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Promoter action of sulphur on the stabilization of pitch spheres

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Elemental sulphur was added into the starting pitch during the preparation of pitch-based spherical activated carbon in order to enhance the stabilization of pitch sphere. Pitch sphere (diameter 0.65–1.0 mm) without adding sulphur needs slow heating rate of 0.5 °C/min, high final temperature of 300 °C and long holding time of 20 h for the successful stabilization in air. While adding elemental sulphur with 2.5–10.0 wt % in total amount into starting pitch decreased the stabilization time significantly, pitch sphere containing 5.0 wt % of sulphur can be stabilized in air very easily at heating rate of 2.0 °C/min up to 270 °C without any holding time, and the successful stabilization time was only 3 h. Pitch molecules reacted with sulphur and some sulphur functional groups, such as C−SH, C−S−C, C=S, O=S=, O=S=O etc., were formed besides the oxygen functional groups under the stabilization condition. All of these sulphur functional groups acted as bridge bonds to make the pitch molecules polymerized so as to high up the softening point of pitch spheres, making the pitch spheres stabilized. Three kinds of sulfocompounds, i.e. H_2S, COS and CS_2 evolved in stabilization process. © *1999 Kluwer Academic Publishers*

1. Introduction

Granular activated carbons made from coal or coconut shells have been commercialized for many years and used in many fields [1–5]. However, the application field of such active carbons was limited because of its insufficient performance. Adsorbents of spherical shape, high mechanical strength and adsorption capacity are requested.

Pitch-based spherical activated carbon of ca. 0.65–1.0 mm diameter with high purity, high mechanical strength and reasonable surface area around 1000 m^2/g is recognized as an excellent adsorbent. Such spherical activated carbon has been prepared from several sources [6–8], where its preparation is intended from commercial available coal tar pitch. So far the remained problem is that the stabilization of the pitch sphere in air to maintain its shape at the successive carbonization is slow, because the diffusion of oxygen into the center of pitch sphere is very slow [9]. Thus increasing cost and limiting application of resultant activated carbon as that for carbon fiber [10].

There were many works focused on the characterization of sulphur in coal [11–14]. It can be seen that sulphur had a good reactivity with aromatic compounds. In the present paper, adding sulphur into the starting pitch was examined to accelerate the stabilization of pitch sphere since the diffusion of oxygen into the center of pitch sphere took too long time.

2. Experimental

2.1. Raw material

Coal tar pitch with softening point of 250 °C was used in the present study. Elemental sulphur was used as an additive to accelerate the stabilization process.

2.2. Preparation of pitch sphere with and without sulphur

The coal tar pitch was blended under stirring with naphthalene of 30 wt % in total amount and then heat treated at 150 °C for 1 h under nitrogen pressure of 0.5 MPa.

The blended pitch was then pulverized into particles of ca. 0.65–1.0 mm. Pitch spheres (PS-0) with diameter of ca. 0.65–1.0 mm were obtained using emulsion method according to the literatures [9, 15].

Elemental sulphur of 2.5–10.0 wt % was blended with pitch at 120 °C before pylverization. Pitch spheres containing 2.5, 5.0 and 10.0 wt % of elemental sulphur, respectively (abbreviated to PS-2.5, PS-5 and PS-10 respectively) were obtained using above method.

2.3. Stabilization and carbonization of pitch spheres

The stabilization of pitch spheres with and without adding sulphur were carried out in air at heating rates of 0.5, 1.0 and 2.0 °C/min up to 270–300 °C and hold for 0 to 20 h. The PS-5 was also stabilized in nitrogen to examine if the sulphur alone could fully stabilize the pitch sphere. The stabilized pitch spheres were then carbonized at 900 °C for 1 h at heating rate of 10 °C/min in nitrogen in order to investigate whether or not the stibilization was sufficient.

2.4. Characterization

2.4.1. Optical microscope observation

The stabilized and carbonized pitch spheres were observed under the optical microscope.

2.4.2. Gas chromatography (GC)

The sulfocompounds evolved from PS-5 during stabilization were analyzed by GC using Flame Photoelectron Detector (FPD).

2.4.3. FT-IR and X-ray photoelectron spectrometry (XPS) analyses

The FT-IR spectra of raw pitch and stabilized pitch spheres were recorded using KBr Disc (FTs 15/90, Biorad Co., USA). The XPS S_{2p} spectrum of PS-5 stabilized in air was measured on XSAM 800 (KRATDS CO., England), using Mg K_α X-ray of 1256.3 eV. Curve-fitting procedure was also carried out based on the model compounds to identify the chemical shifts.

