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Silane modification and characterization of activated carbon

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Abstract Activated carbons have been wildly used as adsorbents for various purpose. When used in a cigarette filter activated carbon can selectively remove a number of the vapor phase compounds to varying degrees of efficiency. To improve the wet-feeling of cigarette smoke with AC in the filter, a new method is developed to chemically functionalize a coal-based activated carbon (AC) based on silanization reaction. Silanization using 3-glycidoxypropyltrimethoxy silane was performed after the oxidized AC was reduced by lithium aluminum hydride.

N_2 and water adsorption, FTIR, and XPS were employed to characterize the changes in the surface morphology, chemistry and physical conditions at different processing stages. Water content analysis in cigarette mainstream smoke (MSS) showed a positive result in the application of modified AC.

Keywords Activated carbon · Silanization · Functional groups · Modification

1 Introduction

Activated carbons (ACs) have been proven to be useful catalyst (Nevskaia and Martin-Aranda 2003; Heinen et al. 2001) as supports for the active phase, or effective adsorbents for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media, or from gaseous environments (Streat and Horner 2000; Suffet et al. 1978; Saha et al. 2001; Biniak et al. 1999). Due to their porous texture and high surface area ($>1000\ \text{m}^2/\text{g}$), activated carbons are finding an increase application in cigarettes filter to remove smoke compounds. Their performance is thought to be determined by their texture and surface chemistry (Rodriguez-Reinoso 1998). However, a major disadvantage by application of ACs in cigarettes filter is agreed to be the dry-feeling of smoke caused by significant water adsorption.

The texture of ACs was proved to be controlled by activation procedure and it's possible to prepare carbons with different proportions of micro, meso and macropores (Wigmans 1986). Carboxyl, carbonyl, phenol, quinone, and lactone groups have been identified in ACs surface (Donnet 1968; Hsieh and Teng 2000; Laszlo and Nagy 1997), meanwhile, a variety of methods have been used to modify the surface groups (Chingombe et al. 2005; Shim et al. 2001; Jia et al. 2002). However, these methods were limited in either chemical/thermal oxidation or reduction by heating under inert gas, however, no evidence was proved to decrease the water adsorption ability.

Organosilanes have been extensively used as coupling agents on hydroxylated surfaces (SiO_2 on Si, Al_2O_3 on Al, glass etc.) (Sagiv 1998; Duchet et al. 1997; Wasserman et al. 1989). Recently, works have mainly been performed on the silanization of oxidized carbon nanotubes (Velasco-Santos et al. 2002), while the silane modification of activated carbons has rarely been practiced.

In the present work, we aim to restrict the water adsorption capacity of ACs by creating more hydrophobic surface groups. The focus is building up an efficient model to modify the surface group using organosilane (3-Glycidoxypropyltrimethoxy silane) as the coupling agent. The coupling process (Plueddemann 1991) can be accomplished via the chemical reaction between the trialkoxy groups of silane molecules and the hydroxyl groups on the ACs, whereas the hydrophobic functional groups of silane molecules can be remained.

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The physical and chemical properties of the modified ACs were characterized by N_2 and water vapor adsorption, FTIR, and XPS data. Moreover, characterization of the cigarettes filter with AC before/after silane modification is also performed.

2 Experimental section

2.1 Materials

The primary coal-based activated carbon (AC), which was generally used in cigarettes filter, was provided by Chifeng Jinyuchang Activated Carbon Corp, China. 3-Glycidoxypropyltrimethoxy silane (GPTMS) with purity of 98% (supplied by Aldrich) was used as the silane functionalization agent. Concentrated nitric acid solution (specific gravity 1.42, 70%) was obtained from Aldrich. All other chemicals and solvents were of analytical grade and used without further purification from the same source (Aldrich).

