PREPARATION AND SURFACE ACID-BASE PROPERTIES OF POROUS CELLULOSE

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Porous cellulose beads were prepared by solubilizing cellulose in sodium hydroxide/urea/sulfourea aqueous solution and then solidifying liquid beads in hydrochloric acid. Scanning electron microscopy (SEM) was used to characterize the morphologies of surface, cross section, and wall structures of the porous cellulose beads, which are folded and porous. The surface acid-base properties of porous cellulose beads were characterized in detail by inverse gas chromatography (IGC). The Lewis basic number K_b was found to be 0.854, which is indicative of a Lewis basic polymeric material. With the discussion of the results of SEM and IGC, a conclusion can be drawn that the porous cellulose beads showed a good ability of adsorbing the smoking tar of cigarettes.

Keywords: Preparation; Characterization; Porous cellulose beads; Inverse gas chromatography; Scanning electron microscopy

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INTRODUCTION

Cellulose and modified cellulose have recently been investigated (Siva et al. 2002) because of wide applications such as adsorbent materials, biodegradable materials, and so on. Especially they, as biodegradable adsorbent materials (Ronny et al. 2006), are widely used in wastewater treatment, absorbent industry, and medication adsorption. Cellulose can interact with adsorbates through hydrogen bonding, complexation, and other interactions. As an adsorbent (Stanley-wood et al. 1986; Liu et al. 2005), in general, cellulose is prepared to be spherical beads to enhance their surface area and adsorbing ability. Many methods have been used to prepare cellulose beads. For example, cellulose beads were prepared by using a solution of cellulose/NMMO/H_2O and sequential cooling, using a reversed-phase suspension technique (Liu et al. 2007).

Smoking tar is of great concern because of the toxic effect to the human beings (Kitamura et al. 2007). Smoking tar contains thousands of harmful substances, such as condensed ring aromatics, phenol, nitrogen-containing compounds and so on (Rustemeier et al. 2002). They could cause acute and even fatal effects when a large dosage is ingested. Evidence has shown that smoking tar is a human carcinogen and causes severe harm to the healthy. Many materials have been studied as adsorbents to remove tar from cigarette smoke, such as, activated carbon and molecular sieves. The investigation has focused on the preparation and characterization of cellulose beads (Liu et al. 2005; Zhou et al.2005; Li et al. 2005) for adsorbing smoking tar (Bi et al. 2005; Singh et al. 2004).

Sorption measurements are very common in the characterization of solid/gas interfaces for various materials (Voelkel 2004; Sun and Berg 2003; Erika 2004). The intermolecular interactions can be classified into two categories, the Lifshitz–van der Waals (LW) interaction and the acid–base (AB) interactions. Since the magnitude of AB interactions is sometimes as much as an order of magnitude stronger than that of LW interactions, they sometimes play a dominant role in adsorption interface related phenomena (Adam 2004; Shi et al. 2007). Inverse gas chromatography is a powerful technique for investigating the acid-base properties of solid surfaces in porous form (Tayssir et al. 2002; Wu et al. 2004; Thielmann 2004; Frank et al. 2004; Narjès et al. 2007). It offers an alternative to the conventional gravimetric or volumetric methods for determining adsorption equilibrium isotherms, due to its simplicity, shorter measurement time, and a wider range of experimental possibilities. It has become widely utilized in recent years.

The Mechanism of Measuring Surface Acid-Base Properties by IGC

Inverse gas chromatography is a useful technique in evaluating the potential for interaction of different components of polymer blends, composites, and multicomponent polymeric systems (Sun et al. 2003; Prithu et al. 1995; Gutierreza, et al.1999; Jean. et al. 1991).

The direct data obtained from IGC is the net retention volume, V_n, given by:

$$V_n = (t_r - t_0)FCJ \tag{1}$$

Here, t_r is the retention time taken for the probe solvent, t_0 that for the non-interacting probe, F is the flow rate of carrier gas in ml/min, and J is the term correcting for the compressibility of the carrier gas, such that:

$$J = 1.5\frac{(P_i / P_o)^2 - 1}{(P_i / P_o)^3 - 1} \tag{2}$$

In Eq. (2), P_i and P_o are the inlet and outlet pressure of carrier gas, respectively. C is a correction factor, allowing for the vapor pressure of water at the temperature of bubble flow meter used to determine the flow rate.

$$C = 1 - P_{\mathrm{H_2O}} / P_o \tag{3}$$

where $P_{\mathrm{H_2O}}$ is the saturated vapor pressure of water at ambient temperature.

$$-\Delta G_a = RT\ln(V_n) \tag{4}$$

Here ΔG_a is the total free energy of adsorption of probe, R is the gas constant, T is the temperature of column, and V_n is the net retention volume.

