Preparation of porous carbons from petroleum coke by different activation methods

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Abstract

Porous carbons were prepared from Shengli petroleum coke (SPC) and Minxi petroleum coke (MPC) by different activation methods with H_2O, KOH and/or $KOH+H_2O$ as active agents. The porous carbons were characterized by nitrogen adsorption at 77 K. It has been found that activation method and component of petroleum coke, of which different kinds of transitional metals on petroleum coke are crucial for preparing high quality porous carbons. Under the identical experimental conditions, the co-activation with KOH and H_2O as active agents in the same activation process, which has been rarely reported in literature, is the easiest method for the preparation of porous carbons with high surface area. The sequence of active agents in terms of difficulty in the preparation of porous carbons with high surface area is as follows: $KOH+H_2O>KOH>H_2O$. A drawback of $KOH+H_2O$ activation in the preparation of porous carbon in this work is found to be its low carbon yield in comparison to KOH activation. Compared with the SPC coke, the MPC coke with higher contents of transitional metal and carbon and lower content of nitrogen is more suitable for making high surface area porous carbons, which is believed to be mainly due to the difference in the contents of transitional metals. Porous carbon with surface area around 2500–3000 m^2/g and carbon yield about 25–30% has been obtained from MPC coke by $KOH+H_2O$ activation with less KOH and shorter activation time in comparison to the traditional methods.
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1. Introduction

Porous carbons, normally called activated carbons, have been widely used in a number of fields, which include sewage water treatment, potable water purification, decolorization, gas separation, oxidative reactions and reductive reactions [1,2]. Basically, the methods for preparation of porous carbons can be grouped into two types, the physical activation method and the chemical activation method [3]. The physical activation method involves carbonization of

a carbonaceous precursor followed by activation of the resulting char in the presence of active agents such as steam, carbon dioxide or a mixture of these gases. In the case of the chemical activation method, the starting feedstocks are first impregnated with an active agent prior to heat treatment. The active agents used in chemical activation process are usually KOH, $ZnCl_2$ and H_3PO_4, H_2SO_4 etc. Both the physical activation method and the chemical activation method have their own merits and disadvantages, which depend on the starting materials and the requirements of porous carbons to be prepared. For the physical activation method, the active agents consumed in the process are cheap and the harmful pollutants released into the environment are relatively less, but the yield of porous carbons is relatively low and it is difficult to produce porous carbons with well-developed pore structure. In the case of chemical activation method, the active agents consumed such as KOH are

expensive and relatively, more harmful pollutants are released into the environment. Nevertheless, the active agents used in the chemical activation method, such as KOH, has dehydrating effect that inhibits the formation of tar [4,5], which helps to enhance the yield of porous carbon and to decrease the activation temperature compared with the physical activation method [6,7]. It is also quite easy for one to prepare high quality porous carbons with well-developed pore structure by chemical activation method.

A number of carbon precursors such as coal and coconut shell have been tested to produce porous carbons by physical activation or chemical activation, separately [7–11], however, in spite of a few papers having reported alkali, calcium and magnesium catalyst can increase the rate of reaction in physical activation, there is little work that has been done about the preparation of high quality porous carbons by co-activation with KOH and H_2O as active agents in the same activation process. Petroleum cokes, which are abundant and cheap (less than $100 per ton and usually be used as burning fuel) in China, have higher carbon content (about 90%) and have been proved to be good starting materials for the preparation of porous carbon. In this paper, two typical Chinese petroleum cokes, Shengli petroleum coke (SPC) and Minxi petroleum coke (MPC) with different components, were tested as the starting materials to produce high surface area porous carbons by chemical activation, physical activation and/or co-activation method. The study was conducted with an aim of establishing the effect or influence of different activation methods and different components, especially the existence of transitional metals in petroleum cokes on the development of porous structure in porous carbons.

2. Experimental

2.1. Analysis of petroleum cokes

The chemical components of the petroleum cokes used in this study were analyzed by element analysis, which give the information on organic constituent part (carbon, nitrogen and hydrogen, etc.) in Table 1, and atomic-absorption spectroscopy [12], which include the information on inorganic constituent part (various metals, such as manganese, iron, nickel and chromium) in Table 2.