2.2 Sample preparation

2.2.1 Oxidative process

Double bonds presented in the aromatic AC structure were oxidized with 5 M nitric acids. The aim of this treatment was to create carboxylic acid moieties on AC and also to remove impurities in the raw material. For this purpose, 5 g of raw AC was dispersed in 100 mL of 5 M HNO_3 at boiling point and stirred for 6 h. The reaction solution was removed and a fresh 100 mL of 5 M HNO_3 was introduced. The reaction was allowed to continue stirring for a further 3 h under the same conditions. A fritted glass filter (porosity 4) was used in all the filtration steps realized during the modification. The solution of oxidized AC was filtered and the filtrate was washed thoroughly with distilled water until no further change in pH could be detected. The residue was dried overnight at 80 °C under vacuum to obtain 5 g of oxidized AC which was stored in closed vials.

2.2.2 Reductive process

The reduction of the oxidized AC was realized using lithium aluminum hydride (LiAlH4). Typically, 2.0 g of oxidized AC was dispersed in toluene by ultrasonication (in a water bath) for 30 min, and then 5 g of $LiAlH_4$ was added gently. The solution was stirred for 3 h at room temperature, followed by adding 200 ml of 2.0 N hydrochloric acid into the solution in order to remove the lithium and aluminum. The reduced AC was obtained by filtration of the solution and washing with toluene, absolute ethanol and acetone sequentially, and then drying in a vacuum oven at 80 °C overnight.

2.2.3 Silanization process

1.0 g of reduced AC was added into a three-neck flask with 75 ml toluene and dispersed through ultrasonication (in a water bath) for 30 min. Then 75 ml of 1.0 wt% toluene solution of GPTMS was added and stirred for 6 h at 60–65 °C for silanization. After the reaction, 30 ml of methanol was added to dilute the unreacted GPTMS molecules. The product was obtained by filtration and followed by ultrasonication in toluene to eliminate physisorbed silane molecules. Then the solution was filtered and washed with methanol, water and acetone sequentially. The silane treated AC was dried in a vacuum oven at 80 °C for 12 h.

2.3 Characterization

2.3.1 Physical and chemical characterization of ACs

N_2 and water vapor adsorption, Fourier transform infrared (FTIR) spectrometry, and X-ray photoelectron spectroscopy (XPS) were used to characterize the changes in surface morphology and chemical structure of the AC after each surface treatment step.

N_2 and water vapor adsorption were carried out at respectively 77 K and 293 K using Quantachrome Autosorb 1. All samples were outgassed at 573 K under high vacuum before analysis. For the FTIR (Nicolet 6700, Thermo Scientific), the ACs were pressed into a pellet with potassium bromide (KBr) and scanned from 500 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1}. The XPS spectra were recorded with a VG Escalab markIIspectrometer (VG Scientific Ltd., UK), using Al Kα excitation radiation (1253.6 eV) and calibrated by assuming the binding energy of carbonaceous carbon to be 284.6 eV. T he XPS curve fitting of C 1s and Si 2p was accomplished by MultiPak V6.0 A (Physical Electronics, Inc.).

2.3.2 Cigarette smoke sample preparation and estimation

Equal amount of original and silane-modified ACs was respectively applied in cigarettes filter using AC 4 charcoal feeding unit (Hauni Maschinenbau AG) and MULFI-ME multifilter rod maker (Hauni Maschinenbau AG). A RM200A Borgwaldt smoking machine (using standard smoking conditions of 1 puff/min, 2 seconds puff duration, puff volume of 35 mL, and smoking to a butt length of 23 mm) was used to collect the cigarette smoke condensate (CSC) from 20 cigarettes.

Before smoking, each Cambridge filter pad (CFP) was conditioned at 22 °C and 60% humidity for at least 24 h. Individual pads were then placed inside the Cerulean filter holders to collect mainstream smoke. Estimation of water content in cigarette mainstream smoke (MSS) was accomplished by Agilent 7890N GC system using method of ISO 10362-1:1999.

