators B Chem* 1999; 60: 184-190.
- Conway BE. Electrochemical supercapacitors. New York: Kluwer-Plenum Pub. Co.; 1999. Frackowiak E, Beguin F. Carbon materials for the electrochemical storage of energy in capacitors. *Carbon* 2001; 39: 937-950.
- Chen X, Zhang Y, Gao XP, Pan GL, Jiang XY, Qu JQ. Electrochemical hydrogen storage of carbon nanotubes and carbon nanofibers. *Int J Hydrogen Energ* 2004; 29: 743-748.
- Rajalakshmi N, Dhathathreyan KS, Govindaraj A, Satishkumar BC. Electrochemical investigation of single-walled carbon nanotubes for hydrogen storage. *Electrochim Acta* 2000; 45: 4511-4555.
- Rodriguez-Reinoso F. The role of carbon materials in heterogeneous catalysis. *Carbon* 1998; 36: 159-171.
- Feron PHM, Jansen AE. The production of carbon dioxide from flue gas by membrane gas absorption. *Energy Convers Manage* 1997; 38: S93-S98.
- Mikhalev Y, Oye HA. Absorption of metallic sodium in carbon cathode materials. *Carbon* 1996; 34: 37-41.
- Li YH, Lee CW, Gullett BK. The effect of activated carbon surface moisture on low temperature mercury adsorption. *Carbon* 2002; 40: 65-72.
- Boudou JP, Paredes JI, Cuesta A, Martinez-Alonso A, Tasco'n JMD. Oxygen plasma modification of pitch-based isotropic carbon fibres. *Carbon* 2003; 41: 41-56.
- Pittman Jr CU, Jiang W, He GR, Gardner SD. Oxygen plasma and isobutylene plasma treatments of carbon fibers: determination of surface functionality and effects on composite properties. *Carbon* 1998; 36: 25-37.
- Pittman Jr CU, He GR, Wu B, Gardner SD. Chemical modification of carbon fiber surfaces by nitric acid oxidation followed by reaction with tetraethylenepentamine. *Carbon* 1997; 35: 317-331.
- Xie F, Phillips J, Silva IF, Palma MC, Mene'ndez JA. Microcalorimetric study of acid sites on ammonia- and acid-pretreated activated carbon. *Carbon* 2000; 38: 691-700.
- Hu CC, Wang CC. Effects of electrolytes and electrochemical pretreatments on the capacitive characteristics of activated carbon fabrics for supercapacitors. *J Power Sources* 2004; 125: 299-308.
- Dastgheib SA, Karan LT, Cheng W. Tailoring activated carbons for enhanced removal of natural organic matter from natural waters. *Carbon* 2004; 42: 547-557.
- Chen JP, Wu S, Chong KH. Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption. *Carbon* 2003; 41: 1979-1986.
- Evans MJB, Halliop E, MacDonald JAF. The production of chemically-activated carbon. *Carbon* 1999; 37: 269-274.
- Otowa T, Nojima Y, Miyazaki T. Development of KOH activated high surface area carbon and its application to drinking water purification. *Carbon* 1997; 35: 1315-1319.
- Yang RT. Adsorption, John Wiley & Sons Inc., Hoboken, New Jersey 2003.
- Abe M, Kawashima K, Kozawa K, Sakai H, Kaneko K. Amination of activated carbon and adsorption characteristics of its aminated surface. *Langmuir* 2000; 16: 5059 -5063.
- Fels JR, Kapteijn F, Moulijn JA, Zhu Q, Thomas KM. Evolution of nitrogen functionalities in carbonaceous materials during pyrolysis. *Carbon* 1995; 33: 1641-1653.
- Perez-Cadenas AF, Maldonado-Hodar FJ, Moreno-Castilla C. On the nature of surface acid sites of chlorinated activated carbons. *Carbon* 2003; 41: 473-478.
- Liu SX, Chen X, Chen XY, Liu ZF, Wang HL. Activated carbon with excellent Chromium (VI) adsorption performance prepared by acid-base surface modification. *J Hazard Mater* 2007; 141: 315-319.
- Wibowo N, Setyadi L, Wibowo D, Setiawan J, Ismadji S. Adsorption of benzene and toluene from aqueous solutions onto activated carbon and its acid and heat treated forms: influence of surface chemistry on adsorption. *J Hazard Mater* 2007; 146: 237-242.
