Effects of micropore development on the physicochemical properties of KOH-activated carbons

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Abstract

Effects of micropore development through varying the KOH/char ratio on the porous, electrochemical, electronic, and adsorptive properties for corn-cob-derived activated carbons (ACs) prepared by means of the KOH activation method were systematically compared. The pore properties of ACs, including BET surface area, total pore volume, micropore volume ratio, bulk density, and product yield based on the raw material were investigated to gain an understanding for the influence of KOH dosage on the pore development. Element analysis and temperature-programming desorption (TPD) were used to obtain the information of chemical composition and surface oxygen functional groups on ACs in order to propose the reaction mechanism of KOH activation. Based on the pore development, KOH-activated carbons can be classified into two groups: a combination of physical activation and chemical KOH etching at low KOH/char ratios (0.5–2) as well as chemically uniform etching at high KOH/char ratios (≥ 3.0). From the adsorption study for five organics with molecular weights varying from 129 to 466 g/mol, the specific adsorption capacity of ACs for organics is independent of their specific surface area. The specific capacitance of ACs reached a maximum as the KOH/char ratio was equal to 3, attributed to a compromise between the specific surface area and electronic resistance of ACs.

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1. Introduction

Activated carbons (ACs) are important industrial materials for various applications because of their high specific surface area (S_p) (Fujimoto *et al.*, 2000; Hsieh and Teng, 2000; Shi, 1996; Tsai *et al.*, 1997; Tseng *et al.*, 2003). In analyzing the pore properties and determining the specific surface area of ACs, N_2 adsorption/desorption isotherms at 77 K are the most popular method (e.g., about 89% of 46 articles using this method to analyze the pore properties of ACs derived from plant raw materials in 2005). Data derived from N_2 adsorption/desorption isotherms do not only provide S_p , total pore volume (V_{pore}), and pore size distribution but also the micropore volume

(V_{micro}) and exterior surface area (S_{ext}) (Tamai *et al.*, 1999; Wang *et al.*, 2005). Moreover, from the shape and hysteresis loop of isotherms, the pore size distribution as well as the shape/structure of pores inside ACs can be reasonably estimated (Sing *et al.*, 1985; Suzuki, 1990). Accordingly, this measurement provides the basic physical properties of ACs. On the other hand, the performances of ACs in certain fields (e.g., electrochemical energy storage/conversion systems) do not only depend on the pore structure but also on the chemical properties of ACs, such as chemical composition and surface functional groups (Minkova *et al.*, 2000; Suzuki, 1990). Accordingly, the influences of physicochemical properties of ACs on their performances in modern industries are very important (Gergove and Eser, 1996; Guo *et al.*, 2005; Wu *et al.*, 2001, 2005a).

The chemical composition of ACs, in terms of the weight percentage of C, H, and O, is usually measured by means of

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Nomenclature

C_S	average specific capacitance (F/g)
K_F	Freundlich constant (mol/kg)(mol/m ³) ⁿ
K_L	Langmuir constant (m ³ /mol)
q_e	amount of adsorption at equilibrium (mol/kg)
q_{mon}	amount of adsorption corresponding to monolayer coverage (mol/kg)
R_S	surface resistivity (Ω/cm^2)
S_{micro}	micropore surface area (m ² /g)
S_p	total BET surface area (m ² /g)
V	volume of the solution (m ³)
V_{micro}	micropore volume (cm ³ /g)
V_{pore}	total pore volume (cm ³ /g)
Y_p	weight ratio of final carbons to the initial dried raw materials

Greek symbol

ρ_b	bulk density (kg/m ³)
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element analyses (Minkova *et al.*, 2000; Oh and Park, 2002). The chemical composition of ACs has been found to depend on the nature of raw materials, activation methods, the dosage of chemical species, and the specific surface area (Minkova *et al.*, 2000; Oh and Park, 2002). However, the relationship between chemical composition and preparation condition as well as the activation mechanism is seldom discussed. Thus, changes in the chemical composition of materials during the activation process cannot be suitably described, which is worthy being investigated.

The surface oxygen functional groups on ACs can be detected by means of infra-red (IR) spectroscopy (Guo and Lua, 1999; Lillo-Rodenas *et al.*, 2003), X-ray photoelectron spectroscopy (XPS) (Qu, 2002; Yoshizawa *et al.*, 2000), and temperature-programming desorption (TPD) (Lillo-Rodenas *et al.*, 2003; Molina-Sabio *et al.*, 1996) while the spectroscopic methods usually provide qualitative information only. Although quantitative information can be obtained from curve fitting of XPS spectra, this technique is an external, superficial analysis tool which cannot obtain the complete distribution of functional groups within ACs. Accordingly, TPD through the evolution of CO₂ and CO in different temperature regions is often recommended for the analysis of surface oxygen functional groups. For example, the steam-activated carbon was found to release more CO in comparison with the CO₂-activated carbon by Stones (Molina-Sabio *et al.*, 1996). Carbon fiber (CFN) treated with nitric acid at various temperatures was reported to release more CO₂ when the treatment was under a low temperature. Recently, we also found that KOH-activated carbons release more CO₂ than the steam-activated carbons (Wu *et al.*, 2005b). The above facts indicate the importance of TPD in getting information of surface functional groups in the field of AC research.

