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Charaterization of Pore Structure and Surface Chemistry of Activated Carbons – A Review

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1. Introduction

There is a rapid development in industries since industrial revolution began in the latter half of the 18th century, which not only significantly promotes development of economy all over the world and prosperity in societies, but also extremely improves our lives. However, a large amount of wastewaters including some toxic and hazardous materials such as some metals ions and some non-biodegraded organic compounds are usually produced in many factories during production process. These pollutants such as simple/complex aromatic compounds in wastewaters discharged from factories such as textiles, rubber, paper, plastic, explosive, pharmaceuticals, petroleum refining and cosmetics factories into ditches/rivers are stable to light and oxidation as resistant to aerobic digestion, causing damage to the aquatic life and food web (Kagalkar, et al., 2010, Saratale, et al., 2011, Tabrez&Ahmad, 2009). The basic properties of simple aromatic compounds are shown in Table 1. The compounds can also cause allergic dermatitis and skin irritation. Furthermore, Most of them have been reported to be carcinogenic and mutagenic for aquatic organisms (Lorenc-Grabowska&Gryglewicz, 2007), so discharging of the pollutants is becoming the most challenging threat to environment safety and even human beings’ lives. The introduction of toxic and/or non-biodegradable compounds in the natural environment has been a world wide serious problem that has been paid more attention to by many environmentalist and research institutions from different countries.




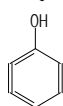
Simple aromatic compounds	Boiling point (°C)	pKa at 25°C	Aqueous solubility at 25°C(g/L)
	80.4	–	1.79
	115.3	5.17	∞
	184.4	4.60	34
	182	9.89	93

Table 1. Basic properties of some simple aromatic compounds (Gokel&Dean, 2004)

To decrease or even eliminate the concentration of the compounds in wastewaters before discharging into environment, the various treatment methods are used for the removal of the pollutants mentioned above from wastewaters, which usually consist of cloud point extraction (Silva, et al., 2009), coagulation using alum (Ghafari, et al., 2009), lime (Foley, et al., 2010), ferric sulphate (Matilainen, et al., 2010) and ferric chloride (Liang, Z., et al., 2009), chemical oxidation (Lee&Von Gunten, 2010) using Fenton reagents (ferrous ion and H_2O_2) (Padoley, et al., 2011), ozone (O_3) (Bundschuh, et al., 2011), chlorine and air (Wang, X., et al., 2011), membrane separation process including nanofiltration (Zahrim, et al., 2011), adsorption (Dos Santos, et al., 2011, Lu, et al., 2011) and so on. Among these, adsorption appears to be one of the best potential and effective methods for removal of pollutants from wastewaters.

The adsorbents can be classified into two types of adsorption materials (natural materials and synthetic ones). Natural adsorbents, usually non-conventional low cost adsorbents used for removal of compounds, include peat/sphagnum moss peat (Naumova, et al., 2011), red mud (Oruh, et al., 2011), coir pith (Parab, et al., 2010), leaves (Chakravarty, et al., 2010), activated sludge (Bassin, et al., 2011, Zhang, C., et al., 2011a), waste organic peel (Feng, et al., 2011), tree fern (Liu, X. L., et al., 2011b), lignite (Al-Asheh, et al., 2003), sawdust (Mane&Babu, 2011), banana pith (Namasivayam, et al., 1998), peanut hull (Tanyildizi, 2011), modified chitosan beads (Liu, B., et al., 2011a), natural biopolymers (Vinod&Sashidhar, 2011), biosorption materials (Montazer-Rahmati, et al., 2011), and minerals such as activated ash/clay (Andersson, et al., 2011) and natural sepiolite (Sevim, et al., 2011). However, the adsorption capacity of the above adsorbents is relatively low.

Usually, there are many types of synthetic or artificial adsorbents (conventional adsorbents) such as activated carbon (AC) (Li, et al., 2010b), resin (Vinodh, et al., 2011), zeolite (Seifi, et al., 2011), and so on used in adsorption operation, but AC is the most widely used adsorbents for removal of inorganic and organic compounds from wastewaters or waste gases because they have excellent capacities for adsorption of compounds derived from their huge surface area, developed pore texture, as well as easy availability (Khan, et al., 1997a, Khan, et al., 1997b, Okolo, et al., 2000, Viraraghavan&De Maria Alfaro, 1998).

According to its various appearance, AC is divided into cylindrical activated carbon (CAC) (Wang, J. C., et al., 2008), granular activated carbon (GAC) (Huang, L., et al., 2011, Saoudi&Hamdaoui, 2011), powder activated carbon (PAC) (Li, et al., 2009a, Li, et al., 2009b, Li, et al., 2010b) and activated carbon fiber (ACF) (Li, et al., 2010a). In terms of extent of its pore development, AC is classified as microporous activated carbon/activated carbon fiber (Li, et al., 2009a, Li, et al., 2010a) and mesoporous activated carbon (Zhang, Y., et al., 2011b). In accordance with range of its use, AC is divided into gas activated carbon and water activated carbon, which are used in treatment of feed/waste gases and waters/wastewaters, respectively.

Usually, AC is prepared from different raw materials such as coal, wood, and so on. It is well known that a type of AC is coal-derived AC. Another one is prepared from woods such as pine wood (Hadi, et al., 2011) and fir wood (Eletsii, et al., 2011), etc. Certainly, AC can be also prepared from various carbon-contained materials (principally plant wastes (Hameed&Daud, 2008, Kula, et al., 2008) in past decades.

It should be noted that high initial cost and costly maintenance of AC including high regeneration temperature and tremendous carbon consumption have greatly restricted its

extensive use in industries. To greatly decrease the cost of AC, the various ACs prepared from non-conventional sources such as coir pith (Agrawal, et al., 2011), sawdust and rice husk (Chen, Y., et al., 2011), pinewood (Tseng, et al., 2003) applied in removal of some compounds have also been investigated and better results have been attained.

The reason why adsorption capacity of adsorbents is high or low is mainly due to pore development and surface groups of AC, which is closely associated with its preparation methods. Here, preparation process of AC should be discussed because it has an important effect on pore structures and surface groups of AC. Preparation of AC includes a primary process and a secondary one which are denoted as carbonization and activation, respectively. Carbonization is followed by activation in sequence. In carbonization process, a large amount of gases, mainly small low molecular weight hydrocarbons-containing molecules or fragments possibly with oxygen (O), nitrogen (N) and sulfur (S), are released from materials surface and adhesion agents from 380 °C to 550 °C in an inert atmosphere due to decomposition of some groups which are readily destroyed. The carbonized materials have primary development of pore structure. In contrary to inert atmosphere used in carbonization process, some activating agents are frequently used in activation process (the secondary process). Gas activating agents consist of vapour, carbon dioxide and air used to further/promote development of pore properties at 600 °C to 980 °C. It is noting that chemical activating agents including phosphorus acid (H_3PO_4), phosphorus pentoxide (P_2O_5) (Izquierdo, et al., 2011), zinc chloride (ZnCl_2) (Cronje, et al., 2011), calcium chloride (CaCl_2) (Hu&Srinivasan, 2001), sodium hydroxide (NaOH) (Vargas, et al., 2011), potassium hydroxide (KOH) (Król, et al., 2011) and potassium sulfide (K_2S) (Huang, Z., 2006) seem to widely applied in preparation of wood-derived ACs which has only the carbonization process. The resulting AC after being cooled down to room temperature must be washed several times in order to eliminate residues of activating agents. After carbonization and activation, ACs have huge surface area, deep developed pore structures and plenty of different types of surface groups are produced. In recent years, combination of a chemical method and a physical one has been also introduced into the activation process and can yield high surface area and developed pore structures (Huang, Z., 2006).

It is well known that principal component of AC is carbon element and surface of AC itself is non-polar, and hence it is concluded that as a whole, AC has hydrophobic surface. Various activation conditions and more or less amount of oxygen AC contacts when it is stored/exposed in air will to some extent implant some/many oxygenated groups on AC surface. The surface groups will alter surface state of AC and subsequently has an influence on its surface chemical properties. This results in the difference in surface chemistry of ACs. When a significant effect of surface chemistry on adsorption and catalysis process is investigated, AC is frequently modified through different treatment methods in order to strengthen or attenuate the surface chemical properties, e.g. surface functional groups. Usually, the properties of the functional groups such as oxygen-containing groups and nitrogen-containing groups of AC surface can be modified by physical, chemical, and electrochemical treatment methods. These methods consist of gas phase oxidation via O_2 or N_2O at different temperatures, various contact times and partial/total pressures, liquid phase oxidation treatments through HNO_3 or H_2O_2 -containing aqueous solutions at various temperatures, concentrations, and reaction times and heat treatment at various high temperatures and in different gaseous environments (N_2 and H_2 and some high pure inert gases such as Ar and He) in order to selectively eliminate some of the functional groups.