2.2. Preparation of porous carbons

In this work, two typical Chinese petroleum cokes, Shengli petroleum coke (SPC) and Minxi petroleum coke

Table 1
Element analysis of petroleum cokes (%)

Samples	C	N	H	Total
SPC	89.26	2.37	4.30	95.93
MPC	92.95	1.05	4.71	98.71

Table 2
Quantitative analysis of petroleum cokes (%)

Samples	Ions			
	Fe^{3+}	Mn^{2+}	Ni^{2+}	Cr^{3+}
SPC	0.13	0.08	–	–
MPC	0.09	0.10	0.51	0.47

–, not found.

(MPC), were used as the starting materials. The preparation of porous carbons was carried out with chemical activation, physical activation and co-activation method, in which KOH, H_2O and KOH+H_2O were used as active agents, respectively. For the chemical activation and the co-activation method, the starting smashed petroleum cokes were soaked in a concentrated solution of KOH for 2 h at room temperature to load KOH, then transferred to a furnace and dried at 423 K for 4 h to completely remove water from the cokes. The cokes loaded with KOH were put into a reactor in which they were heated to 1073 K at a heating rate of 10 K/min and then kept at 1073 K for a period of different time, before being cooled down to room temperature to get semi-products. The semi-products were then washed, first with 0.5 M HCl and then hot and cold distilled water in a sequence, to remove residual alkali completely; then dried at 423 K for 4 h, and finally, porous carbons with different pore structure were obtained. For the physical activation method and the co-activation method, the activations were conducted with a fixed quantity of vapor being continuously put into the reactor at the final activation temperature during the whole activation process. The activation processes mentioned above were all carried out under flowing nitrogen to avoid oxidation of the samples. For all preparation experiments, the weight ratio of KOH to petroleum coke was 2 to 1, and the activation temperature was 1073 K. The yield of porous carbon upon each activation process has been given in Table 3.

2.3. Characterization of porous carbons

The porous carbons were characterized by nitrogen adsorption at 77 K. Before adsorption experiments, all the porous carbons were degassed at 573 K for 2 h. The BET surface area of porous carbons was obtained from nitrogen adsorption in the relative pressure from 10^{-6} to 1.0 using Micromeritics, ASAP2000. The pores size distribution of

Table 3
Yields of porous carbons produced at 1073 K of activation temperature and 30 min of activation time by different activation methods (%)

Active agent	MPC	SPC
H_2O	31	27
KOH	63	56
KOH+H_2O	29	23

PC was obtained by employing the Density Functional Theory [13].

3. Results and discussion

3.1. Chemical components of petroleum cokes

It is known that the quality and pore structure of porous carbons depends, to some degree, on the chemical components of the carbonaceous precursors, the preparation techniques adopted and the process parameters. In this study, the precursors used were two petroleum cokes, the SPC coke and the MPC coke. The main elemental components of these two cokes are shown in Table 1. It can be clearly seen that in comparison to the SPC coke, the carbon content of the MPC coke is higher and the nitrogen content is lower. For these two cokes, the difference in hydrogen content is quite small. This means that under identical preparation conditions, the yield of porous carbons for the MPC coke would be higher than that for the SPC coke, and this can be easily seen from Table 3. In addition to the organic constituents, the inorganic components in petroleum cokes are also important factors that cannot be neglected or underestimated. The inorganic components, i.e. metal elements in the MPC coke and the SPC coke, usually having no fixed dispersion state and no fixed amount due to the flexibility in the components of the raw oil, were analyzed by atomic-absorption spectroscopy, and the results are shown in Table 2. It can be seen that the MPC coke contains 0.51% of nickel, 0.47% of chrome, 0.09% of iron and 0.10% of manganese while in the case of the SPC coke, only 0.13% of iron and 0.08% of manganese are detected. It is believed that the difference in the inorganic components, especially the existence of nickel and chrome in these two petroleum cokes is one of the important reasons why the same treatments to the MPC coke and the SPC coke can lead to porous carbons with different surface areas. It is certain that these metal species in the cokes get involved in the formation of pore structures of the porous carbons, in one way or another. Literature survey shows that little attention has been paid to the influence of the inorganic components in petroleum cokes on the pore development in the final porous carbons. Here we have tried to correlate the surface area of porous carbons prepared from different cokes under identical conditions to the effect of metal elements in cokes, which is discussed in detail in section 3.4.