The Lewis acid–base properties are calculated from ΔG_a, the contribution to the free energy of adsorption by Lewis acid–base (specific) interactions when polar (specific) solvents are injected into the chromatographic column. The expression is:

$$\Delta G_a = \Delta G_a^d + \Delta G_a^s \tag{5}$$

where ΔG_a^d is the dispersive contribution to the total free energy of adsorption, which is determined with *n*–alkanes, and ΔG_a^s is the contribution to the free energy of adsorption by Lewis acid–base (specific) interactions when polar (specific) solvents are injected into the chromatographic column.

From Eqs. (4) and (5), $-\Delta G_a^s$ may be defined as:

$$-\Delta G_a^s = RT \ln\left(\frac{V_n}{V_{n,ref}^d}\right) \tag{6}$$

where, V_n and $V_{n,ref}^d$ are the retention volumes of the polar probe and derived from the n-alkane reference line, i.e. ΔG_a^s results from the distance between the $RT\ln(V_n)$ value of polar solvent and the straight *n*–alkane line.

The enthalpy of specific interactions ΔH_a^s can be determined by studying the variation of ΔG_a^s with the temperature according to following equation (7):

$$\Delta G_a^s = \Delta H_a^s - T\Delta S_a^s \tag{7}$$

where ΔS_a^s is the specific entropy of adsorption. The results of ΔH_a^s were from the slope of the plot of $\Delta G_a^s / T$ vs. 1/*T*. The Lewis acid number K_a and Lewis base number K_b are calculated according to Eq. (8):

$$-\Delta H_a^s = K_a \times DN + K_b \times AN^* \tag{8}$$

In this expression, *DN* and AN^* are the Gutmann's Donor and modified Acceptor numbers of probes, respectively. Plotting $-\Delta H_a^s / AN^*$ against DN / AN^* usually produces a linear correlation, the slope and intercept of which give K_a and K_b, respectively.

EXPERIMENTAL

Materials

Cellulose was purchased from Shandong Gaomi Chemical Fiber Corporation. The degree of polymerization (DP) was 500~600. Blowing Agent AC ($C_2H_4N_4O_2$) was purchased from Tianjing Yongchangsheng Chemical Corporation. Sodium hydroxide, urea, and sulfourea were analytical grade, which were purchased from Beijing Yili Chemical Regents Corporation. For the IGC analysis, the apolar *n*-alkanes probes were *n*-pentane (C_5), *n*-hexane (C_6), *n*-heptane (C_7), *n*-octane (C_8), *n*-nonane (C_9), and *n*-pentane (C_{10}). The polar probes were trichloromethane (TCM), ethyl acetate (Acet.), diethyl ether (ether), and tetrahydrofuran (THF). *n*-pentane (C_5) was taken as the non-interacing probe in this experiment, because the retention time of it was the shortest among all the probes. They are analytical grade solvents and were purchased from Tianjin Kermel Chemical Reagents Development Centre, China. The characteristics of the probe solvents are listed in Table 1.

Table 1. The Characteristics of Probe Solvents

Probe	α(Å^2)	r_l^d(mJ·m^{-2})	$\alpha(r_l^d)^{0.5}$(Å^2(mJ·m^{-2})$^{0.5}$)	AN*(kJ·mol^{-1})	DN (kJ·mol^{-1})
n-C_5	46.1	16.0	184	-	-
n-C_6	51.5	18.4	221	-	-
n-C_7	57.0	20.3	257	-	-
n-C_8	63.0	21.3	291	-	-
n-C_9	69.0	22.7	329	-	-
n-C_{10}	75.0	23.4	363	-	-
TCM	44.0	25.9	224	22.7	0.0
Acet.	48.0	16.5	195	6.3	71.8
Ether	47.0	15.0	182	5.8	80.6
THF	45.0	22.5	213	2.1	84.4

α is molecular area of probe; r_l^d is surface free energy of probe; AN* and DN are the Gutmann's modified acceptor number and donor number of probe, respectively.

