

Preparation and characterization of porous carbons from PAN-based preoxidized cloth by KOH activation

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Received 29 January 2003; accepted 15 October 2003

Abstract

Porous carbons (PCs) were prepared from PAN-based preoxidized cloth with potassium hydroxide (KOH) as active reagent by the chemical activation method. The PCs have been systematically studied by the adsorptions of nitrogen, benzene and iodine. It has been found that the process parameters such as weight ratio of KOH to the starting material, activation temperature and activation time are crucial for preparing high quality PCs. A series of PCs with high BET surface area and well-developed porous structure in which micropores are dominant were obtained with less KOH and shorter activation time in comparison to the traditional methods. The optimum conditions for preparing PCs with high BET surface area from PAN-based preoxidized cloth were given, and the relationships between pore structure and adsorption property of PCs were explored.

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Keywords: A. Porous carbon; B. Activation; C. Adsorption; D. Porosity; Adsorption property

1. Introduction

Porous carbons (PCs), also called activated carbons, have been widely used in sewage water treatment, potable water purification, decolorization, gas separation, oxidative reaction and reductive reaction [1]. Basically, the techniques for preparing PCs can be grouped into two types, i.e. the physical activation method and the chemical activation method. In comparison to the physical activation method, the chemical activation method has drawn much attention because it makes possible to produce PCs with developed pore structure in high yield and at relatively lower temperature, in which the starting materials are simply impregnated with a kind of active agents that function as dehydrating agent and inhibit the formation of tar [2–5]. Up to now, a number of active agents including KOH, NaOH, Na₂CO₃, K₂CO₃, ZnCl₂ and H₃PO₄ and a lot of carbon

precursors such as coal, coconut shell and coke [5–8] have been tested for making PCs with high BET surface area (SBET). The literature survey shows that KOH is one of the most widely used active agents [6–13], and the best value for the weight ratio of KOH to starting material is about 400–600% in order to get high quality PCs [5,14,15]. It is known that KOH is expensive (about \$1000 per ton), thus, it is desirable to reduce the amount of KOH consumed in the chemical activation method. Also, it is noted that relatively little work has been done about preparing high quality PCs with PAN-based preoxidized cloth as starting material.

Here we report that high quality PCs with well-developed microporous structure and high SBET can be prepared from PAN-based preoxidized cloth with less KOH and in shorter activation time (about 30 min). The weight ratio of KOH to the starting material is only 75%. To the best of our knowledge, this has never been reported in the literature.

The pore structure of PC can be well characterized by a number of parameters such as SBET, micropore surface area, pore size distribution. In this work, the pore

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structure and the adsorption property of PAN-based PCs with different activation degrees have been extensively studied and evaluated by nitrogen adsorption, benzene adsorption and iodine adsorption with the aim of establishing the relationships between pore structure and adsorption property of PCs.

2. Experimental

2.1. Sample preparation

In this work, the PAN-based preoxidized cloth (OC) and KOH were used as the starting material and the active agent, respectively. In order to make carbonized cloth (CC), preoxidized cloth was carbonized in a furnace which was ramped to 1073 K at a heating rate of 10 K/min, and was kept at 1073 K for 30 min before being cooled to room temperature.

The starting preoxidized cloths and carbonized cloths were soaked in a concentrated solution of KOH for 2 h at room temperature, then transferred to a furnace and dried at 423 K for 4 h to completely remove water in the preoxidized cloths and carbonized cloths. Then, the dried preoxidized cloths (or carbonized cloths) containing KOH were put into a reactor in which they were heated and activated at different temperatures for a period of different times at a heating rate of 10 K/min, then cooled down to room temperature to get semi-products. The carbonization and activation processes mentioned above were all carried out under flowing nitrogen to avoid oxidation of the samples. The semi-products were washed with 0.5 M HCl, hot water and cold distilled water in a sequence, to remove residual alkali completely; then dried at 423 K for 4 h, and finally, PCs with different pore structure and adsorption property were obtained.