Functional groups of AC surface may be acidic groups and basic ones because the surface chemistry of modified AC is closely associated to the types of heteroatoms (oxygen, hydrogen, nitrogen, et al) other than carbon atom within the carbon matrix (Wibowo, et al., 2007). Some common heteroatoms mainly including oxygen (O), nitrogen (N), phosphorus (P), hydrogen (H), chlorine (Cl) and sulfur (S) introduced in the modification process are bound to the edges of graphite-like layers, forming organic functional groups such as carboxyl groups, lactonic groups, phenolic groups, carbonyl groups, aldehydes, ethers, amino groups and other N-containing groups and phosphates (Salame&Badosz, 2001). The surface functional groups of ACs determine their moisture content, catalytic properties, acid/base character, and adsorption capacity (Salame&Badosz, 2001). Therefore, it is important that the above groups are characterized. However, the surface chemistry characterization of ACs is a complex/difficult task. At present, the characterization methods are better established. In characterization of ACs, it is possible not only to identify the surface chemical groups but also to quantify them.

The objective of this work was to investigate the pore structure and surface chemistry of activated carbons (ACs) due to its effect on adsorption and catalytic property. The present review compiles the work done over the last few decades on types, formation and characterization of surface functionalities of ACs. Special attention is paid to characterization of pore structure and surface groups on ACs by various technologies including N₂ adsorption, scanning electron micrograph, elemental analysis, Boehm Titration, potentiometric titration, Fourier transform infra red/diffuse Fourier infrared transform spectroscopy, X-ray photoelectron spectroscopy, temperature programmed desorption, thermal gravimetric analysis/differential scanning calorimetry, which are illustrated by some examples. Moreover, the most important aspects referring to comparison of different characterization methods are also overviewed in this paper. The present work carried out indicates that various methods have their advantages and disadvantages in investigating the surface groups of ACs and the methods mentioned above must be used to complement each other. As so far, relatively little work has been published and there is considerable scope for more detailed studies on the characterization of surface groups of ACs.

2. Characterization

Adsorption capacity of ACs is dependent on surface area, pore structure and surface groups, polarity, solubility and molecule size of adsorbates; solution pH and the presence of other ions in solution and so on (Radovic, et al., 2001). To investigate and obtain information pertaining to its physical structures and chemistry properties, AC needs to be characterized by various analysis apparatus.

2.1 Physical structure characterization

2.1.1 N₂ adsorption

Surface area and pore structure can be determined by N₂ adsorption (Li, et al., 2010b), mercury porosimetry (García, et al., 2011), capillary condensation (CC) (Liu, Y., et al., 2011c), X-ray Diffraction (XRD) (Tongpoothorn, et al., 2011) and scanning/transmission electron microscope (SEM) (Chingombe, et al., 2005), small angle X-ray scattering (SAXS) (Bradley, et al., 2011).

Here, physical structures of AC analyzed only by liquid Nitrogen adsorption will be introduced in this paper because Nitrogen adsorption are frequently used in investigating the texture of AC. Brunauer-Emmitt-Teller surface area (S_{BET}), Langmuir surface area ($S_{langmuir}$), pore volume and pore distribution of the adsorbents were determined through liquid Nitrogen adsorption at 77 K on a Micromertics ASAP 2020 surface area analyzer (USA). Micropore and mesopore volumes and surface areas of the adsorbents were calculated using Density Functional Theory (DFT). The pore size distribution of adsorbents was determined from adsorption isotherm data using DFT.

Adsorbent	V_{mic} (cm^3/g)	S_{mic} (m^2/g)	V_{mes} (cm^3/g)	S_{mes} (m^2/g)	\bar{r} (nm)	S_{BET} (m^2/g)	$S_{langmuir}$ (m^2/g)
AC	0.305	689	0.069	51	1.103	977	1231±8
ACO1	0.304	777	0.071	50	0.996	903	1135±8
ACO2	0.302	779	0.063	45	0.968	890	1121±8
ACD	0.306	805	0.028	21	0.847	847	1066±5

Note: \bar{r} is median pore radius

Table 2. Textural characterization of the adsorbents (Li, et al., 2009a)

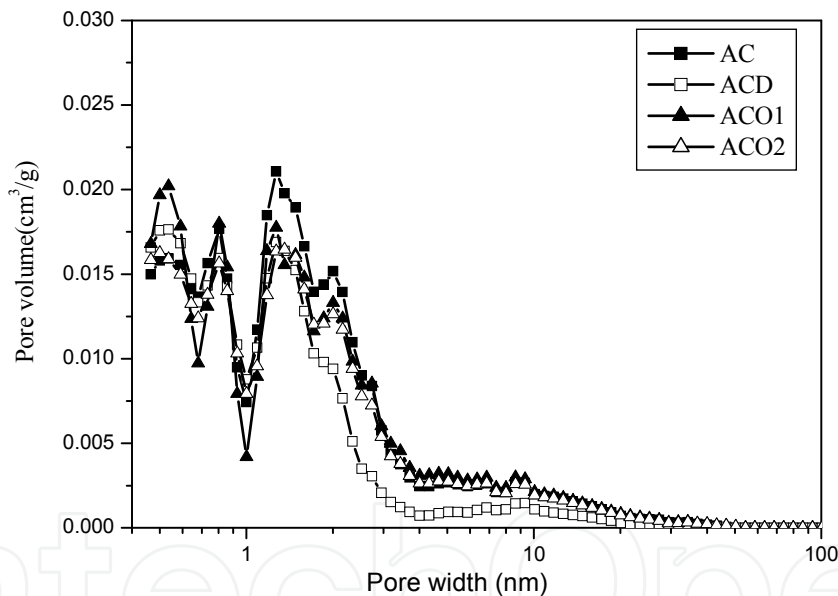


Fig. 1. Pore size distribution of adsorbents (Li, et al., 2009a)

Table 2 suggests that the difference in micro-pore properties, most relevant to adsorption of organic compounds, are small, with similar micro-pore volumes but different micro-pore surface areas, indicating the major difference between them is pore distribution within the micro-pore range as indicated by the mean pore diameter (Table 1). Among the four adsorbents, ACD contains more smaller micropores than the other adsorbents while AC contains less smaller pores in comparison to ACO1 and ACO2. This trend seems correlating well with the ash contents of the adsorbents (Table 4) and suggests that the acid leaching processes remove fine mineral matters from the adsorbents and result in formation of micro-pores, as depicted as Fig. 1. The meso-pore properties (V_{meso} and S_{meso}) of AC, ACO1 and ACO2 are very similar, but that of ACD are significantly smaller than others. These

parameters again correlate well with ash content of the adsorbents, suggesting that there is removal of minerals from the mesopores, which converts them into macro-pores.

2.1.2 Scanning electron micrograph (SEM)

Preparation (Chingombe, et al., 2005)

The surface morphology of the carbons was analyzed using a Cambridge Instrument 360 scanning electron microscope at accelerating voltages of 10–20 kV. Prior to analysis, samples were dried at 373 K and stored in a desiccator overnight. The samples were then put on an aluminum platform for analysis.