Recently, the relationship between the porous structure and electrochemical behavior of ACs is very important because carbons in various forms have been widely used as electrode

materials for electrochemical energy storage/conversion systems, especially for electric double layer capacitors (EDLCs) (Frackowiak and Beguin, 2001; Hsieh and Teng, 2002; Jurewicz *et al.*, 2004; Lufrano and Staiti, 2004; Wei *et al.*, 2005; Wu *et al.*, 2004, 2005b). Although the charge storage of EDLCs is based on the Helmholtz double layers, which is highly reversible, their performances are significantly influenced by the physicochemical properties of ACs, such as pore structure, surface functional groups, and chemical composition, etc. The specific capacitance of ACs can even reach above 100 F/g (Qu, 2002; Wu *et al.*, 2004, 2005b) meanwhile the raw materials of ACs are generally cheap and available. Accordingly, this type of energy storage devices is commercially attractive.

Chemical activation of chars with KOH is very powerful in developing micropores (Wu *et al.*, 2005c), which is recognized to favor the formation of surface oxygen functional groups (Lua and Guo, 2001). In this work, element analysis, TPD, specific capacitance, and specific resistance of KOH-activated carbons in various KOH/char ratios (Tseng and Tseng, 2005) are used to find the influences of micropore development on the chemical composition, distribution of surface functional groups, specific capacitance, and specific adsorption capacity of ACs. Through a comparison of the above information and the results of pore properties measured previously, the influences of physicochemical properties of ACs on the performances in adsorption of organics and EDLCs will be clarified.

2. Materials and methods

2.1. Preparation of carbons by KOH activation

Carbons were prepared from chars activated with KOH, which were carbonized from corncob; a typical two-step process. The preparation procedure has been described in our previous work (Tseng and Tseng, 2005). The weight ratio of KOH/char is set at 0.5, 1, 2, 3, 4, and 6 and the resultant ACs are denoted as CobK0.5, CobK1, CobK2, CobK3, CobK4, and CobK6, respectively.

2.2. Measurements of physicochemical properties

The BET surface area (S_p) of ACs was obtained from the N₂ adsorption isotherm at 77 K with a sorptometer (Porous Materials, BET-202A). The measurement steps and data processing were also described previously (Tseng *et al.*, 2006). Element analysis of ACs was performed using an elemental analyzer (Elementar Co., model Vario EL III).

2.3. Specific resistance measurement

The carrier template (1.5 cm × 1.5 cm) for preparing the test plate samples in the specific resistance measurement was prepared from degreased glass plates. Activated carbon powders were well mixed with 2 wt.% polyvinylidene difluoride (PVdF) binders for 30 min and then *N*-methyl-2-pyrrolidinone (NMP) was dropped into the above mixture and

ground for 30 min. The gas bubbles in the slurry were removed by means of an ultrasonic vibrator for 10 min. Then, the slurry was spread on the template with thickness of 1 ± 0.1 mm, which was dried in an oven at 85°C for 8 h to form the test plates. Four point probe surface resistor meter (Laresta-EP MCP-T360; Mitsubishi Chemical Co.) was used to measure the surface resistance of these test plates and the average value of five replications for each sample was reported in this work.

2.4. Electrode preparation

Activated carbon powders were well mixed with 2 wt.% PVdF binders for 30 min and NMP was dropped into the above mixture and ground to form the coating slurry. This slurry was smeared onto the pretreated graphite substrates and dried in a vacuum oven at 50°C overnight. In order to avoid any unexpected influences, the total amount of AC paste on each electrode was kept approximately constant (ca. 2 mg/cm^2). The pretreatment procedure of the $10\text{ mm} \times 10\text{ mm} \times 3\text{ mm}$ graphite supports (Nippon Carbon EG-NPL, NCK) completely followed our previous work (Wu *et al.*, 2005b). The exposed geometric area of these pretreated graphite supports is equal to 1 cm^2 while the other surface areas were insulated with polytetrafluorene ethylene (PTFE) coatings.

2.5. Capacitance measurements

The electrochemical measurements were performed by means of an electrochemical analyzer system, CHI 633A (CH Instruments). All experiments were carried out in a three-compartment cell. An Ag/AgCl electrode (Argenthal, 3 M KCl, 0.207 V vs. SHE at 25°C) was used as the reference and a platinum wire with an exposed area equal to 4 cm^2 was employed as the counter electrode. A Luggin capillary was used to minimize errors due to iR drop in the electrolytes. The electrolytes used for the electrochemical measurement were degassed with purified nitrogen gas for 25 min before measurements and this nitrogen was passed over the solutions during the measurements. The solution temperature was maintained at 25°C by means of a water thermostat (Haake DC3 and K20).