2.2. Characterization of PCs

The PCs were characterized by adsorption techniques including nitrogen adsorption at 77 K, benzene adsorption at 363 K and iodine adsorption at 298 K. Before adsorption experiments, all the PC samples were degassed at 573 K for 2 h. The parameters of the pore structure of PCs, such as SBET and micropore surface area, were obtained from nitrogen adsorption in the relative pressure range from 10^{-6} to 1.0 using Micromeritics, ASAP2000. The SBET was gained from the BET method [16], and the micropore surface area was obtained from t -plot method [17,18]. The pore size distribution of PC was obtained by employing the density functional theory [19,20].

Iodine adsorption capacity represents the amount of iodine adsorbed on dried carbon adsorbent, mg/g. For each run, about 0.5 g of PC was put into a stoppered

flask with 50 ml of 0.1 mol/l KI/I₂ solution that was shaken at room temperature for 30 min. After filtering off the PC, the filtrate was titrated by 0.1 mol/l standard sodium thiosulfate (Na₂S₂O₃) solution to determine the residual iodine concentration. The adsorbed amount of iodine was worked out from the variation of KI/I₂ solution concentration before and after the adsorption.

Benzene adsorption capacity represents the amount of benzene adsorbed on dried carbon adsorbent, g/g. For each run, about 0.5 g of PC was put in an airproof container filled with benzene gas under 363 K for 1 h, then cooled down to room temperature to measure the weight increase and to calculate the adsorbed benzene [21].

3. Results and discussion

For the chemical activation process, the porous structure and adsorption property of PCs are related to a number of parameters. In this work, we mainly discuss the effects of the parameters such as the starting material, the weight ratio of KOH to starting material, the activation temperature and the activation time on the porosity and adsorption property of PCs.

3.1. Effect of the starting material

In this work, the preoxidized cloth, i.e. the starting material, was impregnated with KOH. After activation and washing, the product from the preoxidized cloth almost turned to powder while the product from the carbonized cloth still remained in a relatively good shape. For the preoxidized cloth-derived PCs and the carbonized cloth-derived PCs, the typical variations in SBET versus the weight ratio of KOH to starting material are shown in Fig. 1, which clearly shows that as the weight ratio increases, the SBETs of the PCs both from preoxidized cloths and carbonized cloths pass through a maximum. In the case of the preoxidized cloth samples, the maximum SBET appears at 75% of the

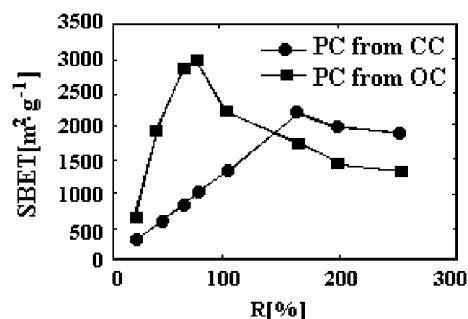


Fig. 1. BET surface area of PCs from preoxidized cloth (OC) and carbonized cloth (CC) versus R value (activation temperature, 1073 K; activation time, 30 min).

KOH weight ratio, while for the carbonized cloth samples, the SBET value seems to increase monotonically and relatively slowly as the weight ratio of KOH increases, and reaches its maximum at about 160% of the KOH weight ratio. It is believed that these differences between the PCs prepared from the preoxidized cloths and the carbonized cloths are due to the reactions taking place during the carbonization step. In the carbonization step, those non-carbon elements in preoxidized cloths such as hydrogen, oxygen, nitrogen and sulfur are removed, while at the same time, the rearrangement in the crystal structure of the preoxidized cloths takes place quickly, resulting in a kind of well-ordered structure that hinders the next step activation reactions [22].