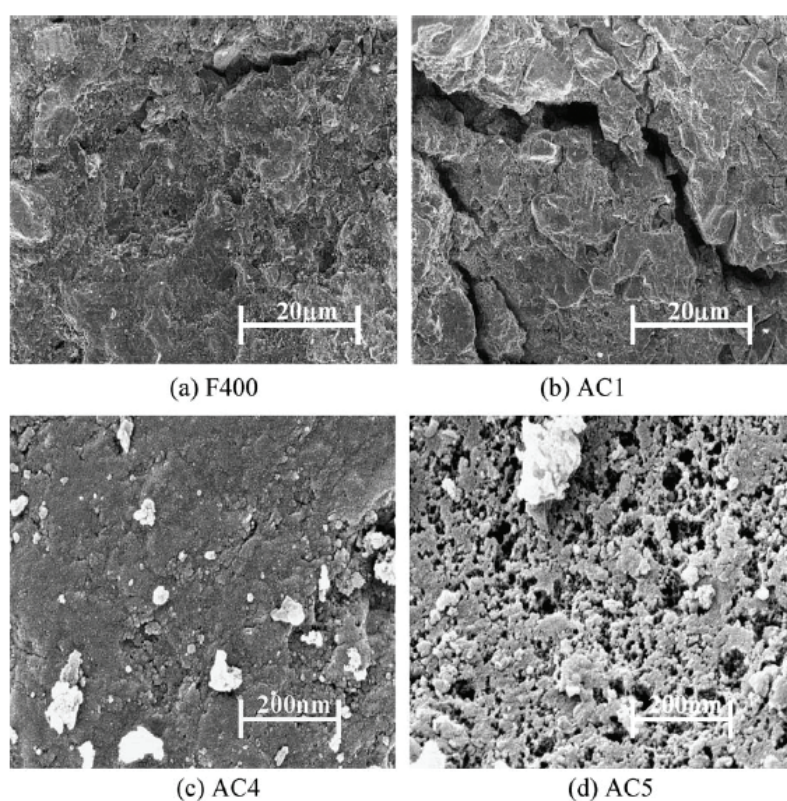


Fig. 2. SEM images of carbon samples before and after modification. (Chingombe, et al., 2005)

Chingombe, et al described the SEM of the samples in Fig. 2 (Chingombe, et al., 2005). There is little difference in the surface morphology of the samples except for some apparent pore widening on AC1 that could have occurred from the oxidation process. It was noticed that the oxidized samples disintegrated to small particles when compared to F400 sample particles. This observation could be linked to the cleavage of C–O bridging bonds on the carbon surface during the oxidation process. The SEM images of AC2 and AC3 were similar in appearance to AC1 image. This implies that post-oxidation treatments of the carbon samples did not make any apparent change in the surface morphology of the adsorbents. The surface morphology for AC4 was compared to that of AC5 and it is readily found that modification of AC4 to produce AC5 had a visual impact on surface morphology. The surface looks spongy and to some extent eroded.

2.2 Surface chemistry characterization

Prior to 1960s, researchers did not know how to characterize surface chemistry of AC. Fortunately, Boehm in 1966 began to make attempt to determinate surface chemistry of AC with acid/base titration theory/method, which makes researchers further analyze/ understand surface chemistry of AC. Thereafter, with the development of science and technologies, more and more characterization methods including elemental analysis, potentiometric titration, Fourier transform infrared/diffuse Fourier infrared transform spectroscopy, X-ray photoelectron spectroscopy, temperature programmed desorption, thermal gravimetric analysis/differential scanning calorimetry, X-ray diffraction (XRD), and so on have been proposed and utilized by researchers all over the world.

2.2.1 Element analyses

Sometimes, contents of elements contained in raw material of AC, e.g. characteristics of raw tobacco residue are provided in the literature (Kilic, et al., 2011). The characteristics of raw tobacco residue were shown in Table 3. From Table 3, it is obviously seen that content of carbon is high and content ash is low, indicating that tobacco residue is suitable for AC production.

Type	Value
Proximate analysis (%)	
Moisture	8.13
Ash	11.73
Volatiles	67.55
Fixed C	12.59
Ultimate analysis (%) (dry-ash basis)	
C	40.95
H	5.21
N	5.99
O*	47.85
H/C	1.52
O/C	0.88
HHV (MJ/kg)	15.07
Structural analysis (%)	
Lignin	8.75
Cellulose	42.30
Oil	3.30

Table 3. Characteristics of raw tobacco residue (Kilic, et al., 2011)

Li, et al determined ash amount and ultimate analyses of the adsorbents in the literature (Li, et al., 2009a). Carbon (C), hydrogen (H), and nitrogen (N) contents of the adsorbents were determined by an element analyzer (Analysensysteme Gmbh Elementar Vario EL), sulfur (S) content was measured by a sulfur analyzer (SC-132, LECO, USA), and oxygen (O) content was calculated by difference. Analytic results were shown in Table 4.

Adsorbent	Ash (wt.%)	C (wt.%)	H (wt.%)	S (wt.%)	N (wt.%)	O (wt.%)
AC	8.32	88.47	0.50	0.46	0.43	1.82
ACO1	7.11	86.89	2.11	0.38	0.83	2.67
ACO2	7.04	86.36	2.04	0.36	0.77	3.49
ACD	0.53	93.40	1.76	0.42	0.58	1.95

Table 4. Ash amount and ultimate analyses of the adsorbents

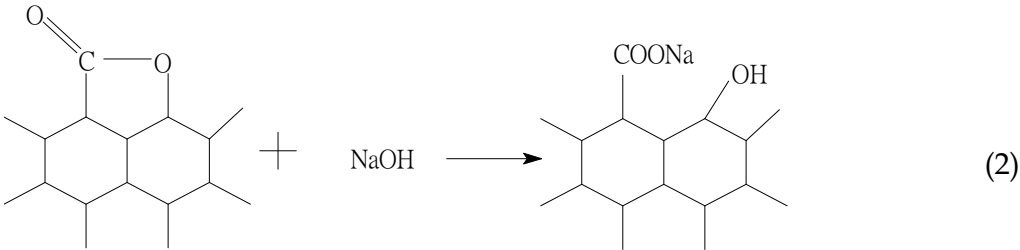
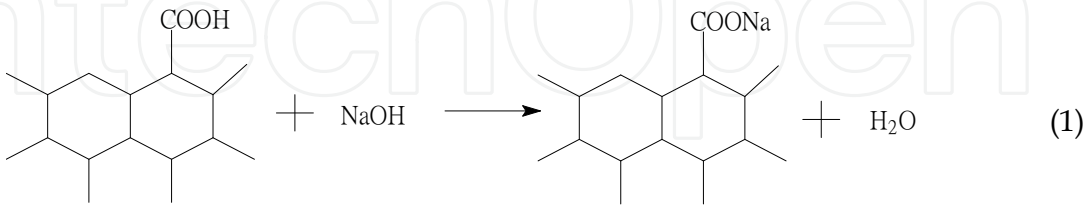
Table 4 shows the composition analysis of the four adsorbents. Among the four adsorbents, AC has the highest ash content at 8.32 wt%. The nitric acid treatment removed some of the ash and yielded adsorbents with medium ash contents, 7.11 wt.% for ACO1 and 7.04 wt.% for ACO2. The HCl/HF treatment removed most of the ash and yielded an adsorbent with the lowest ash content (ACD, 0.53 wt.%). Compared to that of the AC, the higher H, N and O contents for adsorbents ACO1 and ACO2 indicate that the main role of the nitric acid treatment is chemistry modification, with formation of many H, N and O containing groups on the surface; the slightly lower S contents for the acid treated adsorbents indicate that most of the sulfur in the adsorbents is organic.

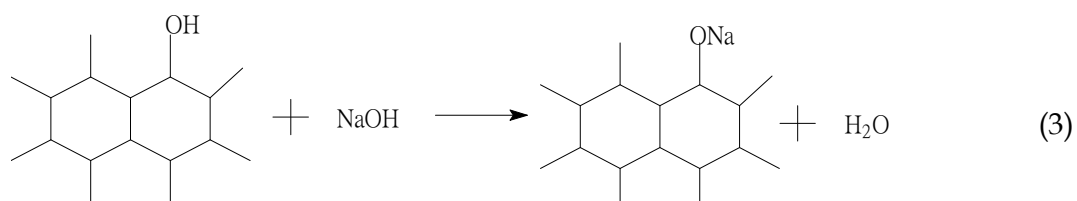
2.2.2 Boehm titration (Ayranci&Duman, 2006, Boehm, 1966, Nevskaia, et al., 2004)

Boehm Titration proposed by Boehm in 1966 is one of many methods to characterize surface chemistry of AC. As so far, the titration based on acid/base titration theory is widely used because it can effectively determine oxygen-containing functional groups of AC surface and obtain information of groups. Boehm titration is based on the theory that acid and base in aqueous solution react with various basic sites and acidic sites of AC which are derived from different oxygenated groups, respectively.