3. Results

3.1. Influence of heating rate and holding time during stabilization on the shape maintenance of pitch spheres

Table I summarizes some optimum stabilization conditions of various pitch spheres.

TABLE I Optimum stabilization conditions of pitch-based spheres

	Stabilization conditions			
Samples	Heating rate (°C/min)	Final temperature (°C)	Holding time (h)	Stabilization time (h)
PS-0	0.5	300	20	>30
PS-2.5	2.0	270	7	10
PS-5	2.0	270	0	3
PS-10	1.0	270	0	5

The PS-0 needed very slow heating rate and long holding time at 300 °C to keep its form during the following carbonization. Adding 2.5–10.0 wt % of sulphur shortened the stabilization time significantly. PS-2.5 needed holding time of about 7 h at 270 °C, at 2.0 °C/min of heating rate. PS-5 needed no holding time under the same stabilization conditions. Further large amount of sulphur of 10.0 wt % (PS-10) needed a slower heating rate of 1.0 °C/min, because the heating rate of 2.0 °C/min caused the deformation of the spheres during stabilization, probably due to excess reactions of sulphur with pitch [16–18].

The optical micrograsphs of some stabilized and carbonized pitch spheres are shown in Fig. 1. Less holding time or higher heating rate clearly caused the deformation of spheres.

The PS-5 stabilized in nitrogen at 300 °C for 10 h could not keep its shape after carbonization, which meant that pitch sphere could not be stabilized effectively by sulphur alone.

3.2. Reaction of pitch spheres during stabilization

3.2.1. Elemental analyses

The elemental analyses of the raw coal tar pitch, stabilized PS-0 and PS-5 are shown in Table II. The oxygen contents and C/H ratio of both stabilized pitch spheres increase significantly. The oxygen content of stabilized PS-0 is larger than that of stabilized PS-5. Ca. 3.0 wt % of sulphur still remained in the stabilized PS-5, probably existing in the form of sulphur functional groups.

3.2.2. Chemical structure characterization of raw coal tar pitch and stabilized spheres

Fig. 2 shows the FT-IR spectra of the raw coal tar pitch, stabilized PS-0 and PS-5. The bands at 3050 cm^{-1} (aromatic C–H), 2720–2960 cm^{-1} (aliphatic C–H) and 870–750 cm^{-1} of both stabilized PS-0 and PS-5 decrease significantly compared to those of raw pitch. While some new bands appeared at 1650, 1750 and 1200 cm^{-1}, which are attributed to carbonyl, ester or aromatic ether groups, respectively [19, 20]. Few sulphur functional group was recognized in the FT-IR spectra due to the disturbing of oxygen functional groups except for the band at 1030 cm^{-1} which is ascribed to sulfoxide group.

Fig. 3 shows the S_{2p} spectrum of stabilized PS-5. The spectrum can be resolved into five signals with binding energy of 162.2, 163.8, 165.9, 167.6 and 170.0 eV, respectively, which can be attributed to $\text{Ph}{-}\text{S}{-}\text{CR}_3$,

TABLE II Elemental analyses of starting pitch, stabilized PS-0 and PS-5

	Elemental analyses (wt %)					
Samples	C	H	O	N	S	C/H ratio
Raw coal tar pitch	91.67	4.64	1.68	0.95	1.06	1.64
Stabilized PS-0	83.86	2.90	10.99	0.99	0.52	2.44
Stabilized PS-5	85.42	3.29	6.66	1.03	2.94	2.17