2.6. Procedure for adsorption experiments

Five solutes, acid blue 74 (AB74), basic brown 1 (BB1), methylene blue (MB), 2,4-di chloro-phenol (2,4-DCP), and 4-chlorophenol (4-CP) with their molecular weight of 466.4, 419.4, 284.3, 163.0, and 128.6 g/mol , respectively, are from Merck. The molecular structures of MB, BB1, and AB74, and the characteristics of chlorinated phenols and dyes have been detailed previously (Wu *et al.*, 2005c). The steps for the adsorption equilibrium experiments completely follow the procedure expressed in our previous study (Tseng *et al.*, 2003).

3. Results and discussion

3.1. Physical properties of activated carbon

The specific (BET) surface area (S_p), total pore volume (V_{pore}), and micropore pore volume ratio ($V_{\text{micro}}/V_{\text{pore}}$) of ACs were estimated from the adsorption/desorption isotherms of N_2 at 77 K in this study. Fig. 1(a)–(f), respectively, show the dependence of S_p , V_{pore} , $V_{\text{micro}}/V_{\text{pore}}$, yield (Y_p), bulk density (ρ_b), and ($Y_p \times S_p$) on the KOH/char ratio. There exists a discontinuity in these properties when the KOH/char ratio is changed from 2 to 3. Based on these phenomena, ACs are qualitatively divided into two groups: group I ACs with the KOH/char ratio varying from 0.5 to 2 and group II ACs with the KOH/char ratio from 3 to 6 (Tseng and Tseng, 2005). We believed that chars were activated by a combination of physical activated and chemical KOH etching to form group I ACs while they were homogeneously etched with KOH resulting in the development of micropores for group II ACs. The above statement is supported by the SEM photographs observed previously; i.e., a twisted outer morphology for group I ACs but smooth, flat surface for group II ACs (Tseng and Tseng, 2005). In Fig. 1(a), the specific surface area rises abruptly when the KOH/char is changed from 2 to 3 but V_{pore} monotonously and gradually increases in Fig. 1(b) although the slope for V_{pore} against KOH/char is started to change at the same range of KOH/char. The above phenomena are attributable to the fact that micropore development is the main reaction in the chemical activation process of chars as the KOH/char ratios are ≥ 3 . This statement is supported by the discontinuity of $V_{\text{micro}}/V_{\text{pore}}$ in the same KOH/char range in Fig. 1(c). Moreover, from the two straight lines in Fig. 1(c), two distinct mechanisms should involve in the activation process, resulting in the presence of groups I and II ACs. Fig. 1(d) shows that the yield of ACs at the KOH/char ratio of 0.5 is lower than that as the KOH/char ratio is equal to 1. This is probably due to the competition of the physical surface pyrolysis and chemical KOH etching when the KOH/char ratio is between 0.5 and 2. Note that a higher coverage of KOH onto the chars (i.e., high KOH/char ratio) will inhibit the physical surface pyrolysis meanwhile the chemical process of KOH etching will be promoted. Thus, yield reaches the highest value at the KOH/char ratio = 1. Fig. 1(e) shows that the bulk density of group I ACs monotonously decrease from 266 to 135 g/m^3 with increasing the KOH/char ratio while no significant variation is found for group II ACs (between 94 and 112 g/m^3). The lower bulk density of group II ACs is attributed to its pure KOH etching process which generates many micropores within the AC cake bread, observed previously in the SEM photographs (Tseng and Tseng, 2005).

It is important and meaningful to gain the information of the yield of BET surface area per unit mass of raw material in the AC researches because it provides the information for the economical assessment of AC preparation and the understanding on the pore variation during the activation process. Fig. 1(f) shows the yield of BET surface area per unit mass of raw material, expressed as $Y_p \times S_p$. In general, curves

Fig. 1. (a) BET surface area (S_p), (b) total pore volume (V_{pore}), (c) micropore pore volume ratio (V_{micro}/V_{pore}), (d) yield (Y_p), (e) bulk density (ρ_b), and (f) yield of BET surface area per unit mass of raw material ($Y_p \times S_p$) of corn-cob-derived, KOH-activated carbons.