Titration principle (Boehm, 1966)

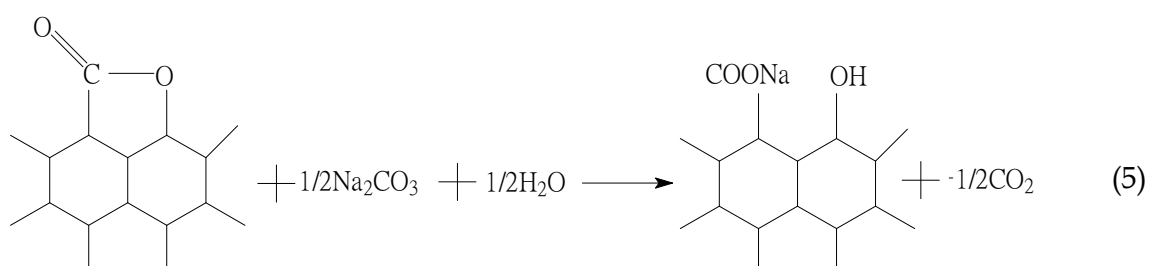
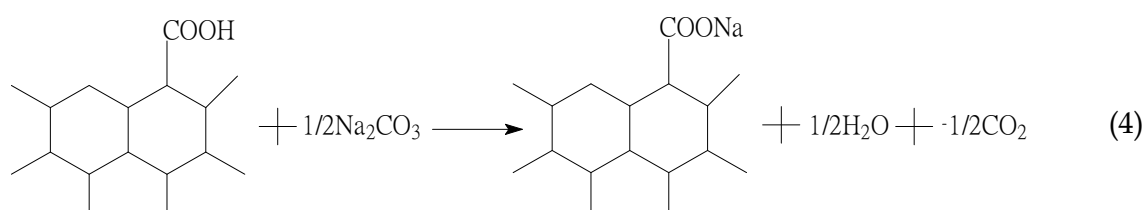
Sodium hydroxide can centralize carboxylic groups, lactonic groups and phenolic groups of AC surface. The reaction processes of sodium hydroxide with carboxyl groups, lactonic groups, phenolic groups are shown in Equations 1-3, respectively.



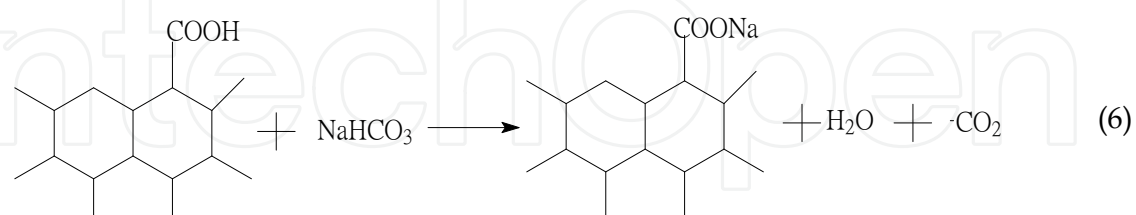


Hydrogen ion of carboxylic groups and phenolic groups is replaced by sodium cation of sodium hydroxide, forming sodium carboxylates and sodium phenolates when sodium hydroxide reacts with carboxylic groups, and phenolic groups of AC surface. In reaction of sodium hydroxide with lactonic groups, sodium carboxylates and phenolic groups are formed.

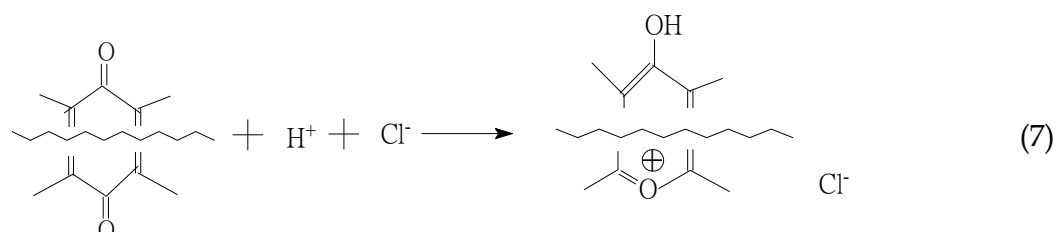
Owing to basic property of sodium carbonate poorer than that of sodium hydroxide, sodium carbonate centralizes only carboxyl groups and lactonic groups, of which reaction processes are shown in Equations 4-5.



Sodium bicarbonate reacts only with carboxyl groups of AC surface, yielding sodium carboxylates due to its poorest basic property among the three bases mentioned above. The Equation 6 describes the above reaction.



Hydrochloric acid can centralize surface base of AC, which is shown in Equation 7.



Preparation and test (Li, et al., 2010a)

Li, et al determined and analyzed the surface functional groups of activated carbon (AC) and activated carbon fiber (ACF). AC and ACF, used as the control adsorbents in the experiments, were commercial coal-based granular activated carbon from Xinhua Chemical Plant (Taiyuan, China) and novel cellulose activated carbon fiber from Shanxi Institute of Coal Chemistry (Taiyuan, China), respectively. AC was crushed into particles of 40–60 mesh size (0.3–0.45 mm) and the ACF was cut into pieces (40 mm × 40 mm); The carbon materials mentioned above were finally dried at 110 °C for 48 h.

To obtain adsorbents with similar textural properties and different surface chemistry, the chemical treatment of ACF by HNO₃ oxidation was carried out in a 500 mL Teflon bottle containing 16 g ACF and 200 mL 5 M nitric acid solution at 70 °C for 6 h. Once the oxidation was complete, the oxidized ACF was repeatedly filtered and washed with distilled water several times to remove the impurities. The oxidized and washed ACF was dried at 110 °C for 48 h. The resulting ACF was designated as ACFN.

An exact amount of adsorbent (0.200 g) was placed in a series of 100 mL well-sealed Teflon bottles containing 25 mL of 0.1 M NaOH, Na₂CO₃, NaHCO₃, and HCl solutions, respectively. After shaking at 150 rpm and 30 °C for 24 h in a thermostatic automatic shaker (HZQ-C, Haerbin, China), the adsorbent was separated from the solutions by filtration, and the filtrates were then titrated with a 0.1 M HCl or NaOH. The number of acidic groups was calculated based on the following assumptions: NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na₂CO₃ neutralizes carboxylic and lactonic groups; and NaHCO₃ neutralizes only carboxylic groups. The number of basic sites was determined from the amount of HCl that reacted with the adsorbents.

Adsorbent	Surface Acidity (mmol/g)	Carboxylic (mmol/g)	Lactonic (mmol/g)	Phenolic (mmol/g)	Surface Basicity (mmol/g)
AC	0.489	0.033	0.327	0.129	0.646
ACF	1.279	0.068	0.911	0.300	1.605
ACFN	3.724	1.409	1.224	1.091	1.383

Note: Surface Acidity and Surface Basicity are the Adsorbent’s surface acidic groups and surface basic groups, respectively.

Table 5. Surface chemistry of the adsorbents determined by Boehm titration (Li, et al., 2010a)

Table 5 showed the acid/base properties of the adsorbents characterized by Boehm titration. From table 5, it is easily seen that the surface property of AC and ACF is totally basic, but that ACFN is acidic. The total surface acidic groups, carboxyl groups, lactonic groups, phenolic groups and basic groups in ACF are much higher than the corresponding parameters in AC, indicating the difference in surface chemistry between AC and ACF resulting from the different preparation of the carbon materials. In addition, contents of total surface acidic groups, carboxyl groups, lactonic groups, phenolic groups but basic groups in ACFN are much higher than those in ACF. It indicates that the HNO₃ oxidation clearly increased the surface acidic groups (carboxylic, lactonic, and phenolic groups) and decreased the basic groups of ACF. It should be noted that other surface functional groups

including anhydrides, pyrones, benzoquinones and benzofurans and nitrogen-containing groups of adsorbents can not be determined by Boehm titration.

It comes to conclusion that the incomprehensive information, instead of total surface information, of oxygen-containing groups of AC can be discovered by results analyses of Boehm titration due to ability of the titration to qualitatively and quantitatively detecting only some surface acidic groups (carboxylic, lactonic, and phenolic groups) and the basic groups.

2.2.3 Potentiometric titration (Zpc Titration) (Dabrowski, et al., 2005, Martin, et al., 2003, Ramrakhiani, et al., 2011)

Potentiometric titration was proposed by Y.Matsura when the effect of surface charge of AC on its adsorption/catalysis abilities began to be concerned about by researchers. At the beginning of potentiometric titration proposed, acidic functional groups of carbon black were only approximately classified into strong acid type ($pK < 7$) and weak acid one ($7 < pK < 11$) due to the researcher's poor understanding of acidic functional groups. Potentiometric titration to some extent has been developed since Y.Matsura, et al. proposed a novel analysis technology, potentiometric titration, to estimate the surface acidity of carbon black with in 1970s, but the potentiometric titration method has been greatly developed since constant distribution of AC surface was investigated by Teresa J., et al, in 1990s. At present, potentiometric titration has been a convenient analysis method of surface chemistry of AC through determining surface charge (Chen, J. P., et al., 2003, Noh&Schwarz, 1990).