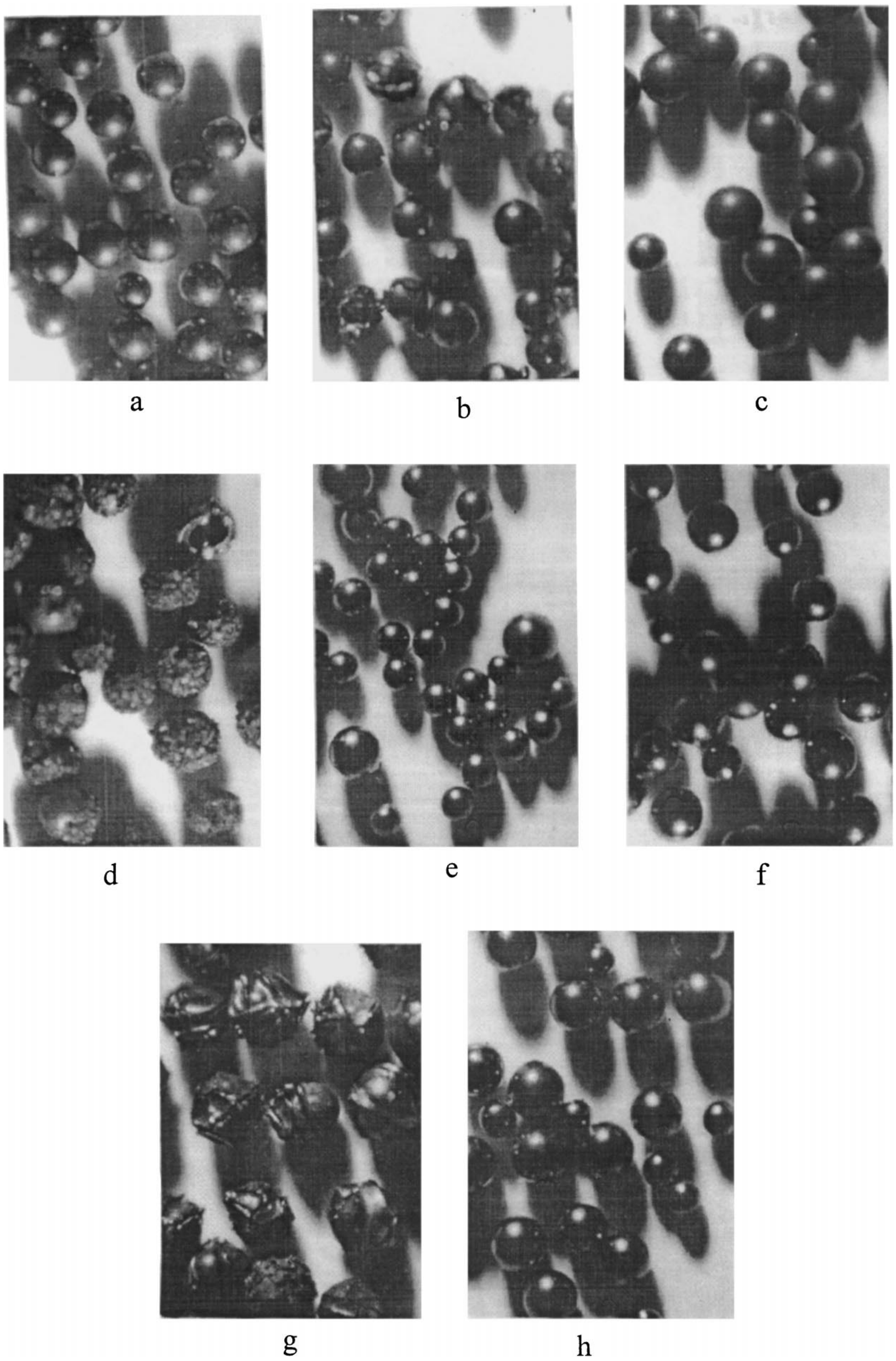

Figure 1 Optical microscopes of pitch sphere before stabilization and some stabilized and carbonized pitch spheres. a: Pitch spheres before stabilization; b: Carbonized PS-0 (stabilization condition: 300 °C, held 15 h, 0.5 °C/min); c: Carbonized PS-0 (stabilization condition: 300 °C, held 20 h, 0.5 °C/min); d: Carbonized PS-2.5 (stabilization condition: 270 °C, held 0 h, 2.0 °C/min); e: Carbonized PS-2.5 (stabilization condition: 270 °C, held 7 h, 2.0 °C/min); f: Carbonized PS-5 (stabilization condition: 270 °C, held 0 h, 2.0 °C/min); g: Stabilized PS-10, 2.0 °C/min; h: Carbonized PS-10 (stabilization condition: 270 °C, held 0 h, 1.0 °C/min).

$S{-}CR_2$ (162.2 eV), $-R{-}SH$, $Ph{-}S{-}Ph$, $-R{-}S{-}R-$ (163.8 eV), $O{=}S{=}$ (165.9 eV), $O{=}S{=}O$ (167.6 eV) and noise signal (170.0 eV) according to literatures [12, 21, 22]. The results clearly indicate that sulphur reacts with pitch molecules during stabilization and forms sulphur functional groups.

3.2.3. Evolution of gaseous sulfocompounds during stabilization

Three kinds of gaseous sulfocompounds, i.e. H_2S, COS and CS_2, were detected in tail gas during the stabilization of PS-5. Fig. 4 shows the evolution profiles of H_2S, COS and CS_2 between 150 and 350 °C during the stabilization, where the heating rate is 2.0 °C/min.

The COS began to evolve at 170 °C, and reached its maximum amount at 330 °C, then decreased. The other sulfocompounds, H_2S and CS_2, began to evolve at 190 °C, reached to their respective maximum amount at 280 and 290 °C, and then decreased to zero at 350 °C.

