

PREPARATION AND CHARACTERIZATION OF POLYMER-BASED SPHERICAL ACTIVATED CARBONS*

Zhao-lian Zhu, Ai-min Li**, Ming-fang Xia, Jin-nan Wan and Quan-xing Zhang

State Key Laboratory of Pollution Control and Resource Reuse, Jiangsu Engineering and Technology Research Center for Organic Toxicant Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, China

Abstract A series of spherical activated carbons (SACs) with different pore structures were prepared from chloromethylated polydivinylbenzene by ZnCl_2 activation. The effects of activation temperature and retention time on the yield and textural properties of the resulting SACs were studied. All the SACs are generated with high yield of above 65% and exhibit relatively high mesopore fraction (me%) of 35.7%–43.6% compared with conventional activated carbons. The sample zlc28 prepared at 800°C for 2 h has the largest BET surface area of $891 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.489 \text{ cm}^3 \text{ g}^{-1}$. SEM and XRD analyses of zlc28 verify the presence of developed porous structure composed of disordered micrographite stacking with large amounts of interspaces in the order of nanometers.

Keywords: Spherical activated carbon; Polymer; Chemical activation; Pore structure; Adsorption.

INTRODUCTION

Activated carbons are widely used as effective adsorbents in many applications such as air separation and purification, pollution control, solvent recovery, catalyst support and energy storage due to their large specific surface area, adequate pore size distribution, high surface activity and high physicochemical stability^[1–6].

Activated carbons are usually prepared from organic precursors of natural or synthetic origins by two traditional methods, namely physical activation and chemical activation. Physical activation basically consists of a carbonization step followed by a step of activation by means of air, carbon dioxide or steam. In chemical activation, the carbonization and activation are accomplished in a single step by carrying out thermal decomposition of the raw material impregnated with certain chemical agents (H_3PO_4 , ZnCl_2 , KOH, NaOH, K_2CO_3 , etc.)^[7]. Chemical activation presents several advantages compared to physical activation, *e.g.*, lower pyrolysis temperatures, high yield and high surface area. Among the chemical activating agents, ZnCl_2 is the most widely used chemical due to its high activating capability and relatively low cost.

The use of natural precursors (*e.g.*, wood and coal) will still limit the purity, strength, physical form and homogeneity of the activated carbon. However, these can be fully overcome by the use of polymeric precursors, where the reproducibility and purity of the precursors are within the control of the manufacturer. Meanwhile, the physical forms and structure can be tailored through the polymer production process. Many polymers have been studied as activated carbon precursors, such as phenolic resins^[8–10], mixtures of furfuryl resin and glycol^[11], vinylidene chloride copolymers^[12], cellulose based materials^[13], polytetrafluoroethylene^[14], poly(ethyleneterephthalate) and polyacrylonitrile^[15]. Spherical activated carbons (SACs) prepared from polymers have received considerable attention for their various potential advantages over activated carbon fibers

* The work was supported by the National Natural Science Foundation of China (No. 50578073) and 863 Project (No. 2006AA06Z383).

** Correspond author: Ai-min Li (李爱民), E-mail: liaimin@nju.edu.cn

Received July 20, 2007; Revised September 13, 2007; Accepted September 19, 2007

(ACFs) and granular activated carbons (GACs), such as extremely low resistance to liquid diffusion, higher adsorption efficiency, better mechanical properties and more resistance to abrasion^[16].

Polydivinylbenzene is one of the most frequently used materials for preparing SACs, however, SACs can not be got by direct carbonization and activation of polydivinylbenzene due to its poor thermostability. In order to preserve the spherical shape of activated carbons, polydivinylbenzene needs to be sulphonated before carbonization, which increases the complicity of preparation process^[17]. The aim of this paper is to prepare and characterize a series of SACs with different pore structure derived from chloromethylated polydivinylbenzene through ZnCl_2 activation. In our studies, polydivinylbenzene was first chloromethylated, then the chloromethylated spherical polymer may post-crosslink in carbonization and activation, which could increase the strength and thermostability of the spheres. So the spherical shape was well preserved after carbonization and activation. At the same time, waste ZnCl_2 from chloromethylation process can behave as the activation agent, which realizes the resource reuse of waste ZnCl_2 . The preparation conditions affecting the yield and textural properties (specific surface area, pore volume and pore size distribution) were investigated. The textural properties of SACs were characterized by N_2 adsorption, XRD, and SEM.