- Li JY, Ma L, Li XN, Lu CS, Liu HZ. Effect of nitric acid pretreatment on the properties of activated carbon and supported palladium catalysts. *Ind Eng Chem Res* 2005; 44: 5478-5482.
- Badie SG, Amina AA, Nady AF. Modification in adsorption characteristics of activated carbon produced by H_3PO_4 under

- flowing gases. *colloid surface A. Physicochem Eng Aspect* 2007; 299: 79-87.
- [36] Li, Li., Li, W.: US20077205248 (2007).
- [37] Tamai H, Nagoya T, Shiono. Adsorption of methyl mercaptan on surface modified activated carbon. *J Colloid Interf Sci* 2006; 300: 814-817.
- [38] Hasenberg, D.M., Refvik, M.D.: WO07070496 (2007).
- [39] Chingombe P, Saha B, Wakeman RJ. Surface modification and characterization of a coal-based activated carbon. *Carbon* 2005; 43: 3132-3143.
- [40] Vinke P, Eijk der van M, Verbree M, Voskamp AF, Bekkum H. Modification of the surfaces of a gas-activated carbon and a chemically activated carbon with nitric acid, hypochlorite, and ammonia. *Carbon* 1994; 32: 675-686.
- [41] Luisa C, Miguel AG, Jose AC, Angel FM, Juan JR. Effects of support surface composition on the activity and selectivity of pd/c catalysts in aqueous-phase hydrodechlorination reactions. *Ind Eng Chem Res* 2005; 44: 6661-6667.
- [42] Marta S, Frank S, Agust F, Azael F, Josep F. Modified activated carbons for catalytic wet air oxidation of phenol. *Carbon* 2005; 43: 2134-2145.
- [43] Li KX, Ling LC, Lu CX, *et al.* Catalytic removal of so₂ over ammonia-activated carbon fibers. *Carbon* 2001; 39:1803-1808.
- [44] Carrott PJM, Nabais JMV, Ribeiro-Carrott MML, Pajares JA. Preparation of activated carbon fibres from acrylic textile fibres. *Carbon* 2001; 39: 1543-1555.
- [45] Stoeckli F, Centeno TA, Fuertes AB, Muniz J. Porous structure of polyarylamide-based activated carbon fibres. *Carbon* 1996; 34: 1201-1206.
- [46] Blanco Lopez MC, Martínez-Alonso A, Tascon JMD. Microporous Texture of activated carbon fibres prepared from nomex aramid fibres. *Micropor Mesopor Mater.* 2000; 34: 171-179.
- [47] Mangun CL, Benak KR, Economy J, Foster KL. Surface chemistry, pore sizes and adsorption properties of activated carbon fibers and precursors treated with ammonia. *Carbon* 2001; 39: 1809-1820.
- [48] Strelko V, Kuts VS, Thrower PA. On the mechanism of possible influence of heteroatoms of nitrogen, boron and phosphorus in a carbon matrix on the catalytic activity of carbons in electron transfer reactions. *Carbon* 2000; 38: 1499-1524.
- [49] Przepiorski J. Enhanced adsorption of phenol from water by ammonia-treated activated carbon. *J Hazard Mater* 2006; 135: 453-456.
- [50] Cheng W, Dastghei SA, Karanfil T. Adsorption of dissolved natural organic matter by modified activated carbons. *Water Res* 2005; 39: 2281-2290.
- [51] Yang L, Wu SN, Chen JP. Modification of activated carbon by polyaniline for enhanced adsorption of aqueous arsenate. *Ind Eng Chem Res* 2007; 46: 2133-2140.
- [52] Lin YR, Teng HS. A novel method for carbon modification with minute polyaniline deposition to enhance the capacitance of porous carbon electrodes. *Carbon* 2003; 41: 2865-2871.
- [53] Radovic LR, Silva IF, Ume JI, Menendez JA, Leony Leon CA, Scaroni AW. An experimental and theoretical study of the adsorption of aromatics possessing electron-withdrawing and electron-donating functional groups by chemically modified activated carbons. *Carbon* 1997; 35: 1339-1348.
- [54] Menendez JA, Phillips J, Xia B, Radovic LR. On the modification and characterization of chemical surface properties of activated carbon: in the search of carbons with stable basic properties. *Langmuir* 1996; 12: 4404-4410.
- [55] Menendez JA, Illan-Gomez MJ, Leony Leon CA, Radovic LR. On the difference between the isoelectric point and the point of zero charge of carbons. *Carbon* 1995; 33: 1655-1657.