corresponding to groups I and II ACs are parabolic. When there is no dosage of KOH (KOH/char ratio = 0), chars are completely activated through the physical pyrolysis process, and the yield of BET surface area per unit mass of raw material is only $46 \text{ m}^2/g$. When the KOH/char ratios equal 1 and 2, on the other hand, values of ($Y_p \times S_p$) are 239 and $238 \text{ m}^2/g$, respectively, which are larger than that of the purely physical pyrolysis AC and that of the steam-activated carbons derived from corn-cob (between 98.1 and $102 \text{ m}^2/g$) (Wu *et al.*, 2001) or pinewood (between 67 and $103 \text{ m}^2/g$) (Tseng *et al.*, 2003). The above enhancement in ($Y_p \times S_p$) is reasonably attributed to the simultaneous occurrence of the physical activation and chemical KOH etching for group I ACs. Moreover, it also suggests that ($Y_p \times S_p$) of a chemical activation process is much higher than those of a physical activation process (e.g., steam

activation). This reveals that chemical etching (by KOH) is much more powerful for micropore development in the interior of chars in comparison with the physical (steam) activation. This statement is supported by the much higher value of ($Y_p \times S_p$) for the pure KOH-activated carbons (i.e., group II ACs). In addition, the yield of BET surface area per unit mass of raw material reaches the highest value of $435 \text{ m}^2/g$ as the KOH/char ratio equals 4. When the ratio is above 4, an over-etching phenomenon is found and harmful to the generation of surface area of ACs.

3.2. Chemical composition of activated carbon

The results of element analysis are listed in Table 1 where corn-cob, cob-char, and CobK0 are respectively indicative of

Table 1
Chemical composition of corncob, char, and activated carbons

Materials	Elemental composition (wt.%)					H/C	O/C
	C	H	N	S	O _{diff}		
Corncob	46.33	6.87	2.49	0.246	44.06	0.150	0.951
Cob-char	74.19	4.38	2.26	0.438	18.73	0.059	0.252
CobK0	87.09	2.47	2.46	0.176	7.80	0.028	0.090
CobK0.5	80.16	2.87	1.57	0.146	15.26	0.036	0.190
CobK1	73.23	3.67	1.45	0.081	21.57	0.050	0.295
CobK2	72.34	3.97	0.97	0.083	22.63	0.055	0.313
CobK3	64.17	5.25	1.12	0.136	29.33	0.082	0.457
CobK4	63.20	5.03	1.34	0.059	30.38	0.080	0.481
CobK6	55.79	6.31	1.15	0.281	36.47	0.110	0.653

O_{diff}: the oxygen is assessed by difference.

raw material dried at 130 °C, carbonized char at 450 °C, and the carbon with physical activation at 780 °C with no KOH addition. The C content is increased from 46 to 87% with the carbonization of raw material and physical surface pyrolysis of chars but an opposite result is found for the contents of H and O, decreased respectively from 6.9 to 2.5% and from 44 to 7.8%. Actually, the composition of five wooden fiber materials (Minkova *et al.*, 2000), with their C content of 47.0–49.5%, H content of 4.6–6.2%, and O content of 43.7–46.7%, is close to that of corncob used in this work. For ACs derived from rice straw with pyrolysis in the oxygen-exhausted condition (Oh and Park, 2002), the contents of both H and O significantly decreased while the C content increased. The above studies and our results shown in this work reveal that carbonization of plant raw materials and physical pyrolysis of chars will cause the significant loss of H and O (probably in the forms of H₂O vaporization and/or CO₂/CO evolution). This effect increasing the C content is most likely due to the limited supply of oxygen.

There are few articles describing the element variations of ACs before and after the chemical activation. The contents of C, H, and O for ACs prepared from corncob and chemically activated with ZnCl₂ (Tsai *et al.*, 1998) were reported to be 90.31, 0.81, and 8.85%, respectively. In addition, the contents of C, H, and O for ACs prepared from palm shells and soaked with H₂SO₄ (Guo *et al.*, 2005) were found to be 83.3, 0.4, and 16.1%, respectively. The results from the above two examples indicates that the content of C is increased and both H and O are decreased when raw materials were chemically activated to form ACs. This trend is similar to that of ACs with the physical activation treatment. However, a reverse trend is found in this study; the C content is decreased from 80 to 56% and that of H and O is respectively increased from 2.9 to 6.3% and from 15 to 36% when the KOH/char ratio is increased from 0 to 6. The above result suggests that the C elements in chars will react with KOH to form oxygen-enriched surface functional groups during the chemical activation process.

For convenient evaluation of the above property, the element residue ratio (δX_i) is defined as the ratio of weight residue of a certain element in char during activation to the weight content of that element in char ($X_{i,\text{char}}$), which can be

calculated as

$$\delta X_i = \frac{X_i \times Y_{i,p}}{X_{i,\text{char}}} \quad (1)$$

where X_i indicates the mass of element i (i.e., C, H, or O) per unit mass of AC. $X_{i,\text{char}}$ is the mass of the corresponding element per unit mass of char. $X_i \times Y_{i,p}$ is indicative of the residual mass of the element i per unit mass of char. Based on the above definitions, δ_i will be equal to 1 if no loss in mass during the activation process is found for the element under study. A low value of δX_i indicates a more loss of the element, implying its higher reactivity to KOH.