Owing to the amphoteric character of the carbon surface derived from the acidic and/or basic functional groups, the surface properties may be influenced by the pH value of the coexisting liquid bulk phase. The effects of surface functionalities on adsorption of organic electrolytes including weak electrolytes such as phenols are usually significantly more complex than porosity effects, and so is their assessment. The attention to the surface charge of the carbon as well as the extent of ionization of the solute should be paid.

It is commonly assumed, that for $pH < pK_a$ adsorption of non-ionized organics does not depend on the surface charge of AC. However, for $pH > pK_a$ the phenolic compound is dissociated, and adsorption of its ionic form depends on the surface charge.

Principle

Potentiometric titration designed to determinate surface chemistry is based on the principle that surface charge of AC is a function of pH value of aqueous solutions. Potentiometric titration measurements are carried out by an automatic titrator.

Determination of potentiometric titration (Dabrowski, et al., 2005)

The pH mode of the titrator was set, then 0.1000 g of AC and 50ml of solution containing 0.1 M $NaNO_3$ were placed in the reaction flask, and finally the mixture including AC and electrolyte was balanced in 298K for 24h. To eliminate the effect of CO_2 in the air, the volume above liquid was protected with N_2 . In measurements with 0.1M NaOH or HCl standard solution, solution was titrated to $pH = 3 \sim 10$. The pH of the solution adjusted to the corresponding potential of the solution is Zpc potential

It should be noted that C1, C2 and C3 represents ACs with different surface chemistry.

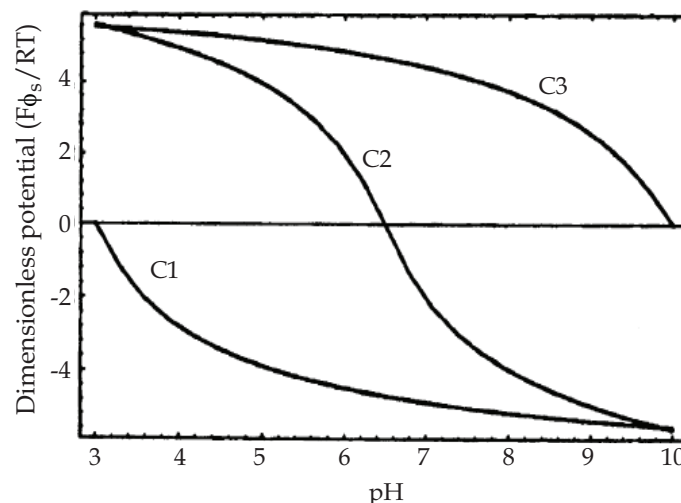


Fig. 3. the relation of surface potential with pH (hypothetical) ACs: C1, acidic carbon ($\text{pH}_{\text{zpc}}=8.0$); C2, amphoteric carbon ($\text{pH}_{\text{zpc}}=6.5$); C3, basic carbon ($\text{pH}_{\text{zpc}}=10.0$) (Radovic, et al., 2001)

Fig. 3 showed the dependence of surface potential on pH for hypothetical ACs supposed by Radovic. The pH value, at which the surface charge is zero, is called the point of zero charge (PZC). For typical amphoteric carbons, the surface is positively charged at $\text{pH} < \text{pH}_{\text{PZC}}$ and negatively charged at $\text{pH} > \text{pH}_{\text{PZC}}$. The so-called isoelectric point, IEP, is denoted as the pH value of zero potential. In practice, pH_{IEP} is usually close to pH_{PZC} , but it is lower than pH_{PZC} of ACs. Potential of C1 is less than zero, indicating the surface of C1 is acidic; Potential of C3 is more than zero, indicating the surface of C3 is basic. It is commonly assumed that for $\text{pH} < \text{pKa}$ adsorption of non-ionized organics does not depend on the surface charge of AC. However, for $\text{pH} > \text{pKa}$ the phenolic compounds is dissociated, and adsorption of its ionic form depends on the surface charge. In accordance with pKa, it is obtained that C1 surface has carboxylic groups and C3 has carbonyls and benzoquinones (Dabrowski, et al., 2005).

From Fig. 3, various acidic or basic groups can not be differentiated by potentiometric titration and specific amount of groups such as carboxylic group, anhydrides, and so on, can not be given by potentiometric titration.

2.2.4 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Azargohar&Dalai, 2011, Chingombe, et al., 2005, Li, et al., 2010a)

The method pertaining to Fourier infrared transform spectroscopy sprang up at the beginning of 20th century and was extremely developed due to the rapid development of technologies on computer and Fourier transform. It, combining Michelson interferometer with computer technology, has many advantages such as short time of measurement, high sensibility and resolution, broad range of measurement spectrum. In 1970s, Kortuum and Griffiths narrated the fundamental of principle of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). DRIFTS is applied in determining the samples with scattering property and strong adsorption capacity, especially AC. Owing to its ability of decreasing or even eliminating the effect of scattering factor derived from performing

process on detecting chemistry, loose powder of some samples is also effectively analyzed. In addition, organic functional groups of AC surface not being detected by common FTIR due to special property of AC, which belongs to a type of blank body, can be determined by DRIFTS (Brown, 1990, Liang, Xiaotian, 1988, Wang, K., et al., 2006, Zhong, 1984).

Principle

Usually, infrared absorption spectra of molecules are vibrational/rotational spectrums of molecules. Infrared absorption spectrums are based on the absorption resulted from transition of vibrational/rotational energy level of molecules. Compared with standard spectrums, information of functional groups of samples can be determined by frequency of absorption band.

Sample preparation (Chingombe, et al., 2005)

F400 is a commercial granular coal-based AC from Chemviron (USA). In the surface modification, F400 was washed with distilled water, and dried at 383 K for 24 h, followed by various treatments including HNO_3 , amination and annealing in H_2 . All other reagents but HNO_3 were analytically pure.

The pre-treated F400 was stirringly oxidized by about 35 wt.% of HNO_3 at 363 K for 6 h. After the oxidation, a fresh HNO_3 solution at the same concentration oxidized the above treated sample for 3 h. The oxidized carbon was then washed with distilled water until no further change in pH could be detected. The resultant water-washed sample (after oxidation) was divided into three portions. The first portion was denoted as AC1, and this is a sample that was washed with water after the oxidation reaction. AC2 was the sample that was washed with 0.1 M NaOH to remove humus that is a byproduct of the oxidation process. The washing was continued until no further coloration from the humic substances could be detected. Reconditioning of the sample to the hydrogen form was performed using 0.1 M hydrochloric acid and further washing with distilled water was done until the pH of the supernatant solution stabilized to a pH of about 4.0. The third sample, denoted as AC3, was as a result of heating the oxidized sample at a temperature of 580 K under vacuum of 2 mm Hg for 12 h to remove humic substances. Prior to the annealing process the sample was conditioned in a flow of hydrogen ($3.3 \times 10^{-6} \text{ m}^3/\text{s}$) for 45 min at ambient temperature. The furnace temperature was then raised at a rate of $10^\circ\text{C}/\text{min}$ until it reached 1173 K where it was maintained for 3 h. After the annealing cycle, the furnace was allowed to cool down and the flow of hydrogen was maintained even during the cooling process.

Operation conditions

Chingombe P., et al. investigate surface groups of ACs through DRIFTS. Fourier Transmission infrared experiments, which were conducted on a Nicolet DXC20 FTIR spectrometer with liquid nitrogen-cooled mercury-cadmium-telluride detector and a Spectra Tech diffuse reflectance accessory (Chingombe, et al., 2005). The preparation process was drying of samples of particle size $<45 \mu\text{m}$ for 24 h at a 383 K and mixture of the dried samples with fine KBr at a ratio of 1:100. In the preparation process, FTIR spectra of samples were recorded at a resolution of 4 cm^{-1} and with 200 scans and an aperture setting of 15. A previously recorded background spectra of water vapour was subtracted from the spectrum of each sample (Dabrowski, et al., 2005).

Results (Chingombe, et al., 2005)

DRIFTS spectra for a series of F400 and oxidized samples were shown in Fig. 4. It is seen that some characterization peaks were at wave numbers 1240, 1610 and 1750 cm^{-1} . The spectra for AC1, AC2 and AC3 have some similar marked curves, indicating the three samples could possess similar surface groups. F400 does not have a characterization peak at 1750 cm^{-1} , and its peak at 1240 cm^{-1} is also less pronounced than that for the other oxidized samples, suggesting that oxidation increase surface groups.