- [56] Menendez JA, Radovic LR, Xia B, Phillips J. Low-temperature generation of basic carbon surfaces by hydrogen spillover. *J Phys Chem* 1996; 100: 17243-17248.
- [57] Shin S, Jang J, Yoon SH, Mochida I. A Study on the effect of heat treatment on functional groups of pitch based activated carbon fiber using ftir. *Carbon* 1997; 35: 1739-1743.
- [58] Seyed AD, Karanfil T. Adsorption of oxygen by heat-treated granular and fibrous activated carbons. *J Colloid Interf Sci* 2004; 274: 1-8.
- [59] Chiang YC, Lee CY, Lee HC. Surface chemistry of polyacrylonitrile- and rayon-based activated carbon fibers after post-heat treatment. *Mater Chem Phys* 2007; 101: 199-210.
- [60] Haque KE. Microwave energy for mineral treatment processes-a brief review. *Int J Miner Process* 1999; 57: 1-24.
- [61] Nabais MV, Carrott PJM, Carrott MMLR, Menendez JA. Preparation and modification of activated carbon fibres by microwave heating. *Carbon* 2004; 42: 1315-1320.
- [62] Van WEJ, Bradshaw SM, Swardt JBD. The dependence of microwave regeneration of activated carbon on time and temperature. *J Microwave Power Electromagn Eng* 1998; 33: 151-157.
- [63] Quan X, Liu XT, Bo LL, Chen S, Zhao YZ, Cui XY. Regeneration of acid orange 7-exhausted granular activated carbons with microwave irradiation. *Water Res* 2004; 38: 4484-4490.
- [64] Valdes H, Sanchez-Polo M, Rivera-Utrilla J, Zaror CA. Effect of ozone treatment on surface properties of activated carbon. *Langmuir* 2002; 18: 2111-2116.
- [65] Jackson, D.P.: US20077219677 (2007).
- [66] Álvarez PM, García-Araya JF, Beltrán FJ, Masa FJ, Medina F. Ozonation of activated carbons: effect on the adsorption of selected phenolic compounds from aqueous solutions. *J Colloid Interf Sci* 2005; 283: 503-512.
- [67] Park SJ, Kim JS. Influence of plasma treatment on microstructures and acid-base surface energetics of nanostructured carbon blacks: N₂ plasma environment. *J Colloid Interf Sci* 2001; 244: 336-341.
- [68] Kodama S, Sekiguchi H, in: D'Agostino, Wertheimer, Favia, Oehr (Eds.), *Plasma Processes and Polymers*. Wiley-VCH, Weinheim 2005; 131.
- [69] Garcia AB, Martinez-Alonso A, Leon CAL, Tascon JMD. Modification of the surface properties of an activated carbon by oxygen plasma treatment. *Fuel* 1998; 77: 613-624.
- [70] Boudou JP, Martinez-Alonzo A, Tascon JMD. Introduction of acid groups at the surface of activated carbon by microwave-induced oxygen plasma at low pressure. *Carbon* 2000; 38: 1021-1029.
- [71] Kodama S, Habaki H, Sekiguchi H, Kawasaki J. Surface Modification of adsorbents by dielectric barrier discharge. *Thin Solid Films* 2002; 407: 151-155.
- [72] Domingo-García M, Lopez-Garzon FJ, Perez-Mendoza M. Effect of some oxidation treatments on the textural characteristics and surface chemical nature of an activated carbon. *J Colloid Interf Sci* 2000; 222: 233-240.
- [73] Wen HC, Yang K, Ou KL, Wu WF, Chou CP, Luo RC, Chang YM. Effects of ammonia plasma treatment on the surface characteristics of carbon fibers. *Surf Coat Technol* 2006; 200: 3166-3169.
- [74] Boudou JP, Paredes JI, Cuesta A, Martínez-Alonso A, Tascón JMD. Oxygen plasma modification of pitch-based isotropic carbon fibres. *Carbon* 2003; 41: 41-56.
- [75] Lee DS, Hong SH, Paek KH, Ju WT. Adsorbability enhancement of activated carbon by dielectric barrier discharge plasma treatment. *Surf Coat Technol* 2005; 200: 2277-2282.
- [76] Pai YH, Ke JH, Huang HF, Lee CM, Zen JM, Shieu FS. CF₄ Plasma treatment for preparing gas diffusion layers in membrane electrode assemblies. *J Power Sources* 2006; 161: 275-281.