Table 1 Textural properties of all ACs

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	Primary adsorption sites Q_0 (mg/g)
Pristine	1050	1022	0.41	0.36	72.7
Oxidized	767	745	0.29	0.26	245.8
Reduced	690	676	0.22	0.20	253.5
Silanized	530	520	0.20	0.18	12.5

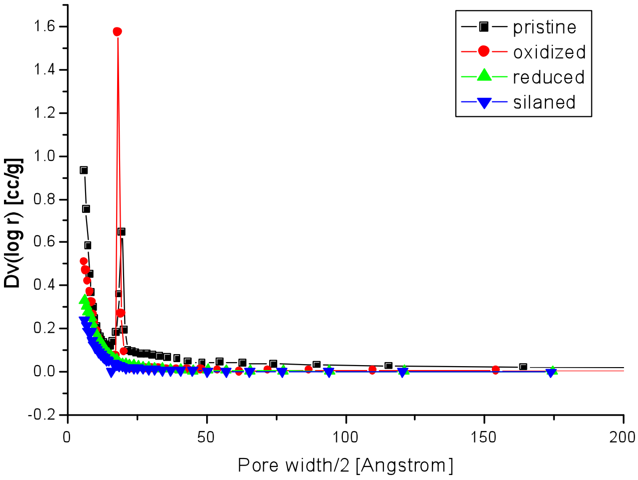

Fig. 1 Pore size distribution for different ACs

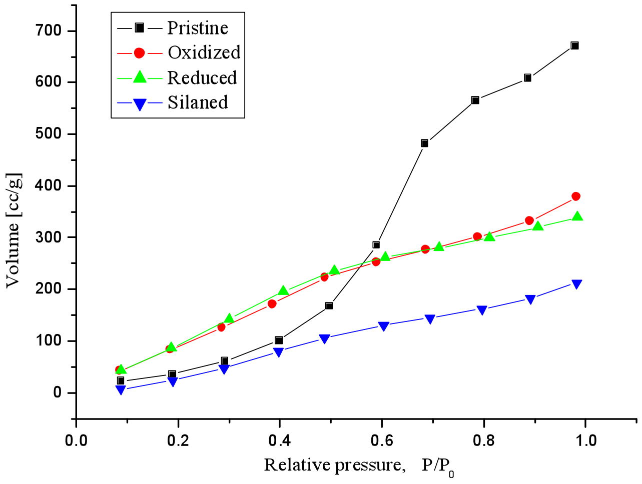

Fig. 2 Water isotherms measured at 298 K on the different ACs

3 Results and discussion

The details of various characterization techniques that were employed for this work are detailed below.

3.1 Texture characterization

Porous texture analysis of these samples was carried out by standard N_2 adsorption. BET equation was used to calculate the surface area. Dubinin-Radushkevich (DR) method was used to estimate the micropore area and volume (Table 1). It can be seen from the results that most of the AC pores are micropores in this case.

BJH pore size distribution for the stated carbons are collected in Fig. 1, which reconfirms the assumption that micropores take primary parts of all the samples. It can be concluded that all surface modification caused varies degrees of decrease in the porous properties and silane functionized one have the smallest surface area and widest average pore width. It's reasonable to assume that the lowering in the surface area and pore volume of modified carbons is the result if an inaccessibility of the probe nitrogen molecules into the internal adsorption sites caused by the presence of increased surface groups at the pore entrance of the graphitic basal planes and possibly by the collapse of some thin pore walls due to the strong action of oxidizing agents.

3.2 Water vapor adsorption

The water adsorption isotherms of the carbons were used to compare the hydrophilicity of the AC. A blank run on all the bulbs showed that water adsorption on the inner surface of the glass was negligible.

Due to high surface tension of water in comparison with other liquid adsorptives, water adsorption is different from that of conventional adsorptives (N_2 or C_6H_6), which don't show adsorption in macropores or in large mesopores (Gregg and Sing 1982). Some researchers considered that up to P/P_0 of about 0.8 water adsorption is due to micropore filling and at higher P/P_0 due to the filling of mesopores and/or macropores (Lodewyckx and Vansant 1999).