EXPERIMENTAL

SACs Preparation

Divinylbenzene-derived spherical polymer (DSP) was synthesized essentially as described^[18, 19]. Briefly, styrene (176 g), divinylbenzene (24 g), dibenzoyl peroxide (2 g) and liquid paraffin (100 g) were mixed in a round-bottomed flask. Subsequently, 1200 g of 1 wt% gelatin solution were added. Polymerization was performed with stirring at 80°C for 12 h. The resultant DSP was filtered and rinsed with hot deionized water at 80°C, and extracted with acetone for 8 h before being dried under vacuum at 60°C. In order to increase the strength of spherical polymer, the DSP was then chloromethylated: DSP (100 g) was swollen in monochloromethylether (600 mL). Subsequently, ZnCl_2 (40 g) was added slowly, and the mixture was stirred continuously at 60°C for 12 h. The chloromethylated spherical polymer (Cl-DSP) was filtered and then extracted with ethanol for 8 h and dried under vacuum at 60°C for 8 h. The content of chlorine in Cl-DSP was around 19%.

The resulting Cl-DSP was mixed with ZnCl_2 solution (30 wt%) obtained by dissolving the waste ZnCl_2 from chloromethylation process in water, and incubated at 80°C for 24 h. After that, the samples were filtered and dehydrated at 110°C for 6 h before being placed in a quartz combustion boat and loaded into a horizontal cylindrical furnace (*i.d.* = 80 mm) under N_2 flow ($150 \text{ cm}^3 \text{ min}^{-1}$). The samples were heated up to 600–900°C at a heating rate of 10 K min^{-1} and maintained at the desired activation temperature for 1–3 h. The samples prepared at temperatures of 600, 700, 800, and 900°C for 2 h were designated as zlc26, zlc27, zlc28, and zlc29, respectively, and those at 800°C for 1 and 3 h as zlc18 and zlc38. The resultant SACs were washed sequentially with 0.5 mol/L HCl solution at 80°C and boiling water to remove excess ZnCl_2 before being dried at 110°C for 24 h and stored in a desiccator for characterization.

SACs Characterization

The specific surface area (S_{BET}) and pore structural parameters of the SACs were determined from the adsorption-desorption isotherm of nitrogen at -196°C (Micromeritics ASAP2010). The S_{BET} was calculated by the BET equation, micropore volume (V_{mi}) and micropore specific surface (S_{mi}) area were obtained using the t-plot method, and pore size distribution (PSD) was determined using the BJH model^[20]. The total pore volume (V_{t}) was obtained by converting the nitrogen adsorption amount at a relative pressure of 0.98 to the liquid nitrogen volume. The mesopore volume (V_{me}) was calculated by subtracting V_{mi} from V_{t} .

The morphology of zlc28 was examined in an SEM (Hitachi S-4300). The zlc28 was coated with platinum by a platinum sputtering device for clear visibility of the surface morphology. The stacking structure of aromatic carbon layers of zlc28 was analyzed with an X-ray diffractometer (ARL-X' TRA, Cu K α radiation at 40 kV and 30 mA, $\lambda = 0.15406 \text{ nm}$), and the X-ray patterns were recorded for 2θ from 10° to 60° at a scan rate of $0.02^\circ \text{ per min}$.

RESULTS AND DISCUSSION

Yield of SACs

The yield of SACs can be calculated from the resultant sample weight and its initial polymer precursor weight. The effects of activation temperature and retention time on the yield of SACs are shown in Fig. 1. The results show that activation temperature and retention time have similar negative effects on the yield. For a 2 h activation retention time, the yield of SACs decreases from 73.9% to 68.6% as temperature is increased from 600°C to 700°C due to elevated release of volatile matters during pyrolysis with temperature increase. Above 700°C, the yield almost remains unchanged. Similarly, at 800°C when the activation retention time is extended from 1 h to 3 h, the yield gradually decreases from 70.2% to 66.1%, indicating the volatile matters have been released almost completely, and the reaction becomes very slow. All the SACs have relatively high yield of above 65%, which is attributed to the fact that ZnCl_2 can inhibit tar formation and increase the carbon yield as well.

