MODIFICATION OF THE ACTIVATION CHARACTERISTICS OF PHENOLIC RESIN-BASED ACTIVATED CARBON SPHERES BY POLYMER-BLENDING METHOD

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Introduction

Activated Carbon Spheres (ACS) are celebrated for their good fluid mechanics characteristics such as homogeneously filling density and exerting little resistance to the passed fluid when used in fixed-bed reactor due to their regular spherical shape. Furthermore, they do not hurt the adsorbate molecule. Thus, they are widely used in blood purification such as hemoperfusion. Recently, a new kind of activated carbon spheres were prepared from phenolic resin successfully by the authors, of which the preparation process was time- and energy-saving than that making from pitch. However, there are still two problems to be solved [1]: The first one is the "core-shell' structure of highly burned ACS because the carbonized spheres possess small porosity and that makes the activating molecules difficulty to penetrate into the inner part of the spheres; The second one is the activated carbon spheres with low burn-off possess small specific surface area. In this study, a new approach called polymer-blending method was tried to solve above issues.

Experimental

Polyvinyl butyral (PVB) was mixed with the novolac-type phenolic resin and hexamethylenetetramine in methanol by a weight ratio of 11.1:100:12.4, followed by blending. After evaporating methanol under reduced pressure, the solid mixture was pulverized into irregular particles and formed into spheres by emulsion method. Phenolic resin-based activated carbon spheres (P-ACS) were obtained by carbonizing and activating the prepared spheres [2]. Thermogravimetry method, nitrogen adsorption method, mercury porosity and SEM were used to analyze the effect of adding PVB on the carbonization, activation and pore structure characteristics of the ACS. P-ACS without PVB was also prepared for comparison.

Results and Discussion

Figure 1 shows the thermogravimetry curve of two kinds of spheres. Phenolic resin spheres begin to pyrolyze slowly at 350°C. The pyrolysis rate increases from 520°C and lasts to 700°C, at which the rate begins to slow down. When the temperature reaches 800°C, a plateau appears, indicating the end of the carbonization process. The final carbon yield was about 73 % of the starting phenolic resin. PVB begins to decompose at about 200°C, a sharp weight loss occurs at 300~450°C and then the pyrolysis almost finishes, leaving only 9 % of carbon residue. The degradation behavior of polymer blend spheres is different from PVB or phenolic resin spheres. The finial carbon yield was 66 % of the starting spheres. Table 1 lists the apparent density of the two kinds of carbonized spheres. The apparent density of polymer blend-derived carbon spheres is smaller than that of the intrinsic carbon spheres, which implies the higher porosity of the former one.

Changes in burn-off of the two kinds of carbon spheres are shown in Figure 2. The burn-offs become larger with the increase of time, and the burning rates exhibit different features. Intrinsic carbon sphere possess the lowest burning rate. The burning rate of polymer blend-derived carbon spheres is faster than the intrinsic carbon spheres. It proves that addition of pore-forming agent can change the activation behavior of intrinsic carbon spheres. Figure 3 shows the SEM photos of intrinsic activated carbon spheres and the polymer blend-derived ones with burn-off of 58.41% and 60.32 respectively. At such burn-off degree, the former one appears 'core-shell structure' but the later one possesses homogeneous structure.

The surface area and pore structure parameters are listed in Table 1. At the almost same burn-off, P-ACS added with PVB posses higher surface area and total pore volume. The mesopore ratio of the polymer blend ones, calculated from the ratio of mesopore volume to total pore volume, is 27.8%. It is also larger than that of the intrinsic ones, which is 23.1%.

There are three mechanisms which are often invoked for explaining the development of porosity during gasification of carbon: 1) the widening of existing pores, 2) the opening

of previously inaccessible pores, 3) the creation of new pores by selective gasification of certain structural components. The processes of 1) and 2) are recognized to be the most important factors [3]. The higher porosity makes the penetration of activating agent into the inner part of carbon spheres much easier, thus the bigger contacting surface area with the carbon matrix, which results in higher burning rate of polymer blend-derived spheres than the intrinsic ones. The easier penetrating into the inner part of carbon also minishes the grads of activating agent along the diameter of carbon sphere, leading to the homogeneous activation of polymer blend-derived carbon spheres. With the progress of activation process, the walls of micropores are ablated and connected into bigger pores. In the polymer blend-derived carbon spheres, there are large amount of initial pores, which provide bigger probability of connection of micropores into bigger pores, thus results in larger mesopore volume of polymer blend-derived activated carbon spheres than that of intrinsic ones.