- [77] Eisenmenger-Sittner C, Schrank C, Neubauer E, Eiper E, Keckes J. Modification of wetting of copper (cu) on carbon (c) by plasma treatment and molybdenum (mo) interlayers. *Appl Surf Sci* 2006; 252: 5343-5346.
- [78] Paredes JI, Martinez-Alonso A, Tascon JMD. Oxygen plasma modification of submicron vapor grown carbon fibers as studied by scanning tunneling microscopy. *Carbon* 2002; 40: 1101-1108.
- [79] Brüser V, Heintze M, Brandl W, Marginean G, Bubert H. Surface modification of carbon nanofibers in low temperature plasmas. *Diamond Relat Mater* 2004; 13: 1177-1181.
- [80] YC Liu, Lu DN. Surface energy and wettability of plasma-treated polyacrylonitrile fibers. *Plasma Chem Plasma Process* 2006; 26: 119-126.
- [81] Zhu Q, Sun J, He C, Zhang J, Wang Q. Influence of plasma treatment on the electroless deposition of copper on carbon fibers. *J Macromol Sci Part A Pure Appl Chem* 2006; 43: 1853-1865.
- [82] Miller, J.R., Zhang, T.: WO07040603 (2007).
- [83] Huang HC, Ye DQ, Huang BC. Nitrogen plasma modification of viscose-based activated carbon fibers. *Surf Coat Technol* 2007; 201:9533-9540.
- [84] Tashima D, Kurosawatsu K, Sung YM, Otsubo M, Honda C. Surface modification of nanoporous materials for electric double layer capacitors application. *Mater Chem Phys* 2007; 103: 158-161.

- [85] Tendo C, Tixier C, Tristant P, Desmaison J, Leprince P. atmospheric pressure plasmas. A Review Spectrochimica Acta Part B 2006; 61: 2-30.
- [86] Rong HQ, Ryu ZY, Zheng JT, Zhang YL. Effect of air oxidation of rayon-based activated carbon fibers on the adsorption behavior for formaldehyde. Carbon 2002; 40: 2291-2300.
- [87] Budinova T, Savova D, Petrov N, *et al.* Mercury adsorption by different modifications of furfural adsorbent. Ind Eng Chem Res 2003; 42: 2223-2229.
- [88] Zhu JL, Wang YH, Zhang JC, Ma RY. Experimental investigation of adsorption of NO and SO₂ on modified activated carbon sorbent from flue gases. Energy Convers Manage 2005; 46: 2173-2184.
- [89] Mugisidi D, Ranaldo A, Soedarsono JW, Hikam M. Modification of activated carbon using sodium acetate and its regeneration using sodium hydroxide for the adsorption of copper from aqueous solution. Carbon 2007; 45: 1081-1084.
- [90] Li ZJ, Del Cul GD, Yan WF, Liang CD, Dai S. Fluorinated carbon with ordered mesoporous structure. J Am Chem Soc 2004; 126:12782-12783.
- [91] Economy J, Foster K, Jung H. Tailoring carbon fibers for adsorbing volatiles. Chemtech 1992; 597-603.
- [92] Shen WZ, Wang H, Liu YH, Guo QJ, Zhang YL. Oxidization activated carbon fiber through nitrocellulose combustion. colloid surface A. Physicochemi Eng Aspects 2007; 308: 20-24.
- [93] Ucer A, Uyanık A, Cay S, Ozkan Y. Immobilisation of tannic acid onto activated carbon to improve Fe(III) adsorption. Sep Purif Technol 2005; 44: 11-17.
- [94] Lee YW, Park JW, Jun SJ, Choi DK, Yie JE. NO_x adsorption-temperature programmed desorption and surface molecular ions distribution by activated carbon with chemical modification. Carbon 2004; 42: 59-69.
- [95] Nian YR, Teng H. Nitric acid modification of activated carbon electrodes for improvement of electrochemical capacitance. J Electrochem Soc 2002; 149: A1008-A1014.
- [96] Hsieh CT, Teng H. Influence of oxygen treatment on electric double-layer capacitance of activated carbon fabrics. Carbon 2002; 40: 667-674.
- [97] Momma T, Liu XJ, Osaka T, Ushio Y, Sawada Y. Electrochemical modification of active carbon fiber electrode and its application to double-layer capacitor. J Power Sources 1996; 60: 249-253.