Preparation of the Porous Cellulose Beads

Cellulose material with 500-600 degree of polymerization was dispersed into an aqueous solution consisting of 8%~12% sodium hydroxide and 6~12% urea /sulfourea at –10 °C (Ruan et al. 2004; Miani et al. 2004). The above mixture was stirred to obtain a viscose, and then a small amount of blowing agent AC was added. The viscose containing bladders were injected into a centrifugal machine to prepare spherical drops, and the spherical drops were solidified in 5% hydrochloric acid aqueous solution to obtain shaggy beads, and then washed and dried at 105 °C for 4 hours. Finally, we obtained porous cellulose beads with 210~270g·L^{-1} packing density and 280~380 μm diameters.

Characterization Method

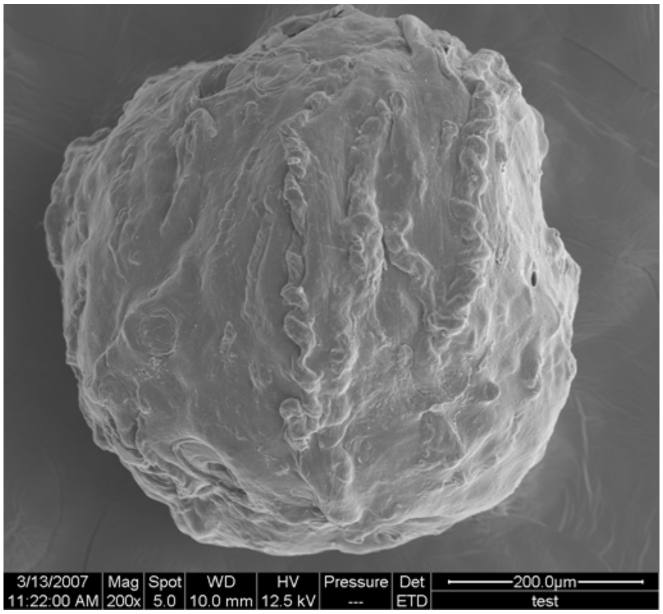
The IGC instrument was a GC-900A gas chromatograph (Shanghai TianPu Analytical Instrument Ltd., China) equipped with a flame ionization detector (FID). Nitrogen was used as the carrier gas. The flow rate was 14.39 mL·min^{-1}, measured from the end of the column with a soap bubble flow meter. The injector and FID were heated to 140 ^{o}C. The probe solvents were injected manually, using a 1.0 μL Hamilton syringe. The injection volumes were 0.1 μL. The column was a stainless steel tube (0.5 m length, 2.56 mm i.d.). It was washed with acetone prior to use. The porous cellulose beads were aged at 100 ^{o}C for 8 h. A weighed amount of 1.0492 g (120–140 mesh) was packed into the column. The IGC experiments were performed at 50, 60, 70, and 80 ^{o}C.

The samples were coated with gold to prevent electrical charging and were observed by a QUANTA 200 Scanning Electron Microscope under vacuum at an acceleration of 20kV.

RESULTS AND DISCUSSION

SEM Characterization

Figure 1, part (a) shows the apparent surface morphological structure of a porous cellulose bead. There are a lot of draped and porous structures on the surface. Part (b) shows the cross-section of a porous cellulose bead. Many cavities were distributed in the interiors of the beads. Draped and porous structures were formed by the blowing agent AC. These structures were considered to be beneficial to absorption properties of the porous cellulose beads. Part (c) shows the inner wall surface and cavities, which enlarge the surface area. The inter- and intra-structures allow the material to interact effectively with adsorbents.



(a)