It is usually difficult to ascribe the peak at 1240 cm^{-1} (a superimposed peak) to a specific groups because the peak of a certain bands is overlapped by that of other bands. The superimposed peaks can be resulted from ether, epi-oxide and phenolic structures in various chemical environments. Beniak et al. reported that tertiary C-N stretching vibration may also result in the contribution of the peak in the region of 1240 cm^{-1} . The C-N contribution can probably explain the lack of a pronounced peak on F400 sample which did not undergo HNO_3 oxidation. The peak at 1610 cm^{-1} can be ascribed to quinone-like structures, and this peak appears in all the samples. Sutherland et al. and Shim et al. have also observed such a peak. As mentioned earlier, the peak at 1750 cm^{-1} appears on the oxidized samples only, but its position on the spectra of the other samples makes it difficult for positive identification. However, Lopez et al. obtained peaks in this region when they modified carbon samples by air oxidation and they assigned it to free carboxyl groups, lactonic groups, esters and carbonyl groups near the hydroxyl groups. The most logical explanation for the peak at 1750 cm^{-1} would be the existence of carboxyl groups that are formed as a result of nitric acid oxidation. This is also supported by the high sodium capacity results on the oxidized samples as opposed to F400 sample.

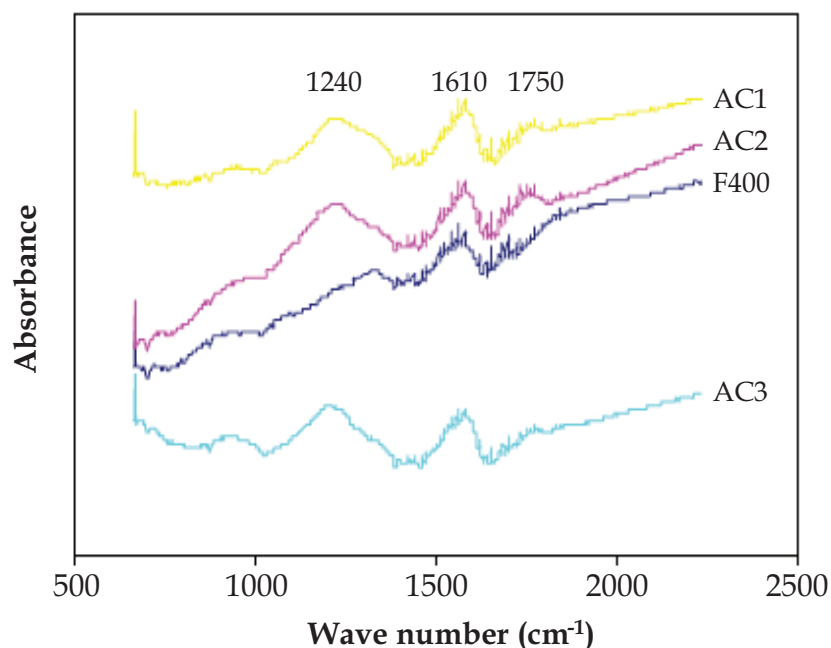


Fig. 4. DRIFTS curves for F400 with different treatments. (Chingombe, et al., 2005)

Owing to the similarity of DRIFTS curves of samples in Fig. 4, another example pertaining to characterization of surface chemistry by DRIFTS below is given to better describe the role of DRIFTS.

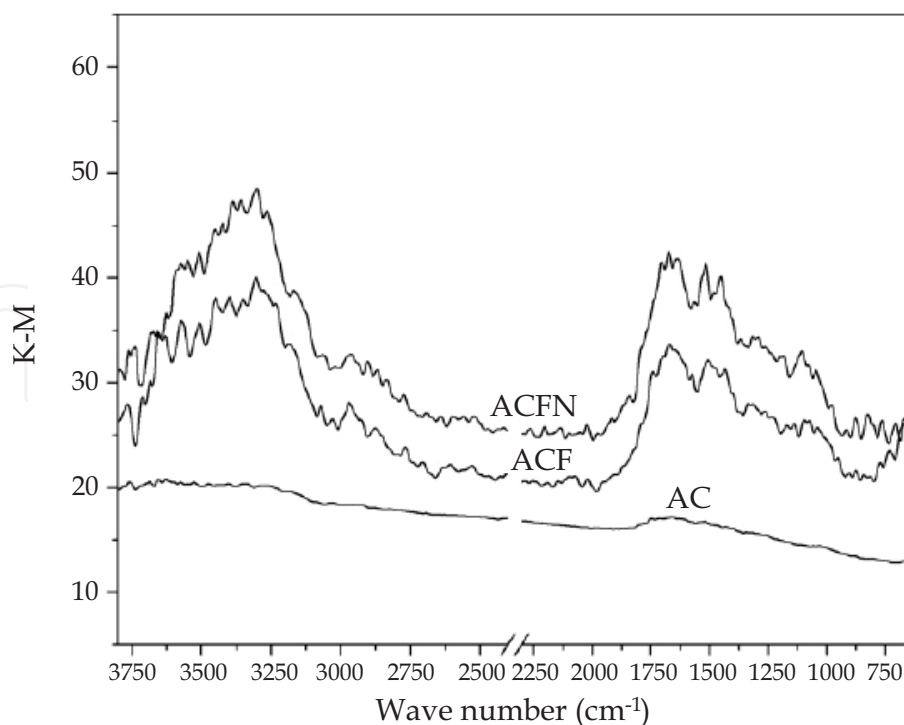


Fig. 5. DRIFTS curves of the adsorbents (Li, et al., 2010a)

The DRIFTS spectra of the adsorbents were shown in Fig. 5. As can be seen, among the three adsorbents, the lowest intensity of bands is in AC, indicating that AC has fewer groups than both ACF and ACFN. Compared with ACF, ACFN has stretching vibrations similar to those of ACF, with the exception of the stronger intensity of bands of the surface functionalities of ACFN with OH of around 3384cm^{-1} , C=O (carboxylic groups, anhydride, lactone and ketene) at 1674cm^{-1} , C–O (lactonic groups, ether, phenol, etc.) including ν_{as} (C–O) at 1300cm^{-1} , and ν_{s} (C–O) at 1110cm^{-1} . This indicates that more oxygen-containing groups have been introduced on ACF surface after HNO_3 oxidation. Although the DRIFTS spectra do not provide quantitative information of the carbon surface chemistry, it can provide other important results, such as nitrogen-containing groups, that could not be detected using the titration method due to their inability to dissociate. Clearly, ACFN has the strong band with the stretching vibrations around 1519cm^{-1} , which can be ascribed to the presence of more nitro groups on the ACF surface.

From the analysis, DRIFTS does not accurately quantify oxygen-containing functional groups, but can acquire carboxyl groups, hydroxyl groups, carbonyls and nitro group produced from HNO_3 oxidation. Furthermore, some absorption peaks can not be ascribed to a specific group due to the overlapping peaks.

2.2.5 X-ray photoelectron spectroscopy (XPS)

The chemical shift effect of inner electron energy level originated from copper oxidation was discovered by Siegbahn K. in 1958, which represented the birth of XPS. XPS technology was fast developed during 1970s and 1980s. From then on, XPS has been not only an important measurement method in research, but also an effective means of analysis and test in controlling industrial quality.

Principle (Wang, K., et al., 2006)

When samples to determine is being exposed by X-ray with enough energy, an inner-shell electron will be bombarded from the sample atoms, producing an ion in an excited state (Equation 8) and XPS can detect the kinetic energy of the bombarded electron.



Kinetic energy of each electron is related with the orbital energy of emission electron, and orbital energy is characteristic of atoms or molecules, so the XPS can be used to qualitatively analyze samples. In a given experimental condition, number of emission electron is generally proportional to the concentration of emitters, so the XPS can also quantify the samples. The depth of samples studied in electron spectrum is less than 5 nm, so XPS is a surface analysis method. Specific binding energy of each electron corresponds to a Gaussian peak, representing a type of functional group.

Experiments (Wang, S.&Zhu, 2007)

To obtain the surface chemistry of AC, samples can be also characterized by XPS. Here, an example of XPS of the samples done by Wang is given below.