- [98] Bleda-Martínez MJ, Morallon E, Cazorla-Amoros D. Polyaniline/porous carbon electrodes by chemical polymerisation: effect of carbon surface chemistry. Electrochimica Acta 2007; 52: 4962-4968.
- [99] Qu DY, Shi H. Studies of activated carbons used in double-layer capacitors. J Power Sources 1998; 74: 99-107.
- [100] Shi H. Activated carbons and double layer capacitance. Electrochim Acta 1996; 41: 1633-1639.
- [101] Tanahashi I, Yoshida A, Nishino A. Electrochemical characterization of activated carbon-fiber cloth polarizable electrodes for electric double-layer capacitors. J Electrochem Soc 1990; 137: 3052-3057.
- [102] Lozano-Castello D, Cazorla-Amoros D, Linares-Solano A, Shiraishi S, Kurihara S, Oya H. Influence of pore structure and surface chemistry on electric double layer capacitance in non-aqueous electrolyte. Carbon 2003; 41: 1765-1775.
- [103] Tanaike O, Hatori HI, Yamada Y, Shiraishi S, Oya A. Preparation and pore control of highly mesoporous carbon from defluorinated PTFE. Carbon 2003; 41: 1759-1764.
- [104] Qiao WM, Korai Y, Mochida I, Hori Y, Maeda T. Preparation of an activated carbon artifact: oxidative modification of coconut shell-based carbon to improve the strength. Carbon 2002; 40: 351-358.
- [105] Oda H, Yamashita A, Minoura S, Okamoto M, Morimoto T. Modification of the oxygen-containing functional group on activated carbon fiber in electrodes of an electric double-layer capacitor. J Power Sources 2006; 158: 1510-1516.
- [106] Fang BZ, Binder L. A novel carbon electrode material for highly improved edlc performance. J Phys Chem B 2006; 110: 7877-7882.
- [107] Fang BZ, Wei YZ, Suzuki K, Kumagai M. Surface modification of carbonaceous materials for edlcs application. Electrochimica Acta 2005; 50: 3616-3621.
- [108] Swiatkowski A, Pakula M, Biniak S, Walczyk M. Influence of the surface chemistry of modified activated carbon on its electrochemical behavior in the presence of Lead (II) Ions. Carbon 2004; 42: 3057-3069.
- [109] Boehm HP. Surface oxides on carbon and their analysis: a critical assessment. Carbon 2002; 40: 145-149.
- [110] Joong SN, James CAS. Effect of hmo₃ treatment on the surface acidity of activated carbons. Carbon 1990; 28: 675-682.
- [111] Papierer E, Dentzer J, Li S, Donnet JB. Surface Groups on nitric acid oxidized carbon black samples determined by chemical and thermodesorption analyses. Carbon 1991; 29:69-72.
- [112] Boehm HP. Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon 1994; 32: 759-769.
- [113] Tamon H, Okazaki M. Influence of acidic surface oxides of activated carbon on gas adsorption characteristics. Carbon 1996; 34: 741-746.
- [114] Papier E, Li S, Donnet J. Contribution to the study of basic surface groups on carbons. Carbon 1987; 25: 243-247.
- [115] Boehm HP. Surface oxides on carbon. High Temp-High Pressures 1990; 22: 275-288.
- [116] Otake Y, Jenkins RG. Characterization of oxygen-containing surface complexes created on a microporous carbon by air and nitric acid treatment. Carbon 1993; 31: 109-121.
- [117] Zhuang QL, Kyotani T, Tomita A. The change of TPD pattern of O₂-gasified carbon upon air exposure. Carbon 1994; 32: 539-540.
- [118] Zielke U, Hüttinger KJ, Hoffman WP. Surface-oxidized carbon fibers: i. surface structure and chemistry. Carbon 1996; 34: 983-998.
- [119] Zhuang QL, Kyotany T, Tomita A. DRIFT and TK/TPD analyses of surface oxygen complexes formed during carbon gasification. Energ Fuel 1994; 8: 714-718.
- [120] Zhuang QL, Kyotany T, Tomita A. Granada, Spain, Ext Abstracts Carbon'1994; 94:466.
- [121] Marchon B, Carrazza J, Heinemann H, Somorjai GA. TPD and XPS studies of O₂, CO₂, and H₂O adsorption on clean polycrystalline graphite. Carbon 1988; 26: 507-514.