3.2. Influence of different activation methods

For a specific petroleum coke, the pore structure of the final products, porous carbons, will largely depend on the activation methods. For the two petroleum cokes used in our study, they were pretreated under identical conditions but activated in different ways. In order to make clear the influence of activation methods on pore development of
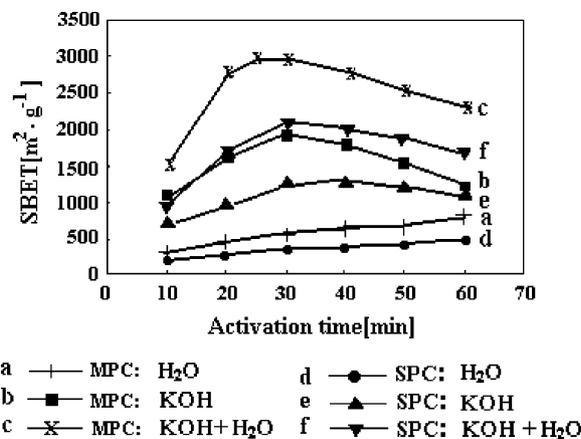

Fig. 1. Variation of surface areas of porous carbons with activation time in different activation methods.

porous carbons, we have measured the BET surface areas of all porous carbons prepared from the SPC coke and the MPC coke by following different activation methods, and have tried to correlate the data of surface area to the activation time with other preparation parameters being exactly the same. The variations of the BET surface areas of porous carbons made from the SPC coke and the MPC coke with activation time are shown in Fig. 1. It can be seen from Fig. 1 that for both cokes used in this study, the surface areas of the porous carbons made by physical activation of H_2O increase monotonically and slowly as the activation time increases, and are less than 1000 m^2/g which are much lower compared with those porous carbons made by chemical activation of KOH or co-activation of $KOH + H_2O$. This clearly demonstrates that the physical activation method is less competitive to the chemical method and/or the co-activation method in terms of surface areas of the carbon products. For those porous carbons made by chemical activation and/or co-activation, both from the MPC coke and the SPC coke, their BET surface areas pass through a maximum as the activation time increases, though the time varies between 25 and 40 min depending on the starting coke and the active agents used. Obviously, the co-activation method with $KOH + H_2O$ as active agent is the easiest method for the preparation of porous carbons in terms of surface area development. The sequence of active agents in terms of difficulty in the preparation of porous carbons with high surface area is as follows: $KOH + H_2O > KOH > H_2O$. The difference in BET surface area of porous carbons made by different activation methods may be explained as follows.

It is well known that physical activation is a heterogeneous, solid-gas reaction that can be diffusion limited, resulting in a higher degree of activation at the particle periphery than at the core, which results the wider distribution of pore in porous carbons [14]. So, porous carbons, especially those porous carbons with high surface area made by physical activation, usually cover micropore, mesopore and macropore. However, in chemical activation process, KOH act as active agent and the reaction primarily

involve the attack of KOH on the carbon atom in the precursor. Cross-linking and increased aromatization are promoted during carbonization, and the former helps to bond otherwise volatile products into the precursor structure before reaching pyrolysis temperatures, which results a consequential reduction in tar formation and increase in the carbon yield that can be easily seen from Table 3, and this will be further discussed in the next paragraph. The KOH is loaded by impregnation on the precursor in chemical activation, which can help the starting materials touch the active agent sufficiently and shorten the diffusion time of active agent. Due to the reason mentioned above, the distribution of pore in porous carbon made by chemical activation is usually narrower than that made by physical activation. The pores of the porous carbons made by chemical activation are mainly belonging to micropore, even the porous carbon with high surface area. In co-activation of $KOH + H_2O$, due to the reaction of KOH and carbon atom located in the skeleton of the precursor, the resulting char have more pores accessible to the steam, which alleviate diffusion limited compared with physical activation. Besides react with carbon atom in most parts of the precursor, the steam in the co-activation can take reaction with carbon atom in the precursor where little KOH exists. Other than the reactions mentioned above, potassium acting as the catalyst can increase the rate of activation of steam and carbon atom [14]. All of the above mentioned in co-activation process helps to produce porous carbon with high BET surface area and narrow pore distribution.

The yield of porous carbons is different according to different activation methods both for the MPC coke and SPC coke. It can be seen from Table 3 that chemical activation can brings porous carbon with higher yield than physical activation. In the co-activation method, due to intense activation between KOH and carbon, together with the reaction between steam and carbon, the yield of porous carbon has been largely lowed, a little less than that of physical activation method and far less than that of chemical activation method. Obviously, more work is needed to enhance the yield of porous carbon in co-activation in future.