It should be noted that the strengths of the PCs from the carbonized cloth and the preoxidized cloth are different, though they may have same SBET value. The strength of the PC product from the carbonized cloth is better than that from the preoxidized cloth, but in the latter case much less KOH is needed. The main objective of this work is to explore techniques for preparing high quality PCs economically. With this in mind, the focus of our work in the following part is concentrated on the preparation of PCs from the preoxidized cloth.

3.2. Effect of the weight ratio of KOH to starting material (R value)

The weight ratio of KOH to starting material (R value) has been found to be a crucial parameter in KOH activation process [14,15]. With the preoxidized cloth as starting material, the effect of the R value on the SBET and the micropore surface area of PCs is shown in Fig. 2. It can be clearly seen that as the R value increases, the SBET increases and reaches a maximum at a R value of 75%, then drops as the R value increases further. This is also the case for the micropore surface area. This implies that some micropores are widened to become big pores during the activation process.

In addition to the SBET and the micropore surface area, the pore size distribution of PCs is another important parameter that needs to be addressed in terms of the effect of the R value. It is known that two

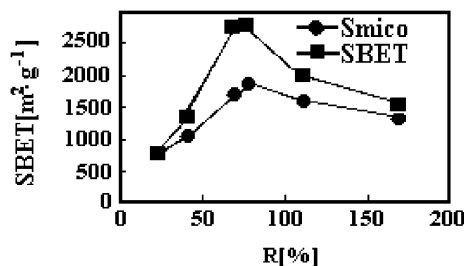


Fig. 2. BET surface area and micropore surface area of PCs versus R value (activation temperature, 1073 K; activation time, 30 min).

mechanisms might be involved in the chemical activation process [15], one is the pore formation mechanism due to the reaction of the chemical active agent and the starting material and the other one is the pore widening mechanism which is caused by the chemical active agent inside the opened pores. Pore widening usually begins when a number of opened pores already exist and the chemical active agent is abundant inside the pores, thus it becomes to be significant when the R value is reasonably high. Fig. 3 shows the adsorption isotherms of samples A, B and C that were obtained at different R values. It shows that an increase in R value (R values of samples A, B and C are 20%, 40% and 75%, respectively) results in a great increase of nitrogen adsorption capacity. The adsorption isotherms of samples A and B are Type I isotherms, in which the knees of the isotherms at about $P/P_0 = 0.05$ are very sharp and the plateaus are fairly flat. It is well known that the adsorption on microporous materials at lower P/P_0 due to micropore filling leads to Type I isotherm. Thus, it is easy to figure out that the pores in samples A and B are mainly micropores. In the case of sample C, the adsorption isotherm differs from that of samples A and B, in which the knee is a glasis, and the slope of the plateau increases due to multi-layer adsorption. When the relative pressure P/P_0 is over 0.90, significant nitrogen uptake can be observed, indicating that mesopores and/or macropores develop significantly in sample C. The pore size distribution of PCs can be calculated on the basis of the adsorption isotherms using the density functional theory. Fig. 4 shows the pore size distribution of these three samples, which are in good accordance with the results of the adsorption isotherms presented in Fig. 3. It can be seen that the pore size becomes wider as the R value increases. For samples A and B, the micropores are dominant and the pore widths are smaller than 2.0 nm, and the pore size distribution is a typical bi-modal micropore distribution; For sample C obtained at a higher R value, the pores are distributed in a

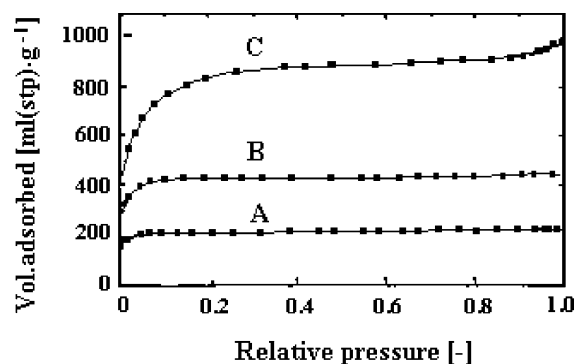


Fig. 3. Adsorption isotherms of PC samples A, B and C obtained at R values of 20%, 40% and 75%, respectively (activation temperature, 1073 K; activation time, 30 min).