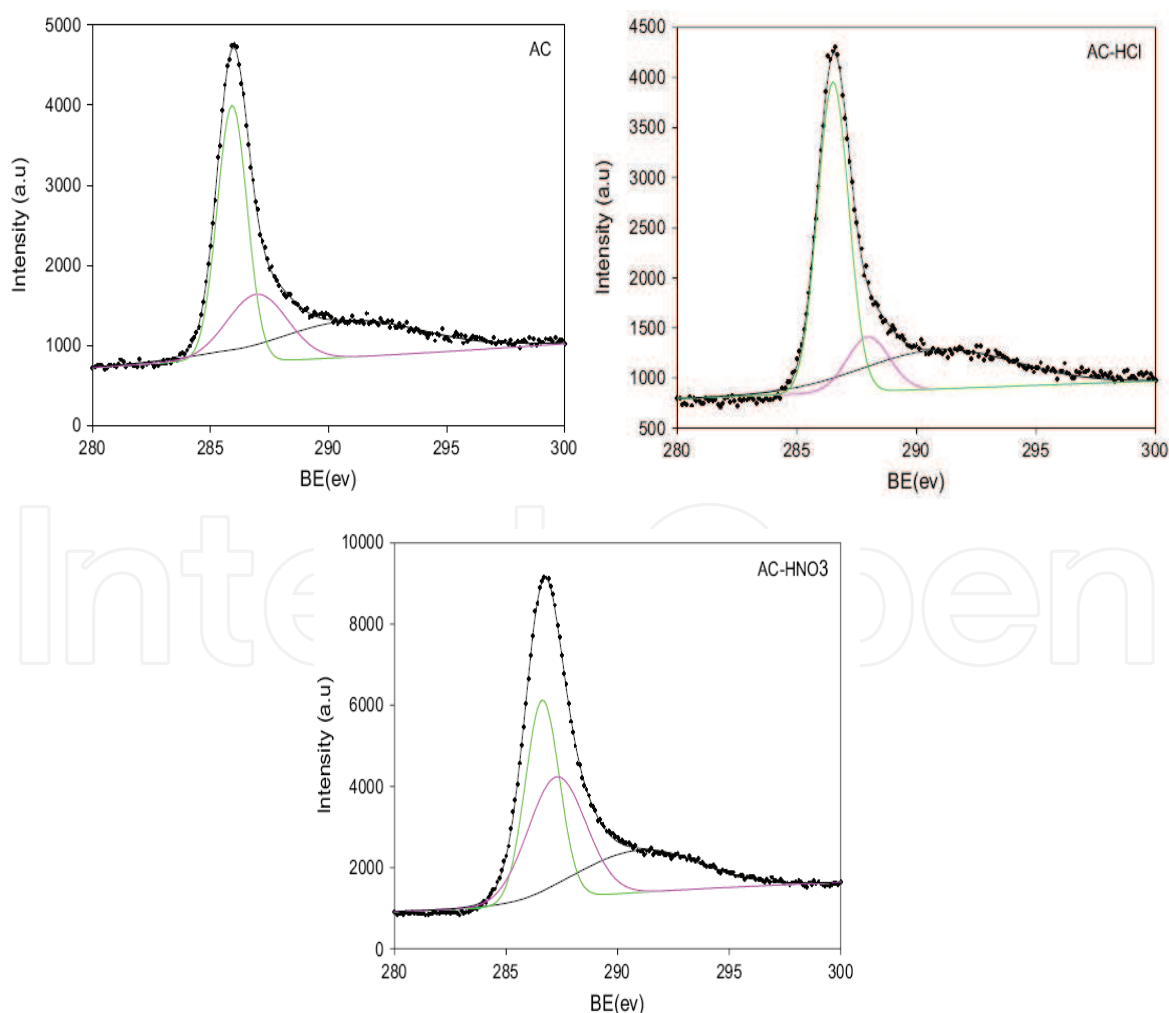


Fig. 6. XPS spectra of C1s on AC surface (Wang, S.&Zhu, 2007)

Wang used the three samples including AC (A commercial activated carbon), AC-HCl (AC treated with 2 M HCl at room temperature) and AC-HNO₃ (2 M HNO₃ for about 24 h at room temperature), and determined the surface chemistry of the above samples by resolution analysis of XPS peaks (Fig. 6).

The XPS measurements were carried out in PHI-560 ESCA system (Perkin Elmer), conditions of which were set at a basic pressure of 2×10^{-7} Torr with Mg Ka excitation at 15 kV and recorded in ΔE constant mode, pass energy 50 and 100 eV.

It should be noted that in measuring functional groups, the content percent (%) of other elements of functional groups to determine can be identified by XPS if the elements (such as C or O) have been given. The distribution of C and O structures can be derived from C1s and XP O1s spectra.

Fig. 6 showed the C1s signals of ACs. It is readily seen that C1s signals of samples are different. The maximum C1s signal on acid-treated carbons are shifted to higher binding energy due to an increase in oxidic species (alcohols, carbonates, or carboxylic groups) and ethers on the carbon surface after acid treatment. The resolution of peak indicates that three functional groups (C-C, C-O and C=O) can be obtained. For AC-HNO₃, C-O and C=O functional groups are much higher than AC and AC-HCl and C=O on AC-HCl is also higher than AC (Wang, S.&Zhu, 2007). Therefore, XPS results confirm that more acidic groups such as carboxylic groups and ethers were produced by acid treatment (Wang, S.&Zhu, 2007).

From analysis of Fig. 6, XPS can monitor oxygen-containing groups, but inaccurately quantify the groups.

2.2.6 Temperature programmed desorption (TPD) (Li, et al., 2009a, Li, et al., 2010a)

TPD is one of temperature-programmed analysis technology to measure structures and properties of catalysts and interaction between reaction molecules. It has been frequently used to identify and quantify oxygen-containing groups on AC through chemical adsorption apparatus or mass spectrum.

Principle

Surface oxygen-containing groups on carbon materials decompose upon heating, releasing CO₂ and/or CO at different characteristic temperatures (Mahajan&Moreno-Castilla, 1980), so it is readily concluded that a certain functional group decomposes at its special/corresponding temperature. Usually, decomposition law in TPD is as follows. For example, the CO₂ produced at temperatures lower than 400 °C may be ascribed to the decomposition of carboxylic acids, and at around 650 °C to the decomposition of lactones. CO₂ and CO released at temperatures about 550 °C account for the decomposition of anhydrides; the CO released at around 700 °C can be attributed to the decomposition of phenolic groups, and beyond 850 °C to the decomposition of carbonyl groups and quinones.

Experiments

To obtain the surface chemistry of AC, samples can be also characterized by TPD experiments. Here, an example of TPD of the samples treated by different methods is given to describe the analysis process (Li, et al., 2009a).

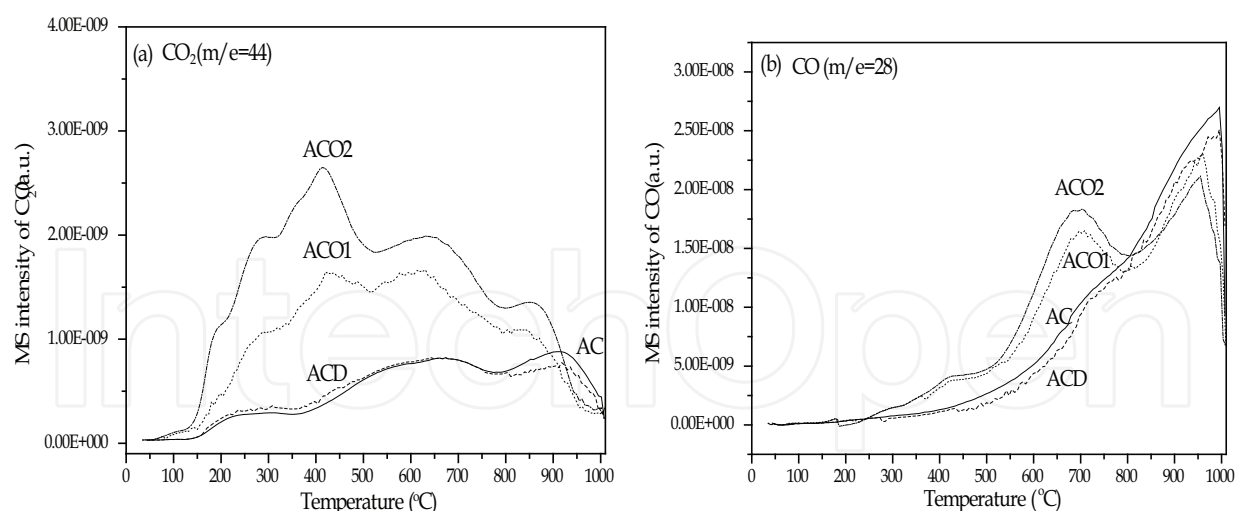


Fig. 7. CO₂ (a) and CO (b) evolution during TPD of the four adsorbents (Li, et al., 2009a)