Fig. 5 also shows evolution profiles of sulfocompounds from PS-5 during the stabilization in nitrogen. Most sulphur evolved as H_2S, very little amounts of CS_2 and COS being detected out at 200–350 °C.

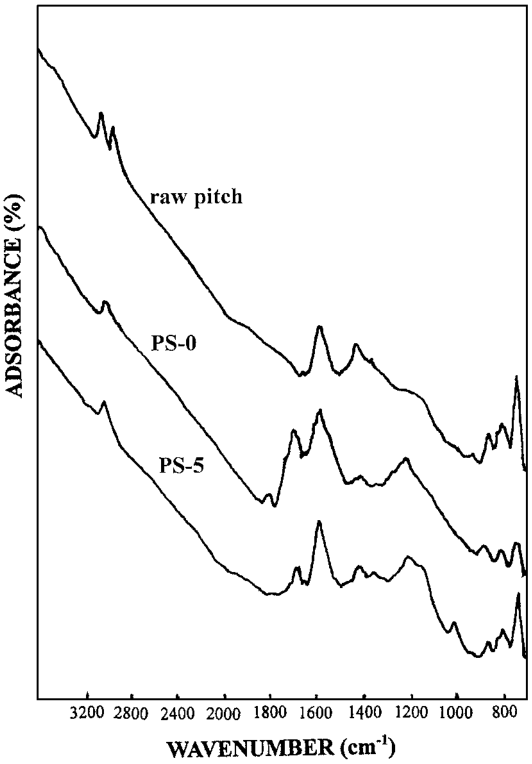

Figure 2 FT-IR spectra of raw coal tar pitch, stabilized PS-0 and stabilized PS-5.

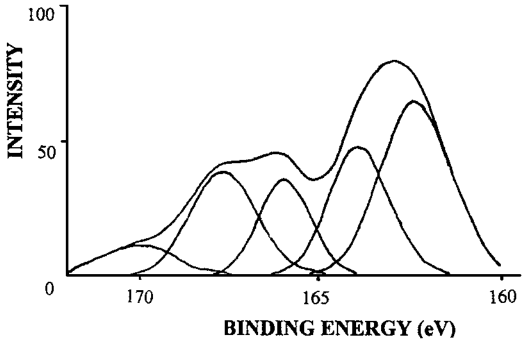

Figure 3 Curve-fitted XPS sulphur 2p spectra of stabilized PS-5.

4. Discussion

PS-0 of 0.65–1.00 mm diameter needed about 30 h for the complete stabilization in air in order to maintain its shape in the carbonization, although the sublimation of naphthalene under the stabilization conditions could produce some pores to allow the diffusion of oxygen into the center of the pitch sphere. Elemental sulphur dispersed in pitch spheres homogeneously reacted with pitch molecules to evolve as H_2S, accelerating the dehydrogenation as a kind of stabilization reactions. Some of sulphur remained in the pitch to form sulfide bridge which can also stabilize the pitch. Such reactions certainly helped the stabilization of pitch, especially the pitch at the core of the sphere. The pitch molecules on outer surface of the sphere are oxidized at the stabilization. The evolution of sulfuocompounds from the center of the sphere leaves pore to accelerate the diffusion of oxygen into center of the pitch sphere. The stabilization in nitrogen failed to maintain the shape of PS-5 at the carbonization process, which indicated that oxidation in air is necessary for the full stabilization.

A reasonable amount of sulphur content in pitch sphere is needed to control the stabilization process. sulphur of 2.5 wt % took 7 h of holding time at 270 °C when the heating rate was 2.0 °C/min. It should be noted that sulphur of 10.0 wt % requires a heating rate of 1.0 °C/min to keep the shape. Too much evolution of sulfuocompounds deformed the shape before the sufficient stabilization.

The evolution of COS and CS_2 from PS-5 was observed during stabilization in air. Oxygen may activate the reactivity of sulphur to carbon. No SO_2 was detected, indicating that sulphur reacted with pitch molecules rather than oxygen. The oxygen content in stabilized PS-5 is less than that in the stabilized PS-0. The remaining sulphur groups contribute directly to the stabilization.