Fig. 2 shows the dependence of δC , δH , and δO on the KOH/char ratio. When the KOH/char ratio is increased from 0 to 1, the coverage of KOH onto the chars is increased, which gradually inhibits the physical activation on the surface of chars. Thus, the residue ratios of H and O are obviously increased from 0.24 to 0.53 and from 0.18 to 0.72, respectively. On the other hand, as the KOH/char ratio is increased from 0 to 0.5, the residual ratio of C is also increased obviously from 0.49 to 0.64 while a decrease in this property is found when the KOH/char ratio is above 0.5. This phenomenon is considered as a sign for the significant contribution of another activation process, i.e., the chemical etching of chars by KOH. This chemical etching is considered to mainly consume C elements in chars and a decrease in the residual ratio of C is found. Note the relatively high dosage of KOH as the KOH/char ratio ranges from 3 to 6 while the residual ratios of both H and O are nearly constant (from 0.58 to 0.65 and from 0.82 to 0.87, respectively). This phenomenon suggests that the consumption (and reaction mechanism) of H and O during the KOH activation are approximately constant when the KOH/char ratio is between 3 and 6. However, the residual ratio of C significantly drops from 0.47 to 0.34 in the same region of KOH/char ratio. The above results suggest that a chemical reaction between KOH and C elements in the char favor the development of micropores. Investigate elements H, O, and C. In the range of KOH/char ratios from 0 to 1, H and O increased with increased KOH consumption. This showed that increased KOH coverage could decrease physical activation; and in the range of KOH/char

Fig. 2. Element residue ratios of H, O, and C (δH , δO , and δC) of corncob-derived, KOH-activated carbons.

ratios from 3 to 6, H and O were almost constant. It meant that sufficient KOH coverage inhibited physical activation.

3.3. Activation mechanism

C_f -KOH reaction is described as (Yang and Lua, 2003):

It is believed that after a serial of reactions during KOH activation, the last product is K_2CO_3 .

Metal potassium (K) is produced during K_2O activation at temperature exceeding 700°C . The possible reactions might be as follow:

To K_2O , Eqs. (5)–(7) are parallel reaction mechanisms. That which reaction mechanism is the main reaction is not easy to be determined. Because the activation temperature was 780°C , the boiling point of potassium, in the study, if the reaction were according to Eqs. (6) and (7), the product element potassium would lose in large amount through vent and exhaust of reaction furnace. From our experimental observations, up to 83% of potassium could be recovered. That is 17% of potassium was lost and 83% of it remained in the final products. This revealed that the main reaction mechanism was Eqs. (2)–(5) in this work. Furthermore, from element residue ratio of H, O, and C, it was found that C loss was much higher the other two elements. It can be inferred that reaction between KOH and C is the main reaction. Thus this paper neglects description on reaction mechanism of H and O.

3.4. Surface functional groups of activated carbons

The main surface functional groups present in the char were reported to be carbonyl groups (e.g. ketone and quinone) and aromatic rings (Arriagada *et al.*, 1997; Gome-Serrano *et al.*, 1996; Lua and Guo, 2001) from the findings of chars derived from peach stone (Arriagada *et al.*, 1997) rookose (Gome-Serrano *et al.*, 1996), and oil-palm stones (Lua and Guo, 2001). For ACs activated at high temperatures (e.g., 900°C) and long activation time (e.g., 60 min) with CO_2 , only aromatic rings remained (Lua and Guo, 2001) since most oxygen-containing functional groups will be desorbed. Due to the fact that significant amount of H and O elements have been found in the KOH-activated carbons in the element analysis results, their surface functional groups should be more fruitful than those described in previous studies. Moreover, the distribution of surface functional groups is usually dependent on the preparation variables for the chemically activated carbons. This property of our KOH-activated carbons will significantly

influence their performances in several applications (Sun *et al.*, 1996; Wu *et al.*, 2005b). Based on this reason, the surface functional groups of ACs are semi-quantitatively analyzed by means of temperature-programming desorption (TPD) in this work (Cheng and Teng, 2003). Typical evolution profiles of CO_2 and CO determined by the TPD method for CobK1 and CobK4 are shown in Fig. 3.

It is well known that CO_2 mainly desorbs under relatively low temperatures (i.e., $<550^\circ\text{C}$), which has been attributed to the presence of anhydrides, lactones, and carboxyl groups (Molina-Sabio *et al.*, 1996; Qu, 2002; Yoshizawa *et al.*, 2000). On the other hand, desorption of CO species, attributable to quinone, hydroxyl, and carbonyl groups, occurs predominately at relatively higher temperatures (ca. above 500°C) (Cheng and Teng, 2003; Kinoshita, 1988; Otake and Jenkins, 1993). Hence, the distribution of oxygen functional groups can be roughly estimated from the TPD results. A comparison of the curves in Fig. 3 reveals several features. First, the relative intensities of CO_2 and CO evolution are increased with increasing the KOH/char ratio. Accordingly, the density of all surface functional groups on CobK4 should be higher than that of CobK1. Second, the increase in the area under the curve corresponding to the CO desorption is more obvious than that that corresponding to the CO_2 evolution when the KOH/char ration is changed from 1 to 4. This suggests that CobK4 should be enriched with the quinone, hydroxyl, and/or carbonyl groups which are electrochemically active. The above results reveal that ACs activated with KOH at a higher KOH/char ratio reserve more fruitful functional groups, especially for the functional groups evolving CO. On the other hand, due to the fact that activation of chars at a low KOH/char ratio has to suffer the physical activation, certain amount of the surface functional groups will lose during the activation process, somewhat similar to the results of physically activated carbons (Lua and Guo, 2001).