Conclusions

Addition of polyvinyl butyral into the novolac-type phenolic resin before spheroidization might change the carbonization and activation behavior of phenolic resin spheres. PVB evaporated as gaseous substances during carbonization and thus left many pores in the carbon matrix. The higher porosity resulted in higher burn-off rate and homogenous activation of such kind of carbon spheres. Both surface area and pore volume was enlarged during process.

References

1.Yang Junbing, Ling Licheng, Liu Lang. Study on the activation characteristics of phenolic resin-based spherical carbon. New Carbon Materials (in Chinese) 1999; 14(4): 11-16.
2.Yang Junbing, Ling Licheng, Liu Lang. Preparation and properties of phenolic resin-based spherical activated carbon. Extended Abstract, 24th Biennial Conference on Carbon. Charleston, (South Carolina, USA), P676-677.
3.Marsh H, Rand B.Process of activation of carbons by gasification with carbon dioxide. I. Gasification of pure poly (furfuryl alcohol). Carbon 1971; 9(1): 47-61.

Table 1. Pore structure parameters of phenolic resin-based activated carbon spheres

	Burn-off (%)	Specific surface area (cm^2/g)	Micropore surface area (cm^2/g)	Total pore volume (cm^3/g)	Mesopore volume (cm^3/g)	Apparent density of carbon spheres (g/cm^3)
P_1	58.41	1202	1000	0.52	0.12	1.1528
P_2	60.32	1396	1107	0.61	0.17	1.0057

P_1: Intrinsic activated carbon spheres;

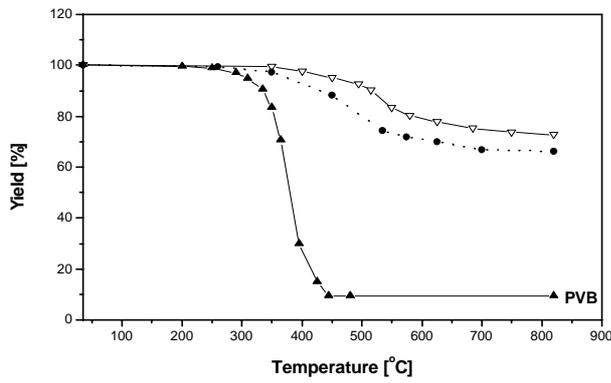P_2: Polymer blend-derived activated carbon spheres.

Figure 1.Thermogravimetric curves of phenolic resin spheres
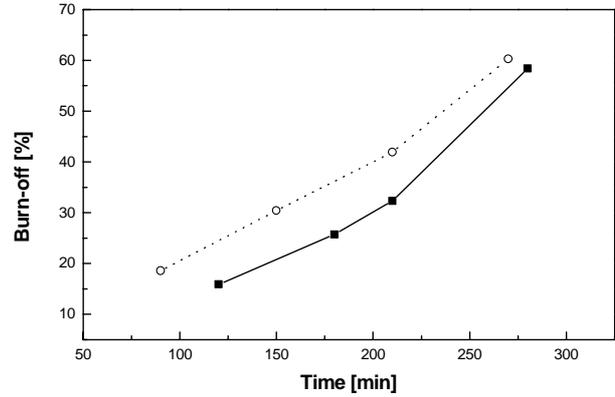Solid line stands for intrinsic spheres; Broken line for polymer blend-derived ones

Figure 2. Burning rate curves of phenolic resin-based carbon spheres
Solid line stands for intrinsic activated carbon spheres; Broken line for polymer blend-derived ones
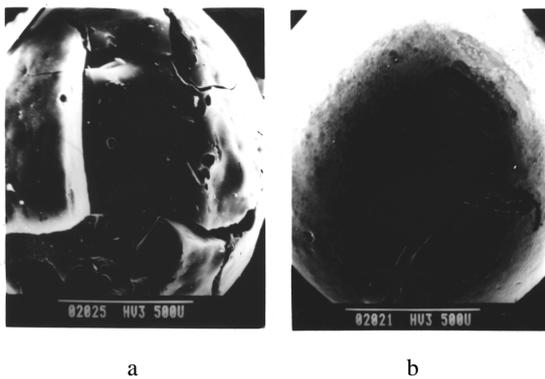

a   b

Figure 3. SEM photo of P-ACS
a stands for intrinsic P-ACS; b stands for polymer blend-derived ones