Fig. 7 showed curves of CO₂ and CO released from the adsorbents during TPD. In Fig. 7, The similar CO₂ and CO release profiles for AC and ACD indicate that the HCl/HF treatment resulted in little change in acid and basic groups on the adsorbents' surface and the main groups on AC and ACD are basic, i.e. carbonyl and quinones. More CO₂ released from ACO1 and ACO2 at temperatures lower than 400 °C and around 650 °C is higher than that AC, indicating carboxylic acids and lactones of AC surface are increased by HNO₃ oxidation; more CO₂ and CO released from ACO1 and ACO2 around 550 °C account for decomposition of more anhydrides; more CO released from ACO1 and ACO2 than that AC at around 700 °C and beyond 850 °C shows that more phenolic groups, carbonyl groups and quinones of AC were formed by HNO₃ treatment. Carboxylic acids, lactones, anhydrides, phenolic groups, carbonyl groups and quinones introduced by HNO₃ treatment can be analyzed by TPD.

It should be noted that some nitrogen-containing functional groups were also produced during HNO₃ oxidation. However, these nitrogen-containing groups can not be better monitored and analyzed due to disturbance of other gases produced in heating. For example, mass charge ratio of 46 can represent NO₂ and CO₂, so NO₂ curve of AC is frequently disturbed by CO₂ released in heating. Furthermore, the information of surface groups of samples obtained by TPD is an indirect analysis result because groups to determine are ascribed only to the CO₂ and CO released from decomposition of groups at different temperature.

Therefore, it draws a conclusion that part of surface groups (the acidic groups such as carboxylic, lactonic, phenolic groups and the basic groups) of AC are determined by TPD, but it does not directly reflect surface chemical properties of AC and only analyze the decomposition behavior of oxygen-containing functional groups. Characterization of surface chemistry through TPD method should be further investigated.

2.2.7 Water vapor adsorption by thermal gravimetric analysis/differential scanning calorimetry (Li, et al., 2009a)

To identify hydrophilic properties of the adsorbents, water vapor adsorption of the adsorbents was measured by a thermal gravimetric analyzer (TGA 409 PC, Netzsch). The

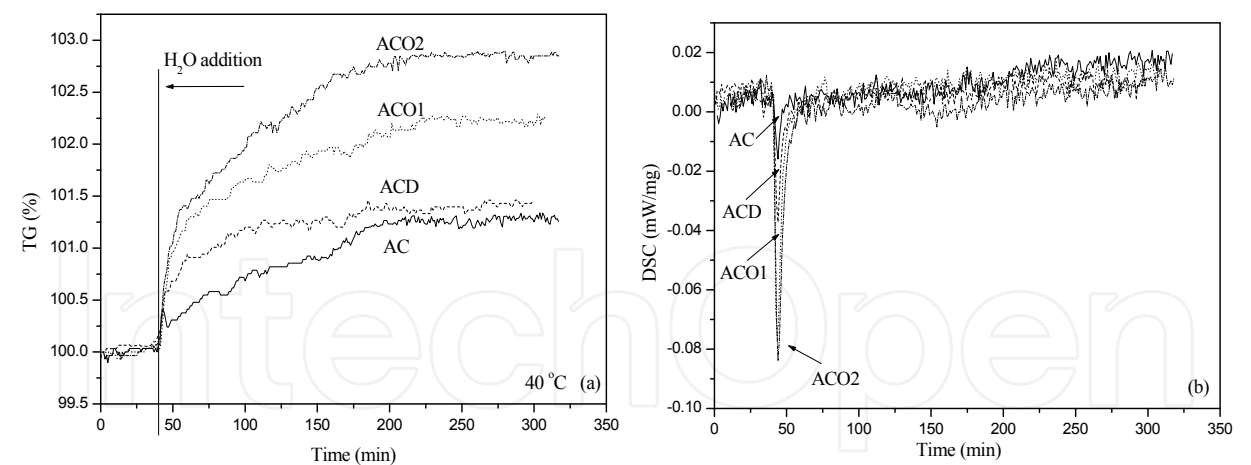


Fig. 8. Water adsorption on adsorbents (AC, ACD, ACO1 and ACO2) (Li, et al., 2009a)

Type	Advantages	Disadvantages
N ₂ adsorption	Determination of micro/ meso pore structure, surface area, average pore diameter and pore distribution	Long process and high expense
SEM	Determination of Pore structure and morphology	Inability of detecting pore distribution
Element analysis	Determinating element C, H, O, N, S, ash content	Inability of specific functional groups
Boehm Titration	Determination of acidic groups (carboxylic groups, lactonic groups, anhydrides, phenolic groups and carbonyl groups) and the basic groups, accurate quantification, large amount of sample, low expense and direct results	Inability of indentifying anhydrides, benzoquinones pyrones and other groups, complex operation, long process. Sample was destroyed
Pzc Titration	less samples, low expense, process slow, indirect results	Inability of indentifying types of some groups, Inability of quantification. Sample was destroyed
DRIFTS	Part of functional groups, nitrogen-containing groups to determine, less samples, medium expense, easy operation, intact samples and direct results	Inability of some absorption to be attributed and approximate quantification
XPS	Medium mass, more samples, high expense and direct results	Inner surface layer in depth less than 5 nm, approximate quantification, high expense and easy operation. Some peaks is difficult to disintegrate and fit.
TPD	Analysis of functional groups decomposing at temperatures lower than 1100 °C, accurate quantitative, a small amount of sample	Medium expense, medium easy and indirect results. Sample was destroyed

Table 6. Comparisons of characterization methods of AC surface chemistry

measurement started with flowing Ar (99.99%, 50 mL/min) over 8.0 mg adsorbent at 40 °C, followed by replacing the Ar stream by water vapour-containing Ar stream (P_{H_2O} of 7.381 kPa) at steady state. The weight increase in the adsorbent after the introduction of water vapour is attributed to water adsorption.

The TG and DSC data in Fig. 8 all show that water adsorption of the adsorbents increases from AC to ACD and then to ACO1 and to ACO2. Clearly, this trend corresponds to the changes in surface acid/basic properties; a higher surface acidity of an adsorbent is consistent with a higher water adsorption capability. Adsorption heat also verifies the trend.

2.3 Comparison of characterization methods

Form the discussion in many examples, characterization methods mentioned above can be used to analyze physical texture and surface chemistry of AC. To further understand the methods, it is important to investigate the advantages and disadvantages between the methods, which were listed below.

Comparisons of characterization methods of AC surface chemistry were shown in Table 6. N_2 adsorption and SEM can be used to better analyze physical structures of AC. It should be noted that in analyzing surface chemistry of AC by Boehm, Pzc Titration and TPD, carboxylic, anhydride, lactonic groups and phenolic groups can be determined, but ketones, aldehydes, ethers, esters, pyrones and other functional nitrogen-containing groups can not be detected, which can be characterized by DRIFTS and XPS. DRIFTS and XPS have the greater advantage of determining nitrogen-containing functional groups than other methods mentioned above.

3. Conclusion

There is the difficulty in analyzing its chemical properties of surface derived from the special nature of activated carbon itself, which is a black body and has complex components on surface, so the different characterization methods are proposed and used. Given the above characterization methods are not perfect in characterizing activated carbon surface chemistry, a variety of characterization methods complement each other to acquire more accurate and more comprehensive surface information. It is predicted that with the development of science and technology, these methods will be continually developed and improved and the nature of surface chemistry of AC will be further understood.

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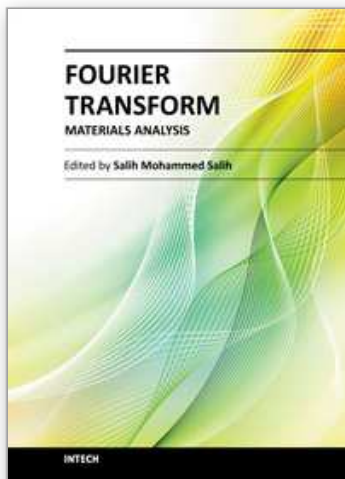
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