Figure 2 shows the water adsorption isotherms of all the samples. It can be seen that the isotherm of the pristine material shows low adsorbate-adsorbent interactions at low reactive pressures followed by a rapid rise in the adsorption amount at higher pressures (type V), typical of water adsorption onto ACs (Sing et al. 1985).

There are two differences that can be derived from the isotherms. First, all the modified ACs have a stronger adsorption of water at low relative pressures. It's well known that surface acidic groups promote water adsorption at low relative pressure, acting as primary adsorption centers for water molecules to first adsorb on, followed by self adsorption among water molecules via hydrogen bonding, leading to the growing of water cluster as the pressure is increased (Rodriguez-Reinoso et al. 1992; Dubinin 1980; Barton et al. 1991; Salame and Bandosz 1999; Stoeckli and Lavanchy 2000). As a result, the adsorption behavior of these carbons would depend chiefly on the role of functional groups with relatively less effect of physical adsorption by dispersive forces on hydrophobic grapheme layers. To compare the hydrophilicity of the ACs, the primary adsorption sites concentrations, Q_0, for each activated carbon was determined using (1), the DS-2 equation (Stoeckli and Lavanchy 2000).

$$C(Q_0 - q)(1 - kq) = q/(P/P_0) \qquad (1)$$

where q is the measured adsorption amount per gram of the carbon, P/P_0 is the relative pressure, c is the kinetic parameter, k is the constant involved in decreasing active site concentration, and Q_0 is the concentration of the primary sites. The Q_0 values, given in Table 1, show that the order of the hydrophilicity of the carbons is Reduced > Oxidized > Prisitine > Silaned with oxidized and reduced ACs significantly improved the hydrophilicity, and this result also reconfirm the efficiency of silanization process.

Another obvious difference is the decrease of adsorbed volume at higher relative pressures, where adsorption occurs in the larger pores and at higher adsorbate concentration. Water adsorption of the original carbon, which contains almost no functional groups, involves the adsorption on hydrophobic carbon surface by weak adsorbent-adsorbate interaction forces. Adsorption by this mechanism is inefficient at a low pressure (low concentration) for a polar molecule like water. However, at a higher pressure, where adsorption occurs in larger pore sizes, the high density of adsorbate in the bulk gas phase can force water molecules to enter and pack inside the pores with the help of self hydrogen bonding and this would lead to a sharp increase of the adsorbed amount as the pressure is increased. On the other hand, adsorption on modified sample employs both functional groups and pore packing effects. However, the pore volume available for physical adsorption inside the pores for these carbons is much reduced caused by the partial blocking of pore entrance due to the presence of introduced surface groups at the edges of graphitic layers. The overall effect is to make the adsorption capacity of modified carbon to be less than that of the original one. Similar results were also demonstrated by Alcaniz-Monge et al. (2001).

3.3 FTIR spectroscopy analysis

FTIR spectra for the activated carbon obtained at different steps are depicted in Fig. 3. Table 2 shows the infrared bands which can be associated with different oxygen functional groups on carbon materials (Fanning and Vannice 1993).

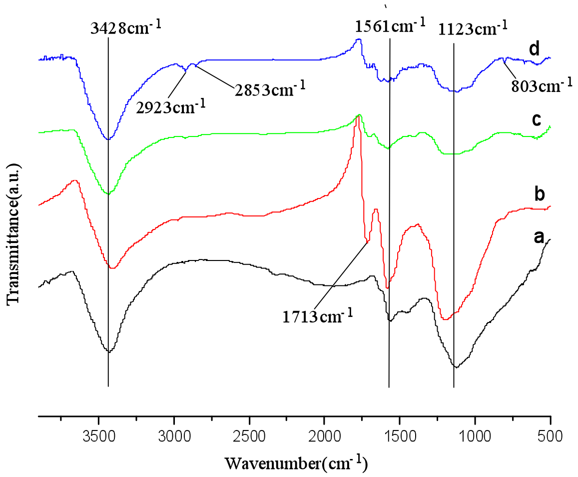

Fig. 3 FTIR spectras of the ACs (*a* Pristine, *b* Oxidized, *c* Reduced, *d* Silanized)

For the pristine AC (Fig. 3a), the bands at 3428 and 1123 cm^{-1} are attribute to the presence of hydroxyl groups (–OH) on the surface, which can be resulted from either oxidation during purification of the raw material or atmospheric moisture present on the AC (Ramanathan et al. 2005). Another peak at 1561 cm^{-1} can be attributed to quinone like structures, and this peak appears in all the samples. Sutherland et al. (1996) and Shim et al. (2001) have also observed such a peak.