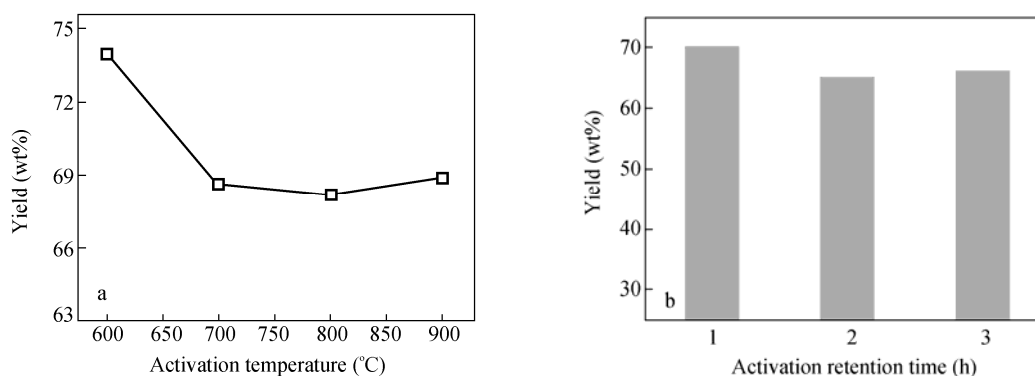


Fig. 1 Effects of activation temperature (a) and retention time (b) on the yield of SACs
The retention time in tests for temperature dependence was 2 h; The temperature in tests for retention time dependence was 800°C.

Nitrogen Adsorption-Desorption Isotherms

Information on the textural properties of porous solids is typically obtained from low-temperature (-196°C) nitrogen adsorption-desorption isotherms. The adsorption capacity of the SACs increases with activation temperature from 600°C to 800°C, revealing the increase in porosity upon activation as a result of continual release of volatiles (Fig. 2a). When the activation temperature changes from 800°C to 900°C, the SACs

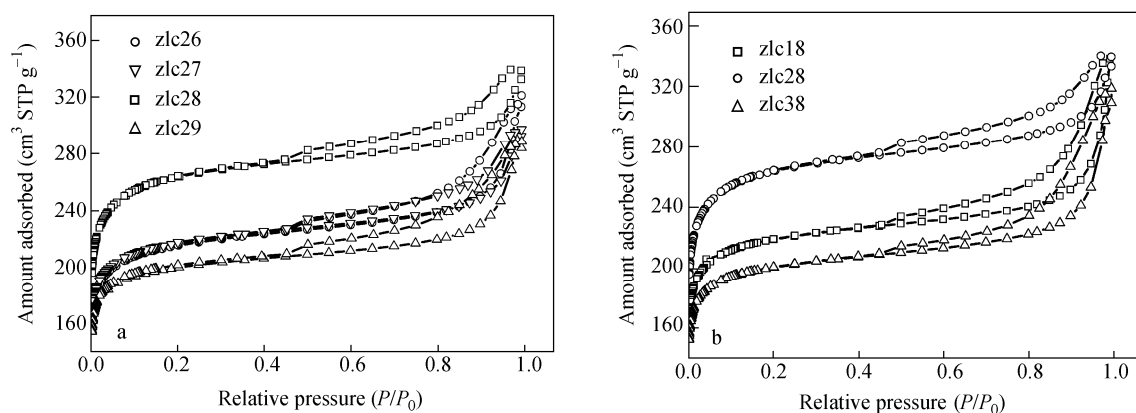


Fig. 2 Effects of activation temperature (a) and retention time (b) on the nitrogen adsorption-desorption isotherms of SACs

adsorption capacity decreases possibly due to sintering and shrinkage of the carbon structure at higher pyrolysis temperatures. N_2 adsorption increases with extending retention time from 1 h to 2 h at 800°C (Fig. 2b), which may result from the increase in porosity due to release of the volatile matter produced in the impregnation. While the decrease of N_2 adsorption, as the retention time is extended from 2 h to 3 h, indicates the pore structure sintering and shrinking upon excess thermal treatment. Additionally, all the SACs exhibit a type IV isotherm with well-pronounced hysteresis loops in the relative pressure range of 0.5–1.0, revealing the presence of mesoporous structure.

BET Surface Area and Pore Volume

Adsorptive capacity, the most important property of SACs, is directly related to the specific surface area and the pore volume. The textural characteristics of SACs are presented in Table 1, and the effects of activation temperature and retention time on the evolution of micropore and mesopore fractions are shown in Fig. 3. The micropore fraction (mi%) was defined as $mi\% = (V_{mi}/V_t) \times 100$ and the mesopore fraction (me%) as $me\% = (V_{me}/V_t) \times 100$. It can be seen that in cases of increasing activation temperature from 600°C to 800°C for 2 h or extending retention time from 1 h to 2 h at 800°C, the increasing amounts of volatile matters are progressively released thereby resulting in the development of porosity, and hence the S_{BET} , S_{mi} , V_t , V_{mi} and mi% gradually increase. However, further increase in activation temperature or retention time results in their decrease, which can be attributed to the fact that severe thermal treatment causes sintering and shrinkage of the pore structure, and meanwhile some micropores are widened into mesopores, as inferred from the increase of me%.