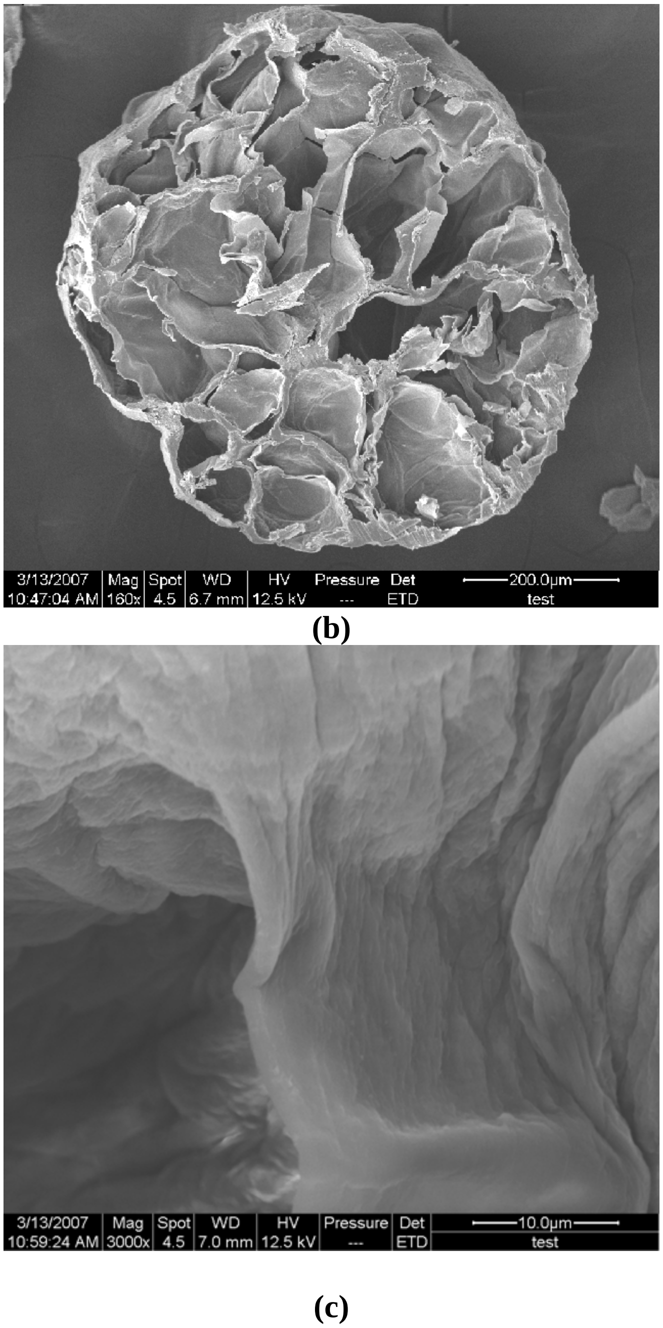


Fig.1. Morphological structure of porous cellulose beads by SEM **(a)** SEM image of apparent surface morphological structure **(b)** SEM image of cross-section **(c)** SEM image of wall surface of cavities.

IGC Surface Characterization

Figure 2 shows a plot of ln(V_n) against 1000/T for *n*-alkanes and polar probes in an IGC experiment. Linear relationships of the plots were obtained. From the values of net retention volumes of the probes, the surface properties of cellulose beads were determined.

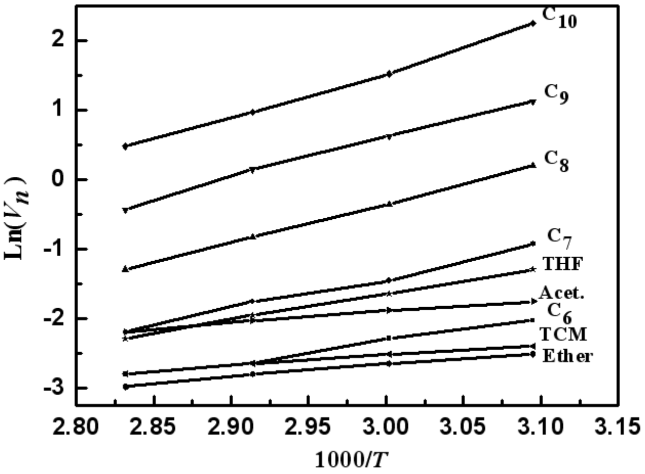


Fig.2. Plot of ln(*V*n) against 1000/T for *n*-alkanes and polar probes

Figure 3 shows results of the free energy of adsorption by Lewis acid-base interactions ΔG_a^s for the polar probes adsorbed on porous cellulose beads at 323.15K. Table 2 lists the data for ΔG_a^s measured at the absolute temperatures shown.