For the oxidized AC (Fig. 3b), a new band appeared at 1713 cm^{-1}. The most logical explanation for this peak would be the existence of carboxyl groups formed as a result of nitric acid oxidation. Lopez et al. (2003) also obtained peaks in this region when they modified carbon samples by air oxidation and they assigned it to free carboxyl groups, lactone group esters and carbonyl groups near the hydroxyl groups.

The FT-IR spectrum of the reduced AC (Fig. 3c) shows the reduction of the –COOH groups to –OH groups, as verified by the disappearance of the band at 1713 cm^{-1} and stronger intensity at the peak of 3428 cm^{-1}.

Compared to reduced AC, two new bands at 2923 and 2853 cm^{-1} associated with the stretching of the methylene groups from the GPTMS molecules appeared (Ma et al. 2006) for the silane-functionalized AC (Fig. 3d). The weak signal at 803 cm^{-1} and the strengthen signal at 1100 cm^{-1} due to Si–OH (Satyanarayana et al. 2000) confirms the presence of GPTMS. The chance of reaction between –OH surface group and the epoxy group, instead of –OCH_3 group, in GPTMS molecules can be neglected under our mild experiment condition. Similar conclusion was also made by Ma et al. (2006).

Table 2 FTIR assignments of functional groups on carbon surfaces

Group or functionality	Assignment regions (cm^{-1})		
	1000–1500	1500–2050	2050–3700
C–O in ethers (stretching)	1000–1300		
Alcohols	1049–1276		
Phenolic groups:			
C–OH (stretching)	1000–1220		
O–H	1160–1200		2500–3620
Carbonates; carboxyl-carbonates	1100–1500	1590–1600	
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

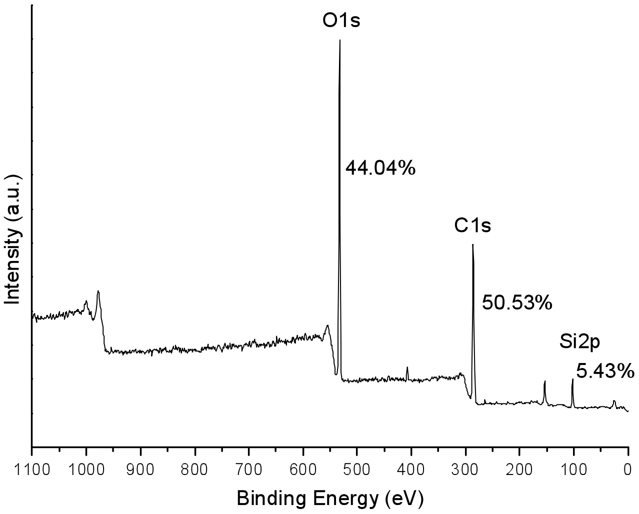

Fig. 4 XPS survey spectra of silane-treated AC

3.4 XPS results

To elucidate the surface state of ACs after silanization, XPS analysis was applied. The XPS survey spectrum (Fig. 4) of silane functionalized AC reveals the presence of silicon on the surface. The atomic percentage of the silicon in the sample stands at 5.43%.

Figure 5 shows the C 1s and Si 2p signals. The C 1s (Fig. 5a) peak of silane-treated AC can be deconvoluted into six fitting curves with peaks at 284.5, 285.2, 286.1, 287.2 and 288.8 eV (Ago et al. 1999), which corresponds to C_g sp^2, C_d sp^3, C–O, C=O and CO–O binding respectively. The relatively high ratio of the contribution between 287.2 and 286.1 eV confirms the change of C=O into C–O groups during reduction process.