Table 1. The textural characteristics of spherical activated carbons

Sample	S_{BET} ($m^2 g^{-1}$)	S_{mi} ($m^2 g^{-1}$)	V_t ($cm^3 g^{-1}$)	V_{mi} ($cm^3 g^{-1}$)	V_{me} ($cm^3 g^{-1}$)
zlc-26	730	560	0.452	0.259	0.193
zlc-27	733	567	0.431	0.263	0.168
zlc-28	891	679	0.489	0.315	0.174
zlc-29	673	535	0.415	0.249	0.167
zlc-18	740	582	0.445	0.269	0.175
zlc-38	677	536	0.439	0.248	0.191

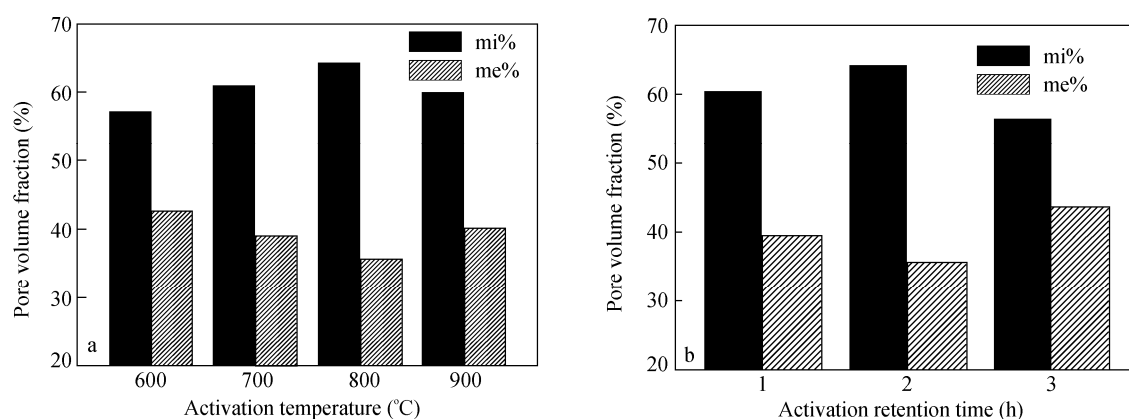


Fig. 3 Effects of activation temperature (a) and retention time (b) on the evolution of micropore and mesopore fractions

The retention time in tests for temperature dependence was 2 h and the temperature in tests for retention time dependence was 800°C.

The SACs prepared exhibit relatively high me% (35.7%–43.6%) compared with that of conventional activated carbons. The effect of $ZnCl_2$ addition is implicated in two competing mechanisms: micropore formation and pore widening^[21]. At low $ZnCl_2$ -to-raw material ratios, micropore formation is the dominant

process; pore widening becomes more important as the ratio increases. In our study, the raw materials were sufficiently impregnated with the concentrated ZnCl_2 solution, which has very high ZnCl_2 -to-raw material ratios. ZnCl_2 remains in the outer layer of the polymer particles and widens the pore size *via* a localized decomposition of the polymer, thus this process enhances mesopore formation, and the resultant SACs have relatively high me%.

Pore Size Distribution

Pore size distribution (PSD), a very important property of adsorbents, determines the fraction of total pore volume accessible to molecules of a given size and shape. According to the classification adopted by the IUPAC, pores are classified as micropores (< 2 nm), mesopores (2–50 nm) and macropores (> 50 nm). It is found that increasing activation temperature from 600°C to 800°C results in the enhancement of micropores as a consequence of the release of volatiles (Fig. 4a). As activation temperature increases from 800°C to 900°C, micropores decrease due to severe thermal treatment resulting in sintering and shrinkage of the pore structure. Figure 4(b) shows that there are increasing micropores and mesopores with extending retention time from 1 h to 3 h. This trend can be explained by the fact that carbon gasification is enhanced by extending activation retention time, thus causing pore deepening and pore widening.