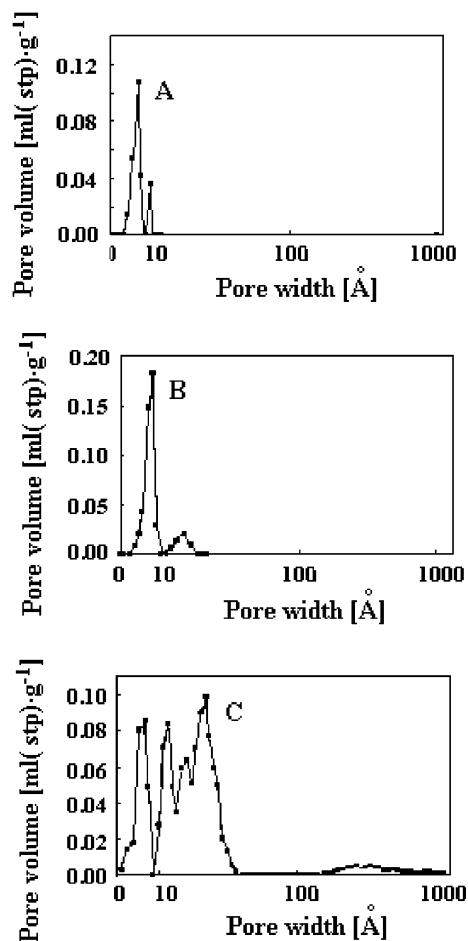


Fig. 4. Pore size distributions of PC samples A, B and C obtained at R values of 20%, 40% and 75%, respectively.

wide range, covering micropore, mesopore and macropore, and the pore size distribution is a typical tri-modal one. Obviously, the pore size distribution of the PCs obtained from preoxidized cloth at different KOH ratios differs substantially from each other. According to the literature, the best R value for preparation of PCs with high SBET from different starting materials is about 400–600%. In our case, the optimum R value is only about 75%. One reason for this may be because the different shapes of the starting materials. PAN-based preoxidized cloth was fabricated using micron-sized fibers which therefore have a larger contact area with the active agent than do the other starting materials which are of a different shape. Another reason is may be the different methods of loading KOH. The KOH is loaded by impregnation in this paper while for the traditional techniques the KOH is usually added in solid state by direct mixing the KOH powder with the starting materials. It is obvious that the former loading method is more favorable to help the starting materials touch the active agent sufficiently. Both reasons mentioned above help to reduce the R value.

3.3. Effect of activation temperature (T)

The influence of activation temperature (T) on the preparation of PCs from preoxidized cloths is presented in Figs. 5 and 6. In the temperature range studied, from 773 to 1173 K, the SBET and the benzene adsorption capacity increase with the increase of T , and reach their maximum values at 1073 K, then decrease as the temperature further increases. In this sense, the optimum activation temperature should be 1073 K. However, it seems that the iodine adsorption capacity of PCs increases continually as the activation temperature increases in the temperature range studied, as can be seen in Fig. 6. The difference in the iodine adsorption and benzene adsorption may be due to the difference in their molecular size. The smallest dimension of the iodine molecule is 0.44 nm, which is bigger than that of the benzene molecule (0.32 nm), so adsorption of iodine is more difficult in micropores in comparison to the adsorption of benzene. Adsorption of iodine may easily take place in relatively big pores in the PCs while the adsorption of benzene is relatively difficult in these big pores because of the difference in affinity of these two molecules to the pore walls inside the PCs. These also imply that high temperature results in the creation and development of big pores in the carbon skeleton structure of PCs. It is known that when the activation temperature is increased to 973 K, K_2O and K_2CO_3 species would be formed due to the reaction of KOH with

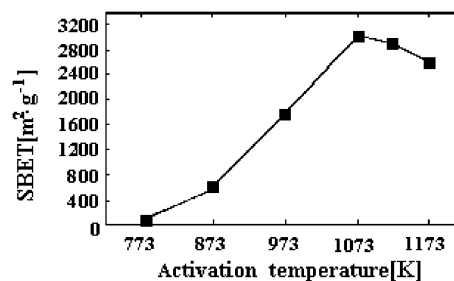


Fig. 5. BET surface area of PCs versus activation temperature (R value, 75%; activation time, 30 min).