- [122] Boudou JP, Parent Ph, Suarez-Garcia F, Villar-Rodil S, Martinez-Alonso A, Tascon JMD. Nitrogen in aramid-based activated carbon fibers by TPD, XPS and XANES. Carbon 2006; 44: 2452-2462.
- [123] Driel J. In Capelle A, Vooys F De. Activated carbon-a fascinating material, the Netherlands. Norit, Amersfoort 1983; 40-57.
- [124] Andrew P, Sherwood MAP. X-ray photoelectron spectroscopic studies of carbon fibre surfaces-II: The effect of electrochemical treatment. Carbon 1983; 21: 53-59.
- [125] Sherwood MAP. Surface analysis of carbon and carbon fibers for composites. J Electron Spectrosc Relat Phenom 1996; 81: 319-342.
- [126] Bascom WD. NASA Contractor Report 178306, Contract NAS1-17918, August 1987.
- [127] Vickers PE, Watts JF, Christian P, Mohamed MC. The surface chemistry and acid-base properties of a pan-based carbon fiber. Carbon 2000; 38: 675-689.
- [128] Estrade-Szwarckopf H. XPS photoemission in carbonaceous materials: A "Defect" Peak beside the graphitic asymmetric peak. Carbon 2004; 42: 1713-1721.
- [129] Zawadzki J. Infrared spectroscopy in surface chemistry of carbons. in chemistry and physics of carbon; Thrower PA. Ed.; Marcel Dekker: New York, 1988; 21: 147-386.
- [130] Fanning PE, Vannice MA. A DRIFTS study of the formation of surface groups on carbon by oxidation. Carbon 1993; 31:721-730.
- [131] Tomaszewski W, Gunko VM, Skubiszewska-Zieba J, Leboda R. structural characteristics of modified activated carbons and adsorption of explosives. J Colloid Interf Sci 2003; 266: 388-402.
- [132] El-Hendawy ANA. Influence of HNO₃ oxidation on the structure and adsorptive properties of comcob-based activated carbon. Carbon 41; 2003: 713-722.
- [133] Przepiorski J, Skrodziewicz M, Morawski AW. High temperature ammonia treatment of activated carbon for enhancement of CO₂ adsorption. Appl Surf Sci 2004; 225: 235-242.
- [134] Terzyk AP. The influence of activated carbon surface chemical composition on the adsorption of Acetaminophen (Paracetamol) *in vitro*: Part II. TG, FTIR, and XPS analysis of carbons and the temperature dependence of adsorption kinetics at the neutral ph. Colloid Surface A 2001; 177: 23-45.
- [135] Sakintuna B, Yurum Y. Preparation and characterization of mesoporous carbons using, a turkish natural zeolitic template/furfuryl alcohol system. Micropor Mesopor Mater 2006; 93: 304-312.
- [136] Meyers CJ, Shah SD, Patel SC, *et al.* Templated synthesis of carbon materials from zeolites (γ , beta, and ZSM-5) and a

- montmorillonite clay (K10): physical and electrochemical characterization. *J Phys Chem B* 2001; 105: 2143-2152.
- [137] Bac CG, Bernier P, Latil S, *et al.* ^{13}C NMR Investigation of carbon nanotubes and derivatives. *Curr Appl Phys* 2001; 1: 149-155.
- [138] Ma Z, Kyotani T, Liu Z, Terasaki O, Tomita A. Very high surface area microporous carbon with a three-dimensional nano-array structure: synthesis and its molecular structure. *Chem Mater* 2001; 13: 4413-4415.
- [139] Darmstadt H, Roy C, Kaliaguine S, Xu G, Auger M, Tuel A. Solid state ^{13}C -NMR spectroscopy and XRD studies of commercial and pyrolytic carbon blacks. *Carbon* 2000; 38: 1279-1287.
- [140] Golzan MM, Lukins PB, Mackenzie DR, Vassalo AM, Hanna JV. NMR evidence for strained carbon bonding in tetrahedral amorphous carbon. *Chem Phys* 1995; 193: 167-172.
- [141] Muller H, Rehak P, Jager C, Hartmann J, Meyer N, Spange S. A concept for the fabrication of penetrating carbon/silica hybrid materials. *Adv Mater* 2000; 12: 1671-1675.
- [142] Zarbin AJG, Bertholdo R, Oliveira MAFC. Preparation, characterization and pyrolysis of poly (Furfuryl Alcohol)/Porous silica glass nanocomposites: novel route to carbon template. *Carbon* 2002; 40: 2413-2422.