3.3. Influence of different activation time

The process parameters, such as activation time, also have much effect on the pore structure of the final products. It can be seen from Fig. 1 that for MPC, the suitable activation time is 25 min in terms of the BET surface area, and this is much shorter than the time reported in literature that is normally around 2 h [15,16]. The possible reasons are 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
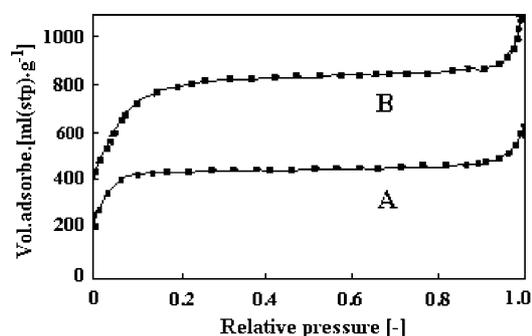

Fig. 2. Adsorption isotherms of porous carbons A and B.

agent sufficiently, which shorten the diffusion time of active agent. The weight ratio of KOH to petroleum coke adopted in this paper is 2–1, much shorter than the optimum ratio reported in literature that is normally more than 3–1, also can be explained by the synergistic effect of KOH and H_2O in co-activation mentioned in section 3.2 and the different methods of loading KOH mentioned above.

Fig. 2 shows the adsorption isotherms of porous carbons that were obtained from MPC coke by co-activation at different activation times. For samples A and B, the activation times are 10 and 25 min, respectively. It can be clearly seen that an increase in activation time results in a great increase of nitrogen adsorption capacity. The adsorption isotherms of samples A and B, especially sample A, are by and large belonging to Type I according to the BET classification, in which the knees of the isotherms at low relative pressure are sharp and the plateaus are generally horizontal. It is well known that the adsorption at lower P/P_0 due to micropore filling leads to Type I isotherm. With this in mind, it is easy to figure out that the pores in sample A and B are mainly micropores. In addition, the slopes of the isotherm plateaus, especially the slope of sample B, increase with the enhanced relative pressure, which due to multi-layer adsorption. Also, significant nitrogen uptakes occur when the relative pressure P/P_0 are over 0.90, especially in sample B, indicating that macropores and/or bigger mesopores develop significantly in these samples. The pores size distributions of porous carbons can be calculated on the basis of the adsorption isotherms using the Density Functional Theory. Fig. 3 shows the pore size distributions of these two samples obtained at different activation times, which agree quite well with the results of the adsorption isotherms presented in Fig. 2. It can be seen that the mesopores and/or macropores becomes abundance as the value of activation time increases. For sample A, the micropores are dominant and the pore width are mostly smaller than 3.0 nm; For sample B, which obtained at longer activation time, the pores are distributed in a relative wide range, besides micropore, mesopore and macropore are important ingredients that cannot be underestimated. This is also the case for the chemical activation method of KOH when SPC coke and MPC coke act as the starting materials
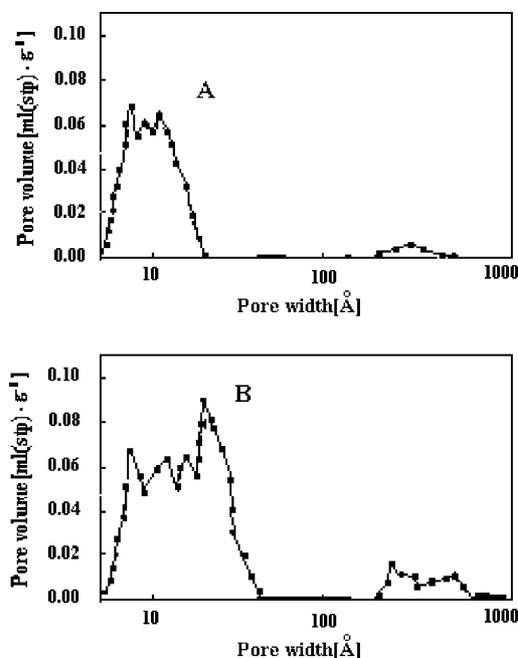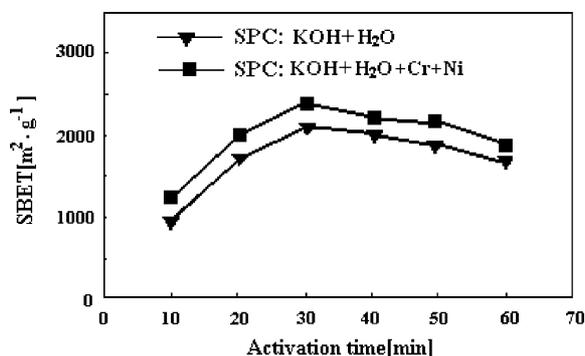
Fig. 3. Pore size distributions of porous carbons A and B.