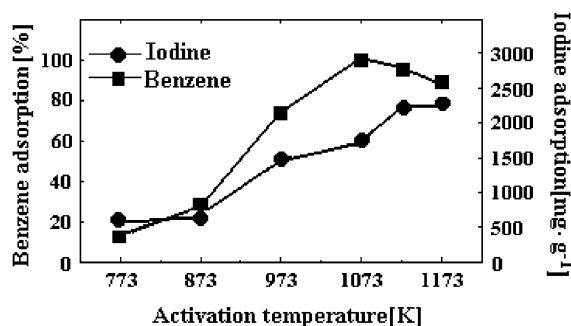


Fig. 6. Benzene adsorption and iodine adsorption of PCs versus activation temperature (R value, 75%; activation time, 30 min).

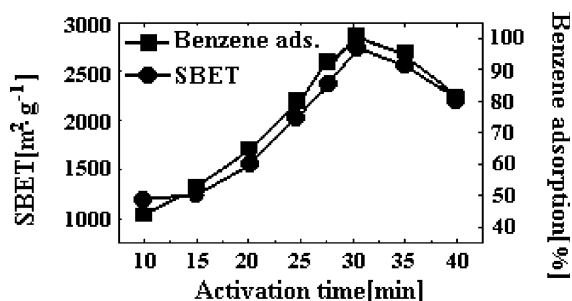


Fig. 7. BET surface area and benzene adsorption of PCs versus activation time (R value, 75%; activation temperature, 1073 K).

carbon. Under the reaction conditions adopted in this study, both the K_2O and K_2CO_3 species can take part in reactions with carbon, which leads to further development of pores [23,24].

3.4. Effect of activation time (t)

The variations of the SBET and the benzene adsorption capacity of PCs with the activation time are shown in Fig. 7. It can be seen that the variation trends of SBET and benzene adsorption capacity with the activation time are quite similar, and more or less, similar to their variation trends in the case of the R value and the activation temperature, as discussed above. It can also be seen from Fig. 7 that as the time increases, the SBET and the benzene adsorption increase and reach a maximum at 30 min, implying that 30 min is the optimum time to produce PCs with high SBET between 2500 and 3000 m^2/g from PAN-based preoxidized cloth by KOH activation.

As can be seen in Fig. 7, the optimum activation time for preparing PCs is about 30 min under conditions adopted in our study, which is much shorter than the time reported in literature that is normally around 2 h [14,15]. It is reported that short activation time is beneficial to preparation of PCs with narrow pore size distribution [15], and this would be extremely useful for preparing carbon molecular sieves.

4. Conclusions

In summary, a series of PCs with high BET surface area and well-developed microporous structure have been obtained with less KOH and shorter activation time in comparison to the traditional methods. PCs with high SBET between 2500–3000 m^2/g can be produced from PAN-based preoxidized cloth by KOH activation. The optimum process parameters are as follows: the weight ratio of KOH to starting material is about 75%, the activation temperature is about 1073 K, the activation time is around 30 min. It has been found that for

the PCs derived from PAN-based preoxidized cloth by KOH activation, the variation trends of the benzene adsorption capacity and the SBET with the activation temperature and the activation time are almost identical.

Acknowledgements

This work was supported by the State Key Laboratory of Heavy Oil Processing at University of Petroleum, China. The authors also wish to thank Prof. M.-Z. Wang and Prof. J.-T. Zheng for their stimulating and helpful discussions.

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