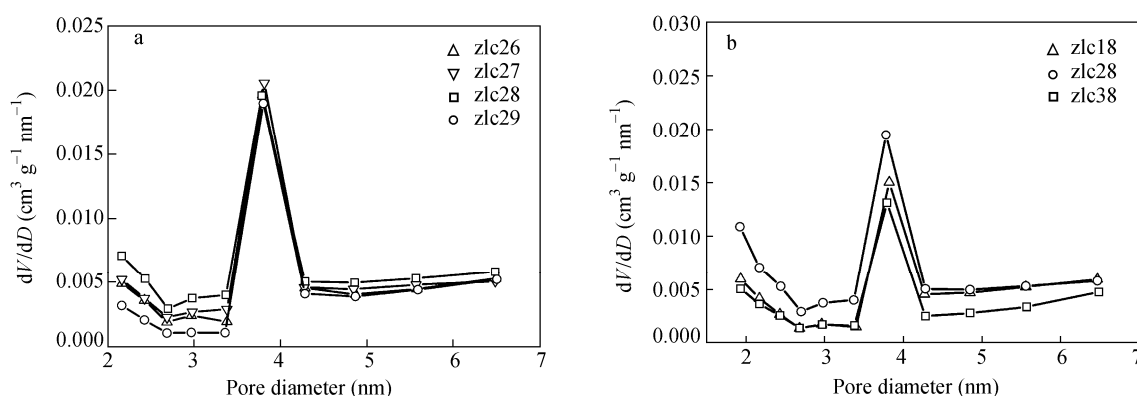


Fig. 4 Effects of activation temperature (a) and retention time (b) on PSD of SACs

Surface Morphology

The morphology of zlc28 was detected in a scanning electron microscope (SEM). The surface of zlc28 is magnified 110 and 30000 times, respectively (Fig. 5). The regular spherical shape of the polymer is well preserved after the activation, which can be attributed to the fact that the chloromethylated spherical polymer further post-crosslinks in activation, which increases the strength and thermostability of the sphere. The micrograph ($\times 30000$) shows that there are large amounts of interspaces in the order of nanometers, revealing a highly developed disorganized porosity.

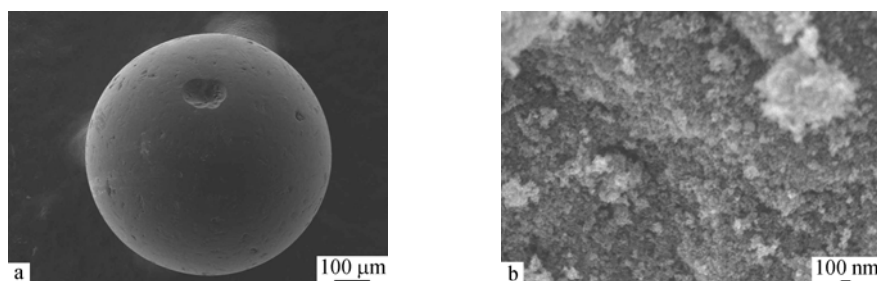


Fig. 5 SEM micrographs of zlc28 at different magnification scales: single sphere magnified 110 times (a), the surface of the sphere magnified 30000 times (b)

Crystal Structure

The X-ray diffraction profile of zlc28 (Fig. 6) shows two very broad diffraction peaks and absence of sharp peaks, which reveals a predominantly amorphous structure^[22]. There are two peaks centered at around 21.5° and 42.9°, corresponding to the (002) and (10) (overlapped 100 and 101) reflections of the disordered stacking of micrographites. From the position of the (002) peak, we can calculate the interplanar distance (d_{002}) by Bragg's Law. Typically, in a crystalline carbonaceous structure, such as graphite, the interlayer distance between two adjacent carbon sheets is 0.335 nm. In this study, the peak at $2\theta = 21.5^\circ$ corresponds to an interlayer distance (d_{002}) of 0.412 nm, which suggests a disordered carbonaceous interlayer different from that of graphite^[23]. The amorphous structure is made up of curved layers of carbon in which the basic building units are distorted six-membered carbon rings. The highly coherent regions are separated by highly defective regions which provide prerequisites for the realization of a high specific surface area.