Figure 5(b) shows a detailed view of the Si 2p spectrum where two components are needed to achieve a suitable fit. The first one has a binding energy of 101.6 eV and corresponds of the bonding of silicon with oxygen coming from the carbon surface (Si–O–C). The other at 103.1 eV is attributed to the silicon participant from the siloxane network (Si–O–Si) resulting from the condensation of silane molecules. These results are in good agreement with the reaction mechanisms of silane, including hydrolysis of $-OCH_3$, condensation to oligomers, hydrogen bond between oligomer and OH groups on the substrate, and the formation of the covalent linkage between silane and the substrate.

3.5 Water content in smoke condensates

Result of the MSS analyze was listed in Table 3. It can be seen that there's an obviously increase in the water content in cigarette smoke after silane modification. By comparing the ratio of water and total particular material (TPM) content, it can be concluded that silane-treated AC was more hydrophobic than the original one. The result is consistent with our smoking quality test, which shows that the cigarette smoke give better score in wet-feeling using silane-treated AC.

4 Conclusion

In this study, we have reported on the chemical functionalization of activated carbons with a functionalized silane: 3-Glycidoxypropyltrimethoxy silane.

Oxidation, reduction and silanization were included in the procedure. The carbons are oxidized and further reduced in order to create, respectively, carboxylic acid and alcohol

Fig. 5 Carbon (**a**) C 1s level, (**b**) silicon Si 2p level of silane-treated AC

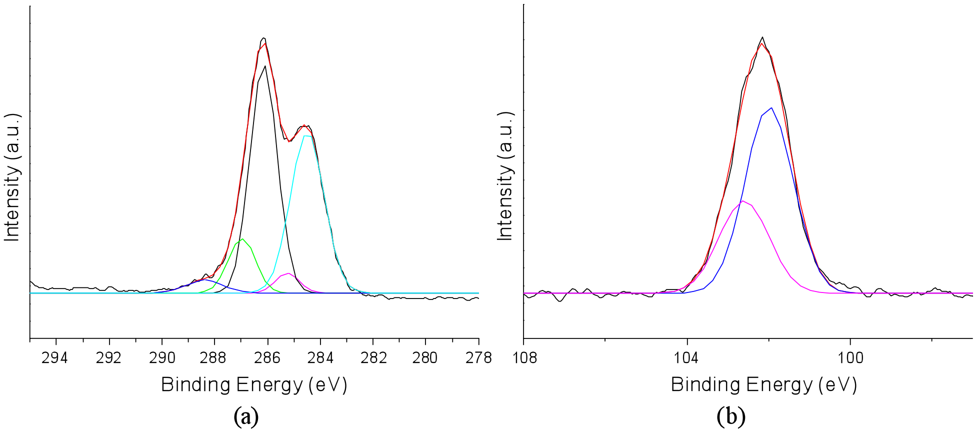

Table 3 Result of the MSS analyze

Sample	TPM (mg/cig)	Nicotine (mg/cig)	Water (mg/cig)	Water/TPM (%)	CO (mg/cig)	Puffs (puff/cig)
Pristine AC	13.62	1.08	1.68	12.33	11.04	6.20
Silaned AC	14.04	1.11	2.36	16.80	11.18	6.39

groups. N_2 and water adsorption isotherm shows a significant loss in microporosity but an increase in hydrophilicity after oxidation process.

The presence of silane molecules is verified by FTIR, and XPS spectra. The two peaks at different binding energies in Si 2p signal indicate that there were two chemical states of Si: Si–O–C and Si–O–Si.

MSS analyze shows a positive result of the application of silane-treated AC. Both the Water/TPM ratio and the smoke total score increase significantly after modification. We are also currently considering other organosilane derivatives with variety of functional groups and applying these ranges of new materials in cigarette filters.

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