3.5. Equilibrium adsorption isotherms for phenols and dyes

Adsorption of organics is studied in this work because ACs with high specific surface area is appropriate for the adsorption of solutes in liquid phase (Tseng and Tseng, 2005). In this work,

Fig. 3. Evolution profiles of CO_2 and CO by temperature-programming desorption for (---) CobK1-AC and (- · - · -) CobK4-AC.

Table 2

Fitting results for the parameters of Langmuir and Freundlich equations for the adsorption of MB, BB1, and AB74 solutes on corncob-derived ACs at 30 °C

Solute	Adsorbent	Langmuir		Freundlich		
		q_{mon} (mol/kg)	Δq_e (%)	$1/n$	K_F (mol/kg) (mol/m ³) ⁿ	Δq_e (%)
MB	CobK0.5	0.44	2.05	0.012	0.44	0.65
	CobK1	1.14	2.75	0.025	1.11	0.81
	CobK2	1.47	1.74	0.023	1.43	1.63
	CobK3	2.34	1.98	0.045	2.27	1.50
	CobK4	2.49	4.37	0.049	2.42	2.45
	CobK6	3.56	5.04	0.078	3.67	4.60
BB1	CobK0.5	0.93	5.93	0.092	0.86	2.54
	CobK1	1.80	4.26	0.149	1.60	1.53
	CobK2	1.96	3.60	0.131	1.86	2.49
	CobK3	2.81	6.61	0.227	2.69	3.63
	CobK4	3.16	4.86	0.285	3.10	3.80
	CobK6	4.08	6.58	0.273	4.39	3.49
AB74	CobK0.5	0.25	6.61	0.239	0.22	4.68
	CobK1	0.43	2.36	0.192	0.42	2.24
	CobK2	0.53	5.47	0.176	0.53	3.12
	CobK3	1.19	2.91	0.146	1.31	1.70
	CobK4	1.51	6.46	0.186	1.01	4.64
	CobK6	1.86	9.09	0.200	2.52	4.90

adsorption isotherms of dyes (MB, BB1, and AB74) and chlorinated phenols (4-CP and 2,4-DCP) on corncob-derived ACs at 30 °C are measured to fit suitable theoretical and empirical equations. Tables 2 and 3 list the fitting values of parameters for the Langmuir and Freundlich isotherm equations, respectively, for the adsorption of the above five organics in aqueous solution. The parameter symbols and data processing of Langmuir and Freundlich isotherm equations follow the same way of our previous study (Wu *et al.*, 2005d).

In order to quantitatively compare the validity of the two isotherm equations under study, a normalized standard deviation, Δq_e (in %), is defined as follow:

$$\Delta q_e (\%) = \sqrt{\frac{\sum [(q_{e,\text{exp}} - q_{e,\text{cal}})/q_{e,\text{exp}}]^2}{N - 1}} \times 100 \quad (8)$$

Table 3

Fitting results for the parameters of Langmuir and Freundlich equations for the adsorption of 4-CP and 2,4-DCP solutes on corncob-derived ACs at 30 °C

Solute	Adsorbent	Langmuir			Freundlich
		q_{mon} (mol/kg)	K_L (m ³ /mol)	Δq_e (%)	Δq_e (%)
4-CP	CobK0.5	1.61	26.3	1.43	7.04
	CobK1	2.26	9.54	1.52	1.90
	CobK2	2.61	35.8	1.97	7.48
	CobK3	4.01	11.1	3.96	12.5
	CobK4	4.69	5.32	2.09	7.92
	CobK6	5.87	7.15	3.73	8.43
2,4-DCP	CobK0.5	2.27	8.39	1.65	2.34
	CobK1	3.42	6.46	2.23	3.73
	CobK2	3.66	25.5	0.69	1.03
	CobK3	5.95	28.1	1.09	4.25
	CobK4	7.84	140	1.13	3.77
	CobK6	8.47	76.6	1.62	3.52

Table 2 shows that the normalized standard deviation, Δq_e , of Langmuir equation is larger (from 1.74 to 9.09%) than that of Freundlich equation (from 0.65 to 4.90%). Table 3 indicates that the results of phenol adsorption is better described by the Langmuir equation with Δq_e from 0.69 to 3.96% in comparison with the Freundlich equation with Δq_e from 1.03 to 12.5%. Although the empirical Freundlich equation more suitably describes the adsorption data of dyes with larger molecular weights, for studying the relationship between the adsorption capacity and KOH/char ratio, the physically meaningful Langmuir parameter, q_{mon} , is employed for a comparison purpose.