Table 2. The Data of ΔG_a^s Measured at Various Absolute Temperatures

T (K)	323.15	333.15	343.15	353.15
TCM	-1.31	-0.55	0.50	1.22
Acet.	2.71	3.42	4.32	4.99
Ether	1.73	2.31	3.04	3.57

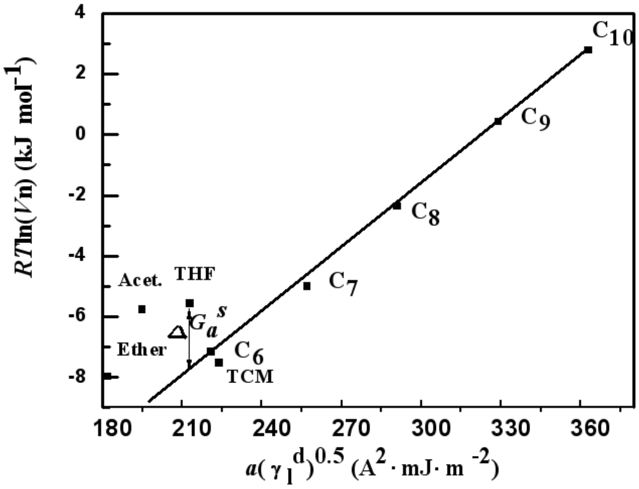


Fig.3. ΔG_a^s for the polar probes adsorbed on porous cellulose bead s at 323.15K

According to Eq (7), the enthalpies of specific interaction ΔH_a^s of all polar probes were obtained from the free energy of specific interactions listed in Table 3. The results are listed in Table 3.

Table 3. The Enthalpies of Specific Interaction ΔH_a^s of all Polar Probes

Probe	TCM	Ethyl acetate	Ether
$-\Delta H_a^s$	18.76	13.10	9.89

Figure 4 shows a plot of $-\Delta H_a^s / AN^*$ against DN / AN^* for polar probes. A fine linear correlation was obtained for the three polar probes. The Lewis acidic number K_a was 0.081, obtained from the slope, and the basic number K_b was 0.854, obtained from the intercept. The result implies that the cellulose bead sample was a Lewis base polymer. This can be elucidated from cellulose molecular structure. The repeated segment of cellulose consists of glucose units, and each unit has hydroxyl groups. The lone electron pairs of oxygen atoms of hydroxyl groups must endow cellulose with a strong Lewis basic property. (Santos et al. 2002; Ceyda et al. 2007).

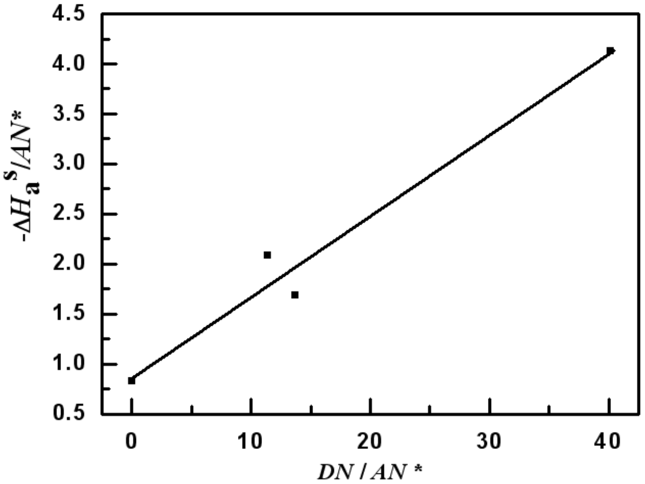


Fig.4. A plot of $-\Delta H_a^s / AN^*$ against DN / AN^* for polar probes

CONCLUSIONS

Porous cellulose beads were obtained by a basic solution–acid solidification method. The surface of the porous cellulose beads was rough, and the inner structures contained many cavities based on scanning electron microscopy. Surface properties of the beads, such as the Lewis acidic number K_a and basic number K_b, were measured by the inverse gas chromatography method. K_a and K_b were 0.081 and 0.854, respectively. The results indicated that the porous cellulose beads were Lewis basic polymeric materials. On the other hand, inter- and intra-surface of the beads contained abundant hydroxyls, which can interact with condensed ring aromatics, phenol compounds by p-π conjugation. These facts showed a good ability of adsorbing smoking tar of cigarettes, which has been proved by the cigarette company.

ACKNOWLEDGMENTS

The authors gratefully thank for the financial supports by Heilongjiang Science Fund for Distinguished Young Scholars (Grant no. JC04-06).

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Article submitted: Sept. 12, 2007; First round of peer-review completed: Oct. 29, 2007; Revised version received and accepted: Nov. 5, 2007; Publication: Nov. 5, 2007.