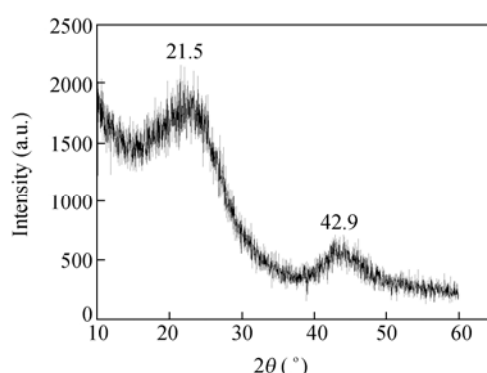


Fig. 6 The X-ray diffraction profile of zlc28

CONCLUSIONS

Spherical activated carbons (SACs) with different pore structures are successfully prepared from chloromethylated polydivinylbenzene by ZnCl_2 activation. The chloromethylated spherical polymer can post-crosslink in activation, which increases the strength and thermostability of spheres. So the spherical shape is well preserved after activation. Increasing the activation temperature or extending the retention time decreases the yield of SACs. All the SACs have relatively high yield of above 65%, as ZnCl_2 can inhibit tar formation and increase the carbon yield. The BET surface area and pore volume increase with either increasing activation temperature from 600°C to 800°C for 2 h or extending retention time from 1 h to 2 h at 800°C as a result of continual release of volatiles, but they decrease thereafter due to sintering and shrinkage of the carbon structure. All SACs exhibit relatively high me% (35.7%–43.6%) compared with that of conventional activated carbons, which can be attributed to the fact that localized decomposition of the polymer widens the pore size at high ZnCl_2 -to-raw material ratios. The resulting SACs consist of disordered micrographite stacking with large amounts of interspaces in the order of nanometers. Waste ZnCl_2 from chloromethylation process can behave as the activation agent, which realizes resource reuse of waste ZnCl_2 .

REFERENCES

- 1 Sircar, S., Golden, T.C. and Rao, M.B., Carbon, 1996, 34: 1
- 2 Magnuson, M.L. and Speth, T.F., Environ. Sci. Technol., 2005, 39: 7706
- 3 Popescu, M., Joly, J.P., Carré, J. and Danatoiu, C., Carbon, 2003, 41: 739
- 4 Besson, M., Gallezot, P., Perrard, A. and Pinel, C., Catal. Today, 2005, 102-103: 160

- 5 Frackowiak, E., *Phys. Chem. Chem. Phys.*, 2005, 9: 1774
- 6 de la Casa-Lillo, M.A., Lamari-Darkrim, F., Cazorla-Amoros, D. and Linares-Solano, A., *J. Phys. Chem. B*, 2002, 106: 10930
- 7 Hu, Z., Srinivasan, M.P. and Ni, Y., *Carbon*, 2001, 39: 877
- 8 Oya, A., Yoshida, S., Alcaniz-Monge, J. and Linares-Solano, A., *Carbon*, 1995, 33: 1085
- 9 Lenghaus, K., Qiao, G.G., Solomon, D.H., Gomez, C., Rodriguez-Reinoso, F. and Sepulveda-Escribano, A., *Carbon*, 2002, 40: 743
- 10 Yue, Z., Economy, J. and Bordson, G., *J. Mater. Chem.*, 2006, 6: 1456
- 11 Wang, Y.X., Tan, S.H., Jiang, D.L. and Zhang, X.Y., *Carbon*, 2003, 41: 2065
- 12 Tamai, H., Kouzu, M. and Yasuda, H., *Carbon*, 2003, 41: 1678
- 13 Huang, J.M., Wang, I.D. and Wang, C.H., *J. Polym. Res.*, 2001, 8: 201
- 14 Tanaike, O., Hatori, H., Yamada, Y., Shiraishi, S. and Oya, A., *Carbon*, 2003, 41: 1759
- 15 László, K., *Microporous Mesoporous Mater.*, 2005, 80: 205
- 16 Yang, J.B., Ling, L.C., Liu, L., Kang, F.Y., Huang, Z.H. and Wu, H., *Carbon*, 2002, 40: 911
- 17 He, B.L. and Huang, W.Q., "Ion Exchange and Adsorption Resins" (in Chinese), The Science and Education Press of Shanghai, Shanghai, 1995, p.361
- 18 Li, A., Zhang, Q., Zhang, G., Chen, J., Fei, Z. and Liu, F., *Chemosphere*, 2002, 47: 981
- 19 Fan, Y., Li, Y. and Ma, J., *Acta Polymerica Sinica*(in Chinese), 2002, (2): 173
- 20 Gregg, S.J. and Sing, K.S., "Adsorption, Surface Area and Porosity", Academic Press, London, 1982, p.84
- 21 Rodriguez-Reinoso, F. and Molina-Sabio, M., *Carbon*, 1992, 30: 1111
- 22 Wang, S. and Lu, G.Q., *Ind. Eng. Chem. Res.*, 1997, 36: 5103
- 23 Lua, A.C. and Yang, T., *J. Colloid Interf. Sci.*, 2004, 274: 594