Adsorption capacity of ACs was found to depend on the features of (a) the physicochemical properties of adsorbents (e.g., surface area, pore size distribution, and functional groups), (b) the physicochemical properties of adsorbates (e.g., molecular weight and size, solubility, polarity, hydrophobic property, functional groups, and pK_a for weak acids or bases), and (c) solution properties (e.g., pH, adsorbate concentration, temperature, presence of competitive solutes, polarity of solvent, etc.). In this work, a parameter, q_{mon}/S_p , was used to evaluate the adsorption capacity per unit surface area (i.e., specific adsorption capacity) of ACs activated in different dosages of KOH for various organics. Based on this definition, the influence of feature (a), the physicochemical properties of ACs, on the specific adsorption capacity for all adsorbates can be systematically investigated since features (b) and (c) are considered to be unchanged.

Fig. 4 shows the dependence of q_{mon}/S_p for dyes (MB, BB1, and AB74) and chlorinated phenols (4-CP and 2,4-DCP) on the KOH/char ratio. The q_{mon}/S_p values for the AC prepared at the KOH/char ratio = 0.5 are very different from the others, probably due to the fact that activation of chars at the KOH/char = 0.5 is mainly contributed by the physical pyrolysis process. For the ACs with their KOH/char ratios from 1 to 6, on the other hand, the q_{mon}/S_p values are approximately the same

Fig. 4. The amount of adsorption corresponding to monolayer coverage of MB, BB1, and AB74 and 4-CP, and 2,4-DCP on corn-cob-derived, KOH-activated carbons.

for any specified organic. This indicates that all ACs exhibit very similar specific adsorption capacity for the above five organics and that the specific adsorption capacity for any one of the five organics is independent of the physicochemical properties of ACs although ACs prepared at different KOH/char ratios generally show very different physicochemical properties. The above phenomenon is attributed to the formation of uniform micropores in the ACs chemically activated by KOH, which is approximately independent of the dosage of KOH when the KOH/char ratio is above a critical value (e.g., 1.0 in this study). In our previous study (Wu *et al.*, 2005d), ACs derived from firwoods with steam activation showed the BET surface area ranging from 527 to 1131 m^2/g . The q_{mon}/S_p values were approximately constant for the adsorption of MB while a loss in the q_{mon}/S_p value up to 32% with increasing the BET surface area for the adsorption of 4-CP was found. This different phenomenon was attributed to the decrease in the proportion of micropores for the steam-activated carbons with increasing the BET surface area, which is harmful to the adsorption of small molecular substances (Wu *et al.*, 2005d).

3.6. Capacitive characteristics of activated carbons

The electrochemical behavior of all KOH-activated carbons was measured to demonstrate the dependence of capacitive performances on the physicochemical properties of ACs. Group I ACs (with the KOH/char ratios of 0, 0.5, 1, and 2) measured in 1 M NaNO_3 at 25 mV/s are shown in Fig. 5(a). Note that all curves in the whole potential region are capacitive-like, indicating that capacitance mainly comes from the double-layer charge/discharge process. In addition, all i - E curves on the positive sweeps are symmetric to those on their corresponding negative sweeps although an irreversible oxidation is found at potentials positive than ca. 0.8 V. The former results indicate that all ACs exhibit the excellent capacitive property in NaNO_3 . The latter result is attributable to the oxygen evolution reaction. Note that voltammetric currents are gradually increased with increasing the KOH/char ratio from 0 to 2, due to the increase in the specific surface of ACs

Fig. 5. Cyclic voltammograms measured at 25 mV/s in 1.0 M NaNO_3 for (a) CobK0, CobK0.5, CobK1, and CobK2; (b) CobK3, CobK4, and CobK6.

with increasing the KOH/char ratio (see Fig. 1(a)). Also note the low ESR of these ACs since the voltammetric currents rapidly reach the plateau values on the positive sweeps of all curves when the direction of potential sweeps is changed from negative to positive. A low ESR should come from a combination of a good electronic conductivity of electrode materials (i.e., ACs) and a low ionic resistance of the electrolyte within the pores of ACs during the charge/discharge tests. From all the above results and discussion, KOH-activated carbons from corn-cob with the KOH/char ratio varying from 0.5 to 2 show the promising potential to supercapacitors.

The CV responses of group II ACs measured in 1 M NaNO_3 at 25 mV/s are shown in Fig. 5(b), which are very similar in shape to the i - E curves in Fig. 5(a). As found previously, a higher specific surface area, a larger pore volume, and a higher density of surface function groups were obtained when the KOH/char ratio was increased. This result should promote the capacitive current density of ACs with increasing the KOH/char ratio from 3 to 6 but an opposite result is obtained. Reasons responsible for this conflict will be clarified in the next section.