Thus sulphur additive was found in the present study a solution to solve a problem in the stabilization of pitch spheres with large diameter. The additive should

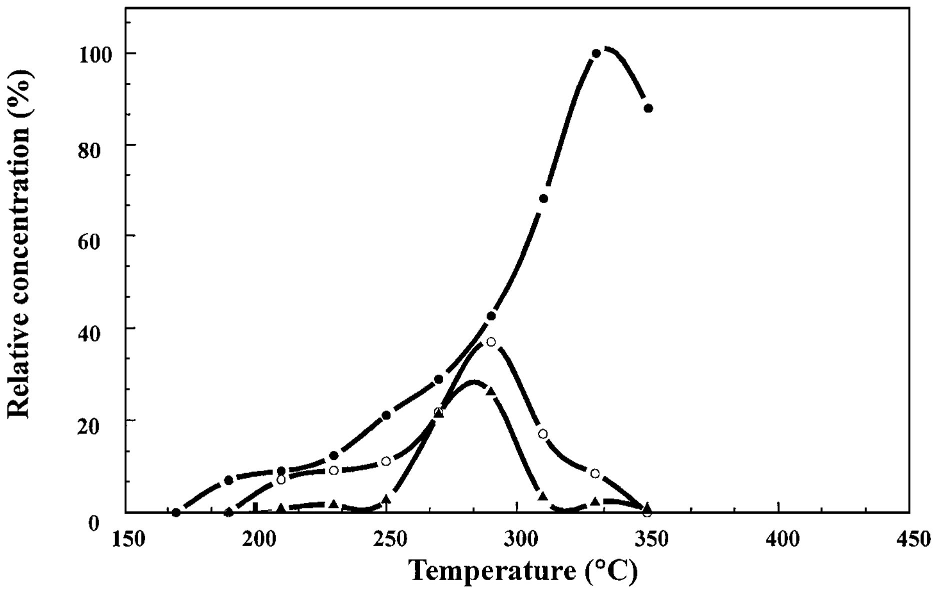

Figure 4 Evolution profiles of sulfuocompounds from PS-5 during stabilization in air. ●: COS; ○: H_2S; ▲: CS_2.

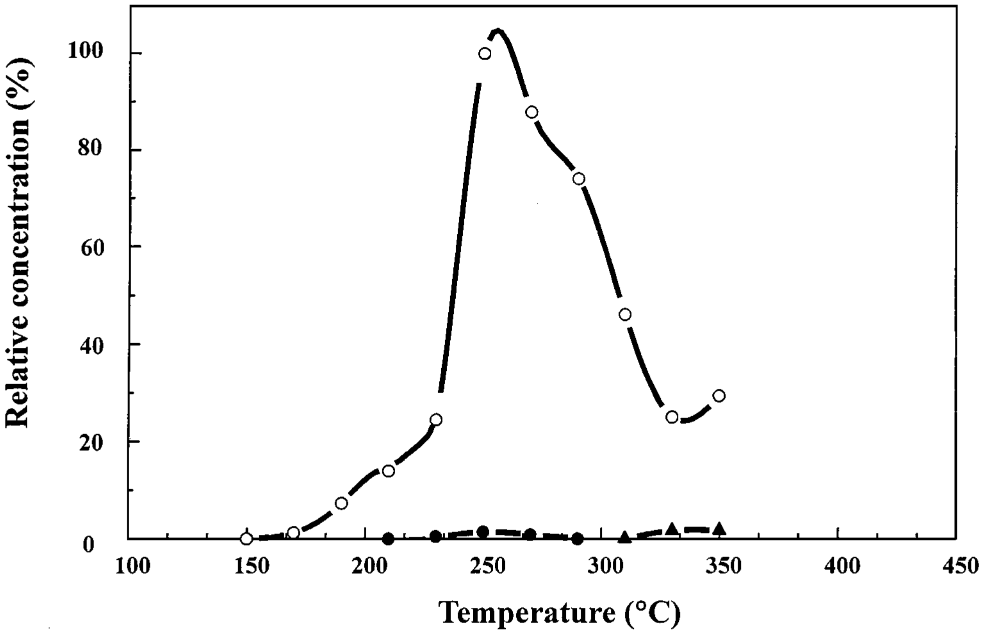

Figure 5 Evolution profiles of sulfuocompounds from PS-5 during stabilization in nitroge. ●: COS; ○: H_2S; ▲: CS_2.

not react with pitch molecules during blending, otherwise, the softening point of pitch will rise. The additive should react with pitch exclusively under the stabilization conditions. The evolution of H_2S during stabilization and carbonization may be a problem because it is a serious pollutant to the atmosphere. The H_2S should be trapped.

5. Conclusion

Elemental sulphur in the pitch sphere can react with pitch molecules under air stabilization conditions to stabilize the pitch sphere through its condensation as the sulphur functional groups acted as bridge bonds. At the same time, H_2S, COS and CS_2 evolve from the inside of pitch sphere, forming channels which allow the rapid diffusion of oxygen into the center of pitch sphere, accelerating the stabilization process.

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