Fig. 4. Variation of surface areas of porous carbons with activation time before and after the transitional metals appended.

and the co-activation method of $KOH+H_2O$ when SPC coke act as the starting materials. Obviously, the process parameters play a role in the development of pore structures of porous carbons. More work is needed in future to clarify the effect of other process parameters, such as the activation temperature and the weight ratio of active agent to the starting material on the pore structure of the final products.

3.4. Effect of transitional metals present in cokes

It also should be noted that the BET surface area of porous carbons made from the MPC coke is consistently higher than that from the SPC coke under identical activation conditions, as shown in Fig. 1, which implying these two cokes have different behaviors during the activation process.

As discussed above, there are some differences in inorganic components of the two cokes used in this study. It can be seen from Table 2 that the MPC coke contains nickel, chrome, iron and manganese metals, while for the SPC coke, only iron and manganese are detected. The difference in the inorganic components, especially the existence of nickel and chrome in these two petroleum cokes, to some degree, is the reasons that porous carbons from the MPC coke have higher surface areas than those from the SPC coke under identical conditions.

In order to verify the effect of the transitional metals (nickel and chrome) on the pore development, we added some nickel and chrome metals into the SPC coke in which no such metal were detected, and prepared porous carbons following the same procedure with $KOH+H_2O$ as active agent. For both nickel and chrome metals, the weight ratios

of added metal to the SPC coke was 0.5 wt%. The variation of surface areas of porous carbons with activation time before and after the transitional metals appended is shown in Fig. 4. It is clear to note that the surface areas of the carbons from the SPC coke loaded with nickel and chrome are consistently higher than those from the original SPC coke. Undoubtedly, the nickel and chrome species present in the coke play an important role in the pore development of porous carbons. Here these transitional metals act as catalyst, which help to reduce the activated energy of the reactions between carbon and active agents and to speed up these reactions. As can be seen in Figs. 1 and 4, the optimum activation time for preparing high surface area porous carbons is about $20\sim30$ min in our case, which is much shorter than the optimum time reported in literature that is normally around 2 h and is discussed as above [13, 15,16].

The preliminary results presented here have shown that porous carbons with high BET surface area can be prepared from the MPC coke with a shorter activation time and low weight ratio of KOH to raw material by co-activation method when $KOH+H_2O$ is used as active agent. The transitional metals present in petroleum coke play an important role in the development of pore structures of porous carbons. More work is needed in future to clarify the respective effect of these transitional metals in the cokes.

4. Conclusions

Porous carbons with surface area around 2500–3000 m^2/g have been produced from the MPC coke by co-activation with $KOH+H_2O$ as active agent. The co-activation process with $KOH+H_2O$ as active agent, which has been rarely reported as active agent to prepare porous carbons in the same procedure, is the easiest method for making porous carbons with high surface areas. The SPC coke and the MPC coke have different behaviors during the activation process, which due to the transitional metals, especially nickel and chrome metals present in the cokes

acting as catalyst for activation reaction. In comparison to the SPC coke, the MPC coke with higher carbon content and with chrome and nickel metals detected is a better coke precursor for preparing high surface area porous carbons. The weight ratio of KOH to petroleum coke is 2–1 in our case, which is much shorter than the optimum ratio reported in literature that is normally more than 3–1. The optimum activation time for preparing high surface area porous carbons from MPC in the co-activation method with KOH + H$_2$O as active agent is about 25 min in this paper, which is much shorter than the optimum time reported in literature that is normally around 2 h. Besides different activation methods, the process parameters in a certain activation method, such as the activation time in the co-activation method, also have effect on the pore structure of the porous carbons. Increasing the activation time unto 25 min in the co-activation method increased the BET surface area of porous carbons made from MPC coke. The yield of porous carbon in KOH + H$_2$O activation in this work is much less than that of KOH activation, and this should be seriously considered in further study.

Acknowledgements

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