The influence of KOH dosage during the activation of chars on the capacitive current density of resultant ACs measured in 0.5 M H_2SO_4 (see Fig. 6) is very similar to that observed in Fig. 5. On the other hand, the capacitive current densities obtained in H_2SO_4 are generally higher than that of the corresponding AC measured in the neutral electrolyte (Fig. 5).

Fig. 6. Cyclic voltammograms measured at 25 mV/s in 0.5 M H_2SO_4 for (a) CobK0, CobK0.5, CobK1, and CobK2; (b) CobK3, CobK4, and CobK6.

This phenomenon has been found in our previous work (Wu et al., 2004, 2005b, 2006), which was found to be independent of the activation methods. The above difference in voltammetric currents is attributable to (i) the better conductivity of acidic electrolytes due to the proton hopping mechanism (Wu et al., 2004); (ii) the increase in the electrochemically accessible surface areas of these highly porous carbons because of the excellent mobility of protons in the acidic medium; (iii) the redox reactions of surface functional groups involving the exchange of electrons and protons. Recently, effects of pH on the specific capacitance of carbon cloth electrodes have been systematically investigated by Anderas and Conway (2006). A 30% loss in specific capacitance has been attributed to the disappearance of the redox transition of surface quinone groups when pH of the electrolytes is varied from 0 to 11, further supporting our statements.

The effect of KOH dosage in the char during the chemical activation on the specific capacitance (C_s) of ACs is clearly shown in Fig. 7. In this work, the specific capacitance of ACs is estimated from the CV curves according to the following equation (Hu and Wang, 2004):

$$C_s = \frac{q^*}{\Delta E \times w} \quad (3)$$

where C_s , q^* , ΔE , and w indicate the specific capacitance, voltammetric charges integrated from the negative sweeps, potential window of CV, and mass of ACs, respectively. Note

Fig. 7. The dependence of specific capacitance (C_s) measured in NaNO_3 and H_2SO_4 , and specific resistance (R_s) of corncob-derived, KOH-activated carbons on the KOH/char weight ratio.

that C_s reaches a maximum value when the KOH/char ratio is equal to 3 and that the highest values of C_s in NaNO_3 and H_2SO_4 are equal to 106 and 127 F/g, respectively. Actually, ACs may be over etched by the formation of too many micropores, which will reduce their electronic conductivity, probably resulting in the lower specific capacitance. Hence, the specific resistance (R_s) of all ACs was measured and represented in Fig. 7. In this figure, the specific resistance of ACs is approximately independent of the KOH dosage when the KOH/char ratio is equal to/below 2. On the other hand, as the KOH/char ratio is increased from 2 to 6, R_s rises very obviously. The increase in R_s is attributable to the breakage of carbon/graphite chains due to an over-etching of ACs as well as the simultaneous formation of surface oxygen functional groups when the KOH/char ratios are above 2. Based on the above results and discussion, C_s will increase with the continuous increase in S_p for group I ACs because their specific resistance is approximately constant. For group II ACs, a compromise between increasing S_p and decreasing R_s results in the maximum C_s for the AC with the KOH/char ratio equal to 3 and C_s will monotonously decrease with the continuous development of micropores.

Based on the above findings, ACs with low R_s is ideal for the supercapacitor application. Note that C_s of group II ACs with the KOH/char ratio of 3, 4, and 6 was expected to be 148, 188, and 269 F/g in 1.0 M NaNO_3 if their R_s was kept as low as that of group I ACs. Although the problem for the high specific resistance of ACs is not solved in this work, the above information is helpful in screening the raw materials and activation methods for searching ACs with high specific surface area and low specific resistance for the application of supercapacitors.

4. Conclusions

According to the discontinuity in several physical properties of ACs chemically activated at various KOH/char ratios, two competitive reaction paths for the pore development are proposed to dominate the activation process: physical activated and etching of carbon with KOH. Very low and high yields of

BET surface area per unit mass of raw material (in terms of $S_p \times Y_p$), 46 and 435 m²/g, are found for the former and latter paths, respectively. From the element residue ratio of C, H, and O, physical activation causes a large drop in the residue ratio of H and O while KOH etching in chars shows high O and H residual ratios, attributable to the main consumption of C in this activation method. From TPD, KOH etching promotes the formation of surface oxygen functional groups, especially for quinone, hydroxyl, and carbonyl groups. The specific resistance of ACs starts to rise with increasing the dosage of KOH at the KOH/char ratio of 2, attributable to the over-etching of chars and the formation of surface oxygen functional groups. For the specific capacitance, the maximum C_s of the AC with the KOH/char ratio equal to 3 results from a compromise between increasing S_p and decreasing R_s . However, this property does not affect the specific adsorption capacity of ACs for all organics studied in this work.

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